



# MATERIALS PHYSICS AND MECHANICS



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#### MATERIALS PHYSICS AND MECHANICS

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# МЕХАНИКА И ФИЗИКА МАТЕРИАЛОВ

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# FINITE ELEMENT MODELLING OF CERAMOMATRIX PIEZOCOMPOSITES BY USING EFFECTIVE MODULI METHOD WITH DIFFERENT VARIANTS OF BOUNDARY CONDITIONS

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**Abstract.** The paper presents an investigation of effective properties of piezocomposites of piezoceramic/polycrystallites type by using the effective moduli method, the computer modeling of representative volumes with random structure of granular heterogeneity and the finite element method to solve the homogenization problems. The effective moduli, obtained from the problems with different boundary conditions on the edges of representative volumes, are analyzed.

**Keywords:** piezoelectricity, two-phase piezocomposite, effective moduli, representative volume, finite element method, finite element software

#### **1. Introduction**

Piezoceramic composite materials have received considerable attention due to their application in sensors, actuator and other piezoelectric devices. In order to improve the efficiency of these materials, the piezoelectric composites based on piezoceramic matrices has been developed recently. Porous piezoceramic materials appeared perspective for use as the elements for acoustic transmitters and as renewable energy sources. As it turned out, in comparison with dense ceramics, porous piezoceramics had small acoustic impedance, but sufficiently high values of piezoelectric sensitivities and thickness piezomoduli. However, porous piezoceramics is less strong compared with dense ceramics. To improve the mechanical properties of porous piezoceramics, more rigid crystallites can be added into ceramic composites.

The classification of piezoelectric composites was initiated by Newnham's connectivity theory. In compliance with this theory, the ceramomatrix or polycrystalline piezocomposites can be classified as two or three phase composites with 3-0 connectivity (with closed or separate inclusions). The ceramomatrix or polycrystalline composite piezoceramic having sizes of inclusions, lesser that 100  $\mu$ m may be accepted as a quasi-homogeneous medium with some effective moduli for most applications.

The material properties of porous or polymer-crystalline piezocomposites with mixed connectivities (3-0, 3-3 or 0-3) have been evaluated using different theoretical and computational models in [1–19] and others. Thus, the use of Marutake's and Bruggeman's approximations for calculation of effective moduli of piezocomposites was offered [19]. The approximate equations for elastic, dielectric and piezoelectric constants of diphasic piezocomposite form 3-0 to 3-3 connectivity were obtained in [1] based on simplified model

combing cubes and 3-3 models. Some cubic models also were used in [2,14]. The modified cubes matrix method was proposed for analysis of the piezocomposite with different connectivity in [9] and other papers of the same authors. The dilute, self-consistent, Mori-Tanaka and differential micromechanics theories were extended in [3] to consider the effective characteristic of piezocomposite materials. The application of each theory was based on three-dimensional static solution of an ellipsoidal inclusion in an infinite piezoelectric media. Theoretical models including optimization techniques and homogenization methods have also been proposed for piezocomposite in [17].

In the present work, we have developed the effective moduli method and finite element technique in accordance with [4,5,20,21]. Theoretical aspects of the effective moduli method for inhomogeneous piezoelectric media were examined. Four static piezoelectric problems for a representative volume that allow finding the effective moduli of an inhomogeneous body were specified. These problems differ by the boundary conditions, which were set on a representative volume surfaces: mechanical displacements and electric potential  $(u\phi)$ , mechanical displacements and normal component of electric displacement vector (uD), mechanical stress vector and electric potential  $(\sigma\phi)$ . Respective equations for calculation of effective moduli of piezoelectric media with arbitrary anisotropy were derived.

Based on these equations the full set of effective moduli for ceramomatrix composite piezoceramics having wide injection range was calculated with help of finite element method realized in the ANSYS package and in the new software ACELAN-COMPOS. Inclusions were modeled by using "granule" algorithm in ACELAN-COMPOS package. Then, the representative volume models generated in ACELAN-COMPOS were transferred to the ANSYS finite element package, where the effective moduli of the composite were calculated.

#### 2. Mathematical models and the effective moduli method

As is known, in linear approximation for piezoelectric materials there are a linear relations between mechanical and electric fields. These dependences are called the constitutive relations and can be presented in the following four equivalent forms [22]:

$$\mathbf{T} = \mathbf{c}^{E} \cdot \mathbf{S} - \mathbf{e}^{*} \cdot \mathbf{E}, \ \mathbf{D} = \mathbf{e} \cdot \mathbf{S} + \mathbf{\epsilon}^{S} \cdot \mathbf{E},$$
(1)

$$\mathbf{S} = \mathbf{s}^{E} \cdot \mathbf{T} + \mathbf{d}^{*} \cdot \mathbf{E}, \ \mathbf{D} = \mathbf{d} \cdot \mathbf{T} + \boldsymbol{\varepsilon}^{T} \cdot \mathbf{E},$$
(2)

$$\mathbf{T} = \mathbf{c}^{D} \cdot \mathbf{S} - \mathbf{h}^{*} \cdot \mathbf{D}, \ \mathbf{E} = -\mathbf{h} \cdot \mathbf{S} + \boldsymbol{\beta}^{S} \cdot \mathbf{D},$$
(3)

$$\mathbf{S} = \mathbf{s}^{D} \cdot \mathbf{T} + \mathbf{g}^{*} \cdot \mathbf{D}, \ \mathbf{E} = -\mathbf{g} \cdot \mathbf{T} + \boldsymbol{\beta}^{T} \cdot \mathbf{D}.$$
(4)

Here,  $\mathbf{T} = \{\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{23}, \sigma_{13}, \sigma_{12}\}$  is the array of the mechanical stress components  $\sigma_{ij}$ ;  $\mathbf{S} = \{\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, 2\varepsilon_{23}, 2\varepsilon_{13}, 2\varepsilon_{12}\}$ , is the array of the strain components  $\varepsilon_{ij}$ ;  $\mathbf{D}$  is the electric flux density vector or the vector of electric displacement;  $\mathbf{E}$  is the electric field intensity vector;  $\mathbf{c}^{E}$ ,  $\mathbf{c}^{D}$  are the  $6 \times 6$  matrices of elastic stiffness moduli at constant electric field and at constant electric displacement, respectively;  $\mathbf{e}$ ,  $\mathbf{d}$ ,  $\mathbf{h}$ ,  $\mathbf{g}$  are the  $3 \times 6$  matrices of piezoelectric moduli (stress coefficients, charge coefficients, strain coefficients, voltage coefficients, respectively);  $\mathbf{e}^{S}$ ,  $\mathbf{\varepsilon}^{T}$  are the  $3 \times 3$  matrices of dielectric permittivity moduli at constant electric displacement, rechanical stress, respectively;  $\mathbf{s}^{E}$ ,  $\mathbf{s}^{D}$  are the  $6 \times 6$  matrices of elastic compliance moduli at constant electric field and at constant electric displacement, mechanical strain and at constant mechanical stress, respectively;  $\mathbf{s}^{E}$ ,  $\mathbf{s}^{D}$  are the  $6 \times 6$  matrices of dielectric field and at constant electric displacement, respectively;  $\mathbf{\beta}^{S}$ ,  $\mathbf{\beta}^{T}$  are the  $3 \times 3$  matrices of dielectric impermittivity moduli at constant mechanical strain and at constant mechanical stress, respectively;  $(\dots)^{*}$  is the transpose operation; and  $(\dots) \cdot (\dots)$  is the scalar or internal product operation. The different material constants from (1) - (4) are connected through each other by the relations:

Finite element modelling of ceramomatrix piezocomposites by using effective moduli method with...

$$\mathbf{s}^{E} = (\mathbf{c}^{E})^{-1}, \ \mathbf{s}^{D} = (\mathbf{c}^{D})^{-1}, \ \mathbf{\beta}^{S} = (\mathbf{\epsilon}^{S})^{-1}, \ \mathbf{\beta}^{T} = (\mathbf{\epsilon}^{T})^{-1}, \ \mathbf{c}^{D} = \mathbf{c}^{E} + \mathbf{e}^{*} \cdot \mathbf{h}, \ \mathbf{s}^{D} = \mathbf{s}^{E} - \mathbf{d}^{*} \cdot \mathbf{g},$$
(5)  
$$\mathbf{\epsilon}^{T} = \mathbf{\epsilon}^{S} + \mathbf{d} \cdot \mathbf{e}^{*}, \ \mathbf{\beta}^{T} = \mathbf{\beta}^{S} - \mathbf{g} \cdot \mathbf{h}^{*}, \ \mathbf{e} = \mathbf{d} \cdot \mathbf{c}^{E}, \ \mathbf{d} = \mathbf{\epsilon}^{T} \cdot \mathbf{g}, \ \mathbf{g} = \mathbf{\beta}^{T} \cdot \mathbf{d}, \ \mathbf{h} = \mathbf{g} \cdot \mathbf{c}^{D}.$$
(6)

Thus, if one of the sets of material moduli is known, { $\mathbf{c}^{E}$ ,  $\mathbf{e}$ ,  $\mathbf{\epsilon}^{S}$ }, then all other sets ({ $\mathbf{s}^{E}$ ,  $\mathbf{d}$ ,  $\mathbf{\epsilon}^{T}$ }, { $\mathbf{c}^{D}$ ,  $\mathbf{h}$ ,  $\mathbf{\beta}^{S}$ }, or{ $\mathbf{s}^{D}$ ,  $\mathbf{g}$ ,  $\mathbf{\beta}^{T}$ }) can be determined. In this section we show that for a composite material one can select such homogenization problems, from which we can directly determine one of the sets of effective material moduli: { $\mathbf{c}^{Eeff}$ ,  $\mathbf{e}^{eff}$ ,  $\mathbf{e}^{eff}$ ,  $\mathbf{s}^{Seff}$ }, { $\mathbf{s}^{Seff}$ },  $\mathbf{s}^{Seff}$ ,  $\mathbf{s}^{Seff$ 

We will consider a ceramomatrix piezocomposite as a two-phase composite in which the first phase (matrix) is a piezoceramic material, and the second phase is the elastic inclusions. Let  $\Omega$  is the representative volume of heterogeneous ceramomatrix piezocomposite materials,  $\Omega = \Omega^{(1)} \cup \Omega^{(2)}$ ;  $\Omega^{(1)}$  is the volume occupied by the primary material of the matrix;  $\Omega^{(2)}$  is the volume or the set of the volumes occupied by the material of the inclusions;  $\Gamma = \partial \Omega$  is the boundary of the volume, **n** the vector of the external unit normal to  $\Gamma$ ,  $\mathbf{u} = \mathbf{u}(\mathbf{x})$  is the displacement vector-function,  $\varphi = \varphi(\mathbf{x})$  the electric potential function,  $\mathbf{x} = \{x_1, x_2, x_3\}$  is the vector of the Cartesian coordinates.

In order to determine the effective moduli of this composite material, we will consider four set of the homogenization problems [20, 21]. The first set is used most often and is based on the following boundary-value problem

$$\mathbf{L}\left(\mathbf{V}\right)\cdot\mathbf{T}=0,\ \mathbf{V}\cdot\mathbf{D}=0,\tag{7}$$

$$\mathbf{T} = \mathbf{c}^{E} \cdot \mathbf{S} - \mathbf{e}^{*} \cdot \mathbf{E}, \ \mathbf{D} = \mathbf{e} \cdot \mathbf{S} + \mathbf{\epsilon}^{S} \cdot \mathbf{E},$$
(8)

$$\mathbf{S} = \mathbf{L}(\nabla) \cdot \mathbf{u}, \ \mathbf{E} = -\nabla \varphi, \ \mathbf{L}^*(\nabla) = \begin{bmatrix} \partial_1 & 0 & 0 & 0 & \partial_3 & \partial_2 \\ 0 & \partial_2 & 0 & \partial_3 & 0 & \partial_1 \\ 0 & 0 & \partial_3 & \partial_2 & \partial_1 & 0 \end{bmatrix}, \ \nabla = \begin{cases} \partial_1 \\ \partial_2 \\ \partial_3 \end{cases},$$
(9)

$$\mathbf{u} = \mathbf{L}^*(\mathbf{x}) \cdot \mathbf{S}_0, \ \varphi = -\mathbf{x} \cdot \mathbf{E}_0, \ \mathbf{x} \in \Gamma,$$
(10)

where  $\mathbf{S}_0 = \{S_{01}, S_{02}, S_{03}, S_{04}, S_{05}, S_{06}\}$ ;  $S_{0\beta}$  are some constant values that do not depend on **x**;  $\mathbf{E}_0$  is some constant vector.

Note that the problem (7)–(10) should be solved in an inhomogeneous volume  $\Omega$ , where  $\mathbf{c}^{E} = \mathbf{c}^{E(j)}$ ,  $\mathbf{e} = \mathbf{e}^{(j)}$ ,  $\mathbf{\varepsilon}^{S} = \mathbf{\varepsilon}^{S(j)}$  for  $\mathbf{x} \in \Omega^{(j)}$ , j = 1, 2. We consider the elastic material of inclusions as a piezoelectric material with their elastic stiffness and dielectric permittivities moduli and with negligible piezomoduli.

In the case of ceramomatrix piezocomposite of 6*mm* class, in order to determine its ten independent effective moduli ( $c_{11}^{E\,\text{eff}}$ ,  $c_{12}^{E\,\text{eff}}$ ,  $c_{33}^{E\,\text{eff}}$ ,  $c_{44}^{E\,\text{eff}}$ ,  $e_{31}^{\text{eff}}$ ,  $e_{33}^{\text{eff}}$ ,  $e_{33}^{\text{eff}}$ ,  $e_{33}^{e\,\text{eff}}$ ,

$$u\varphi - \mathbf{I}. \quad S_{0\beta} = S_0 \delta_{1\beta}, \ \mathbf{E}_0 = 0 \implies c_{1k}^{E\,\text{eff}} = \left\langle \sigma_{kk} \right\rangle / S_0; \ k = 1, 2, 3; \ e_{31}^{\text{eff}} = \left\langle D_3 \right\rangle / S_0, \tag{11}$$

$$u\varphi - \text{II.} \quad S_{0\beta} = S_0 \delta_{3\beta}, \ \mathbf{E}_0 = 0 \implies c_{k3}^{E \text{ eff}} = \left\langle \sigma_{kk} \right\rangle / S_0; \ k = 1, 2, 3; \ e_{33}^{\text{eff}} = \left\langle D_3 \right\rangle / S_0, \tag{12}$$

$$u\varphi - \text{III. } S_{0\beta} = S_0 \delta_{4\beta}, \ \mathbf{E}_0 = 0 \implies c_{44}^{E \text{ eff}} = \langle \sigma_{23} \rangle / S_0; \ e_{15}^{\text{eff}} = \langle D_2 \rangle / S_0, \tag{13}$$

$$u\varphi - \text{IV. } \mathbf{S}_0 = 0, \ E_{0l} = E_0 \delta_{1l} \implies e_{15}^{\text{eff}} = -\langle \sigma_{13} \rangle / E_0; \ \varepsilon_{11}^{\text{Seff}} = \langle D_1 \rangle / E_0, \tag{14}$$

$$u\varphi - V. \ \mathbf{S}_{0} = 0, \ E_{0l} = E_{0}\delta_{3l} \implies e_{3k}^{\text{eff}} = -\langle \sigma_{kk} \rangle / E_{0}; \ k = 1, 2, 3; \ \varepsilon_{33}^{\text{seff}} = \langle D_{3} \rangle / E_{0},$$
(15)

where  $\delta_{ij}$  is the Kronecker symbol; and the angle brackets denote the averaged by the volume  $\Omega$  values:

$$<(...)>=\frac{1}{|\Omega|}\int_{\Omega}(...)d\Omega.$$
(16)

The boundary conditions (8) are the linear essentially boundary conditions, which for a homogeneous piezoelectric comparison medium provide the constant stresses, electric fluxes, strains, and electric intensity fields. However, as has been shown in [20,21], we can use for the homogenization problems other boundary conditions, which also provide the constant stresses, electric fluxes, strains, and electric intensity fields for a homogeneous comparison medium.

Thus, instead of the boundary conditions (10), we can consider the natural boundary condition for the stress with known constant tensions and the essentially electric boundary condition with the known linear electric potential function:

$$\mathbf{L}^{*}(\mathbf{n}) \cdot \mathbf{T} = \mathbf{L}^{*}(\mathbf{n}) \cdot \mathbf{T}_{0}, \ \varphi = -\mathbf{x} \cdot \mathbf{E}_{0}, \ \mathbf{x} \in \Gamma.$$
(17)

Again, in the case of ceramomatrix piezocomposite of 6*mm* class, for determination full set of effective moduli  $(s_{11}^{E \text{ eff}}, s_{12}^{E \text{ eff}}, s_{33}^{E \text{ eff}}, s_{34}^{E \text{ eff}}, d_{31}^{e \text{ eff}}, d_{31}^{e \text{ eff}}, d_{15}^{e \text{ eff}}, \varepsilon_{11}^{T \text{ eff}}, \varepsilon_{33}^{T \text{ eff}})$ , we can solve five boundary problems (5) – (7). (14) with various values of  $\mathbf{T}_0$  and  $\mathbf{E}_0$ , having set only one of the components  $T_{0\beta}$ ,  $E_{0l}$  ( $\beta = 1, 2, ..., 6$ ; l = 1, 2, 3) in the boundary conditions (17) not equal to zero:

$$\sigma \varphi - \mathbf{I}. \quad T_{0\beta} = T_0 \delta_{1\beta}, \ \mathbf{E}_0 = 0 \implies s_{1k}^{E \text{ eff}} = \left\langle \varepsilon_{kk} \right\rangle / T_0; \ k = 1, 2, 3; \ d_{31}^{\text{eff}} = \left\langle D_3 \right\rangle / T_0, \tag{18}$$

$$\sigma\varphi - \text{II.} \quad T_{0\beta} = T_0 \delta_{3\beta}, \ \mathbf{E}_0 = 0 \implies s_{k3}^{E \text{ eff}} = \left\langle \varepsilon_{kk} \right\rangle / T_0; \ k = 1, 2, 3; \ d_{33}^{\text{eff}} = \left\langle D_3 \right\rangle / T_0, \tag{19}$$

$$\sigma \varphi - \text{III.} \ T_{0\beta} = T_0 \delta_{4\beta}, \ \mathbf{E}_0 = 0 \implies s_{44}^{E \,\text{eff}} = \left\langle \varepsilon_{23} \right\rangle / T_0; \ d_{15}^{\text{eff}} = \left\langle D_2 \right\rangle / T_0, \tag{20}$$

$$\sigma\varphi - \text{IV. } \mathbf{S}_0 = 0, \ E_{0l} = E_0 \delta_{1l} \implies d_{15}^{\text{eff}} = \langle \mathcal{E}_{13} \rangle / E_0; \ \mathcal{E}_{11}^{T\text{eff}} = \langle D_1 \rangle / E_0, \tag{21}$$

$$\sigma\varphi - \mathbf{V}. \ \mathbf{S}_0 = 0, \ E_{0l} = E_0 \delta_{3l} \implies d_{3k}^{\text{eff}} = \left\langle \varepsilon_{kk} \right\rangle / E_0; \ k = 1, 2, 3; \ \varepsilon_{33}^{T \text{eff}} = \left\langle D_3 \right\rangle / E_0.$$
(22)

If we assume the the essentially mechanical boundary condition with the known linear displacements and the natural electric boundary condition with known constant normal component of electric flux vector

$$\mathbf{u} = \mathbf{L}^*(\mathbf{x}) \cdot \mathbf{S}_0, \ \mathbf{n} \cdot \mathbf{D} = \mathbf{n} \cdot \mathbf{D}_0, \ \mathbf{x} \in \Gamma,$$
(23)

then for transversely isotropic ceramomatrix piezocomposite we can solve five boundary problems (7) – (9), (23) with various values of  $\mathbf{S}_0$  and  $\mathbf{D}_0$ , having set only one of the components  $S_{0\beta}$ ,  $D_{0l}$  ( $\beta = 1, 2, ..., 6$ ; l = 1, 2, 3) in (23) not equal to zero, and from the solution of these problems we directly obtain the effective moduli  $c_{11}^{D\text{eff}}$ ,  $c_{12}^{D\text{eff}}$ ,  $c_{13}^{D\text{eff}}$ ,  $c_{33}^{D\text{eff}}$ ,  $c_{44}^{D\text{eff}}$ ,  $h_{31}^{\text{eff}}$ ,  $h_{35}^{\text{eff}}$ ,  $\beta_{33}^{S\text{eff}}$ :

$$uD - I. \quad S_{0\beta} = S_0 \delta_{1\beta}, \ \mathbf{D}_0 = 0 \implies c_{1k}^{D \text{ eff}} = \langle \sigma_{kk} \rangle / S_0; \ k = 1, 2, 3; \ h_{31}^{\text{eff}} = -\langle E_3 \rangle / S_0,$$
(24)

$$uD - \text{II.} \quad S_{0\beta} = S_0 \delta_{3\beta}, \ \mathbf{D}_0 = 0 \implies c_{k3}^{D \text{ eff}} = \langle \sigma_{kk} \rangle / S_0; \ k = 1, 2, 3; \ h_{33}^{\text{eff}} = -\langle E_3 \rangle / S_0, \tag{25}$$

$$uD - \text{III. } S_{0\beta} = S_0 \delta_{4\beta}, \ \mathbf{D}_0 = 0 \Rightarrow c_{44}^{Den} = \langle \sigma_{23} \rangle / S_0; \ h_{15}^{en} = -\langle E_2 \rangle / S_0, \tag{26}$$

$$uD - IV. \mathbf{S}_{0} = 0, \ D_{0l} = D_{0}\delta_{1l} \implies h_{15}^{\text{eff}} = -\langle \sigma_{13} \rangle / D_{0}; \ \beta_{11}^{\text{str}} = \langle E_{1} \rangle / D_{0}, \tag{27}$$

$$uD - V = \mathbf{S}_{0} - D_{0} - D_{0}\delta_{0} \implies h^{\text{eff}} = -\langle \sigma_{13} \rangle / D_{0}; \ k = 1, 2, 3; \ \beta^{\text{seff}} = \langle F_{0} \rangle / D_{0} \tag{28}$$

$$uD - V$$
.  $\mathbf{S}_0 = 0$ ,  $D_{0l} = D_0 \delta_{3l} \implies h_{3k}^{\text{ent}} = -\langle \sigma_{kk} \rangle / D_0$ ;  $k = 1, 2, 3$ ;  $\beta_{33}^{\text{bon}} = \langle E_3 \rangle / D_0$ . (28)  
At last, we can consider the natural mechanical and electric boundary conditions with

the known constant tensions and the normal component of electric flux vector:  $\mathbf{L}^*(\mathbf{n}) \cdot \mathbf{T} = \mathbf{L}^*(\mathbf{n}) \cdot \mathbf{T}_0, \ \mathbf{n} \cdot \mathbf{D} = \mathbf{n} \cdot \mathbf{D}_0, \ \mathbf{x} \in \Gamma.$  (29) Finite element modelling of ceramomatrix piezocomposites by using effective moduli method with...

Now for transversely isotropic ceramomatrix piezocomposite we solve five boundary problems (7) – (9), (29) with various values of  $\mathbf{T}_0$  and  $\mathbf{D}_0$ , having set in (29) only one nonzero components  $T_{0\beta}$ ,  $D_{0l}$  ( $\beta = 1, 2, ..., 6$ ; l = 1, 2, 3), and after solving these problems we at first obtain the effective moduli  $s_{11}^{D\text{ eff}}$ ,  $s_{12}^{D\text{ eff}}$ ,  $s_{33}^{D\text{ eff}}$ ,  $s_{44}^{D\text{ eff}}$ ,  $g_{31}^{\text{ eff}}$ ,  $g_{33}^{\text{ eff}}$ ,  $g_{15}^{\text{ eff}}$ ,  $\beta_{11}^{T\text{ eff}}$ ,  $\beta_{33}^{T\text{ eff}}$ :

$$\sigma D - \mathbf{I}. \quad T_{0\beta} = T_0 \delta_{1\beta}, \ \mathbf{D}_0 = 0 \implies s_{1k}^{D \text{ eff}} = \left\langle \varepsilon_{kk} \right\rangle / T_0; \ k = 1, 2, 3; \ g_{31}^{\text{eff}} = -\left\langle E_3 \right\rangle / T_0, \tag{30}$$

$$\sigma D - \text{II.} \quad T_{0\beta} = T_0 \delta_{3\beta}, \quad \mathbf{D}_0 = 0 \implies s_{k3}^{D \text{ eff}} = \left\langle \mathcal{E}_{kk} \right\rangle / T_0; \quad k = 1, 2, 3; \quad g_{33}^{\text{ eff}} = -\left\langle E_3 \right\rangle / T_0, \quad (31)$$

$$\sigma D - \text{III.} \ T_{0\beta} = T_0 \delta_{4\beta}, \ \mathbf{D}_0 = 0 \implies s_{44}^{D \text{ eff}} = \left\langle \varepsilon_{23} \right\rangle / T_0; \ g_{15}^{\text{eff}} = -\left\langle E_2 \right\rangle / T_0, \tag{32}$$

$$\sigma D q - \text{IV. } \mathbf{T}_0 = 0, \ D_{0l} = D_0 \delta_{1l} \implies g_{15}^{\text{eff}} = \left\langle \mathcal{E}_{13} \right\rangle / D_0; \ \beta_{11}^{T \text{eff}} = \left\langle E_1 \right\rangle / D_0, \tag{33}$$

$$\sigma D - \mathbf{V}. \quad \mathbf{T}_0 = 0, \ D_{0l} = D_0 \delta_{3l} \quad \Rightarrow \quad g_{3k}^{\text{eff}} = \left\langle \varepsilon_{kk} \right\rangle / D_0; \ k = 1, 2, 3; \ \beta_{33}^{T \text{eff}} = \left\langle E_3 \right\rangle / D_0. \tag{34}$$

For each set of these problems from found effective moduli we can calculate for "equivalent" effective homogeneous medium the other moduli from the constitutive equations (1) – (4) and the relations (5), (6). We note, that effective moduli, found from different problems  $u\varphi$ ,  $\sigma\varphi$ , uD, and  $\sigma D$ , will differ, i.e.  $(\mathbf{c}^{\text{Eeff}})_{u\varphi} \neq (\mathbf{c}^{\text{Eeff}})_{uD} \neq (\mathbf{c}^{\text{Eeff}})_{uD} \neq (\mathbf{c}^{\text{Eeff}})_{\sigma D}$ , etc.

Further, all these problems will be solved in a representative volume  $\Omega$  numerically by the finite element method.

#### 3. Averaging of inclusions for polycrystalline piezoceramic

For the case of polycrystalline elastic inclusions, we must calculate at the first stage the effective moduli for material of inclusions. At the next stage, we will study piezocomposite with isotropic inclusions as two-phase composite according to the approaches described above. As an example, we shall consider  $PZT/\alpha - Al_2O_3$  composite material.

For calculation of average moduli of inclusions, we shall take into account, that inclusions represent the crystallites of sapphire ( $\alpha$ -corundum) Al<sub>2</sub>O<sub>3</sub>. These inclusions are the crystals of system  $\overline{3}m$  [23], which crystallographic axes are oriented in random manner with respect to the global Cartesian coordinate system. In crystallographic axes, its moduli have the following structure

	$c_{11}^{r}$	$c_{12}^{r}$	$c_{13}^{r}$	$c_{14}^{r}$	0	0					
	$c_{12}^{r}$	$c_{11}^{r}$	$c_{13}^{r}$	$-c_{14}^{r}$	0	0			$\int c^r$	0	0 ]
$\mathbf{c}^r$ –	$c_{13}^{r}$	$c_{13}^{r}$	$c_{33}^{r}$	0	0	0		$\mathbf{e}^r$ –	0	$c^r$	
ι –	$c_{14}^{r}$	$-c_{14}^{r}$	0	$c_{44}^{r}$	0	0	,	е —	0	0 0	$\begin{bmatrix} 0 \\ c^r \end{bmatrix}$ ,
	0	0	0	0	$c_{44}^{r}$	$c_{14}^{r}$				0	<i>E</i> <sub>33</sub>
	0	0	0	0	$c_{14}^{r}$	$c_{66}^{r}$ _					
whee	r	(-r)	rs	10							

where  $c_{66}^r = (c_{11}^r - c_{12}^r)/2$ .

In this connection, the effective moduli can be defined as the average moduli of monophase polycrystallite of trigonal system [21]. Here, the averaging of crystallites moduli on every of the possible orientations of crystallographic axes can be implemented in implicit form [24]. As a result, the inclusions can be considered as isotropic material, which effective moduli are expressed through the initial stiffness moduli  $c_{\alpha\beta}^r$  and the flexibility or compliance moduli  $s_{\alpha\beta}^r$  under well-known formulas [24].

The Voight's averaging gives the following values for the effective bulk module  $K_V^{(2)}$ and shear module  $\mu_V^{(2)}$ 

$$K_{V}^{(2)} = \frac{1}{9} \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} c_{\alpha\beta}^{r} , \qquad \mu_{V}^{(2)} = \frac{1}{30} \left( 3 \sum_{\alpha=1}^{3} c_{\alpha\alpha}^{r} + 6 \sum_{\alpha=4}^{6} c_{\alpha\alpha}^{r} - \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} c_{\alpha\beta}^{r} \right),$$

Alternative averaging on Reuss for flexibility or compliance tensors allows one to find the inverse values for the effective moduli  $K_R^{(2)}$  and  $\mu_R^{(2)}$ :

$$(K_R^{(2)})^{-1} = \sum_{\alpha=1}^3 \sum_{\beta=1}^3 s_{\alpha\beta}^r , \qquad (\mu_R^{\text{eff}})^{-1} = \frac{1}{15} \left( 6 \sum_{\alpha=1}^3 s_{\alpha\alpha}^r + 3 \sum_{\alpha=4}^6 s_{\alpha\alpha}^r - 2 \sum_{\alpha=1}^3 \sum_{\beta=1}^3 s_{\alpha\beta}^r \right),$$

At the averaging of trigonal system polycrystallite the given formulas can be rewritten in the form [24]:

$$K_{V}^{(2)} = \frac{1}{9} (2c_{11}^{r} + c_{33}^{r} + 2(c_{12}^{r} + 2c_{13}^{r})), \ \mu_{V}^{(2)} = \frac{1}{30} (7c_{11}^{r} + 2c_{33}^{r} - 5c_{12}^{r} - 4c_{13}^{r} + 12c_{44}^{r}),$$
(35)

$$(K_{R}^{(2)})^{-1} = 2s_{11}^{r} + s_{33}^{r} + 2(s_{12}^{r} + 2s_{13}^{r}), \ (\mu_{R}^{(2)})^{-1} = \frac{2}{15}(7s_{11}^{r} + 2s_{33}^{r} - 5s_{12\alpha}^{r} - 4s_{13}^{r} + 3s_{44}^{r}).$$
(36)

According to the Hill's approach for the final values of effective moduli of a monophase polycrystalline material, we shall take the arithmetic middling values obtained by averaging on Voight and Reuss:

$$K^{(2)} = (K_V^{(2)} + K_R^{(2)})/2, \ \mu^{(2)} = (\mu_V^{(2)} + \mu_R^{(2)})/2.$$
(37)

Then, the average values of Young's module  $E^{(2)}$ , Poisson's coefficient  $v^{(2)}$ , and stiffness moduli  $c_{11}^{(2)}$ ,  $c_{12}^{(2)}$  for inclusion material can be found by using the standard formulas from  $K^{(2)}$  and  $\mu^{(2)}$ 

$$E^{(2)} = \frac{9K^{(2)}\mu^{(2)}}{(3K^{(2)} + \mu^{(2)})}, \ \nu^{(2)} = \frac{(3K^{(2)} - \mu^{(2)})}{(6K^{(2)} + 2\mu^{(2)})}.$$
(38)

$$c_{11}^{(2)} = \frac{(1 - \nu^{(2)})E^{(2)}}{(1 + \nu^{(2)})(1 - 2\nu^{(2)})}, \ c_{12}^{(2)} = \frac{\nu^{(2)}E^{(2)}}{(1 + \nu^{(2)})(1 - 2\nu^{(2)})}.$$
(39)

The averaging of dielectric permittivities on every of the possible orientations of crystallographic axes leads to isotropic dielectric medium with effective permittivity  $\varepsilon^{(2)}$ :

$$\varepsilon^{\text{eff}} = (2\varepsilon_{11}^r + \varepsilon_{33}^r)/2.$$

$$\tag{40}$$

Thus, the inclusions from sapphire crystallites of trigonal system can be modelled by isotropic material with effective elastic moduli  $E^{(2)}$ ,  $v^{(2)}$  or  $c_{11}^{(2)}$ ,  $c_{12}^{(2)}$  and dielectric permittivitie  $\varepsilon^{(2)}$ , expressed by moduli of sapphire  $c_{\alpha\beta}^r$ ,  $s_{\alpha\beta}^r$ ,  $\varepsilon_{ii}^r$  from formulas (35) – (40).

#### 4. Models of representative volumes

As a representative volume element, we consider a cube evenly divided into smaller piezoelectric cubic finite elements with eight nodes. For a mixed two-phase composite, such element can have piezoelectric properties of the first phase or of the second phase. We use the 3-0 algorithm from ACELAN-COMPOS package for simulation of inclusions as granules, consisting of one or more structural elements not connected with other granules [25–27]. In this algorithm, the representative volumes consist of domains with  $8 \times 8 \times 8$  elements. Number 8 for the domain division was chosen for the convenience of implementing numerical procedures to generate data structures and verify the phase connectivity.

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The input user data are the boundary granule size and the maximum quantum of inclusions in the representative volume. Random choice of the supporting element for the granules ensures in the result the stochastic distribution of material properties in the representative volume element. The granule grows in the domain of  $8 \times 8 \times 8$  element size according to an algorithm that allows the granule to be shaped as close to the ball as possible, while avoiding highly elongated elements.

Each domain is created by a partially random way, and the representative volumes of  $8m \times 8m \times 8m$  order are formed in the result of generating the sequence of domains along three coordinate axes. Thus, each resulting domain differs from the other. Nevertheless, it maintains the connectivity of the main phase and the connectivity of the total volume structure, formed by a 3-0 connectivity algorithm from ACELAN-COMPOS package. A detailed description of this algorithm is contained in [26,27].

Some examples of the representative volume element for m = 2 (eight domains) and for m = 3 (twenty seven domains) are shown in Fig. 1 and Fig. 2, respectively. In these figures the cases (*a*) and (*b*) correspond to the percentage of inclusions p = 10 %, and the cases (*c*) and (*d*) correspond to the percentage of inclusions p = 60 %.

At the next step, the generated structures were transferred to ANSYS finite element package, where all further operations were carried out.



**Fig. 1.** Example of a representative volume elements  $16 \times 16 \times 16$ : (*a*) whole volume with 10 % of inclusions, (*b*) elastic elements in volume with 10 % of inclusions, (*c*) whole volume with 60 % of inclusions, (*d*) elastic elements in volume with 60 % of inclusions



**Fig. 2.** Example of a representative volume elements  $32 \times 32 \times 32 : (a)$  whole volume with 10 % of inclusions, (b) elastic elements in volume with 10 % of inclusions, (c) whole volume with 60 % of inclusions, (d) elastic elements in volume with 60 % of inclusions

Then, the problems (7) - (9) with (10), (17), (23) or (29) were solved for the representative volume using finite element technology and ANSYS package. In the end, in the ANSYS postprocessor the average characteristics (stresses, strains, electric fluxes and electric intensity fields) were automatically calculated by (16) according to (11) - (15), (18) - (22), (24) - (28), or (30) - (34), and thus the full sets of the effective material moduli of piezocomposite were obtained. We used an eight-node finite element SOLID5 with the displacements and the electric potential as degrees of freedom in each node and with capability of piezoelectric analysis. Computing experiments were performed in ANSYS software of 11.0 version. However, the developed programs in macrolanguage APDL ANSYS will work in higher versions of ANSYS that support piezoelectric analysis and finite element SOLID5.

#### **5.** Numerical examples

To provide an example, we consider a PCR-1/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> composite material. For the dense piezoceramic PCR-1 we take the following values of material constants [28]:  $c_{11}^{E(1)} = 15.3 \cdot 10^{10}$ ,  $c_{12}^{E(1)} = 8.7 \cdot 10^{10}$ ,  $c_{13}^{E(1)} = 8.7 \cdot 10^{10}$ ,  $c_{33}^{E(1)} = 12.7 \cdot 10^{10}$ ,  $c_{44}^{E(1)} = 2.6 \cdot 10^{10} (N/m^2)$ ,  $e_{31}^{(1)} = -2.1$ ,  $e_{33}^{(1)} = 12.4$ ,  $e_{15}^{(1)} = 11.3$  (C/m<sup>2</sup>);  $\varepsilon_{11}^{s(1)} = 572\varepsilon_0$ ,  $\varepsilon_{33}^{s(1)} = 304\varepsilon_0$ , where  $\varepsilon_0 = 8.85 \cdot 10^{-12}$  (F/m) is the dielectric permittivity of the vacuum. We assume the following values of material moduli of sapphire [29]:  $c_{11}^r = 49.7 \cdot 10^{10}$ ,  $c_{12}^r = 16.3 \cdot 10^{10}$ ,  $c_{13}^r = 11.1 \cdot 10^{10}$ ,  $c_{33}^r = 11.54\varepsilon_0$ . Then, after the calculation by formulas (32)–(37) we obtain the averaging moduli of ( $\alpha$ -corundum as an isotropic phase:  $E^{(2)} = 40.26 \cdot 10^{10}$  (N/m<sup>2</sup>);  $\nu^{(2)} = 0.23$ ;  $c_{11}^{(2)} = 46.88 \cdot 10^{10}$  (N/m<sup>2</sup>),  $c_{12}^{(2)} = 14.22 \cdot 10^{10}$  (N/m<sup>2</sup>);  $\varepsilon^{(2)} = \varepsilon^{\text{eff}} = 10\varepsilon_0$ . For the representative volume, we take  $8m \times 8m \times 8m$  element structures with number m = 3, which provide close convergence of the computational results.

We are going to analyze the relative effective moduli. For example,  $r(c_{\alpha\beta}^{Eeff}) = c_{\alpha\beta}^{Eeff} / c_{\alpha\beta}^{E}$ are the values of the effective moduli  $c_{\alpha\beta}^{Eeff}$ , related to the corresponding values of the moduli  $c_{\alpha\beta}^{E}$  for the dense piezoceramic without inclusions, and so on.

Table 1 shows the effective elastic stiffness moduli with a different percentage of inclusions for  $u\varphi$ -problems (7) – (15),  $\sigma\varphi$ -problems (7) – (9), (17) – (22), uD-problems (7)–(9), (23) – (28), and  $\sigma D$ -problems (7) – (9), (29) – (34).

Relative	Boundary	Percentage of inclusions					
moduli	problem	10	20	30	40	50	60
	uφ	1.128	1.261	1.406	1.581	1.767	1.931
$r(e^{E \operatorname{eff}})$	$\sigma \varphi$	1.116	1.222	1.352	1.502	1.676	1.837
$r(c_{11})$	иD	1.128	1.261	1.407	1.581	1.767	1.933
	$\sigma D$	1.115	1.225	1.352	1.505	1.683	1.842
	uφ	1.047	1.098	1.146	1.198	1.254	1.310
$r(e^{E \operatorname{eff}})$	$\sigma \varphi$	1.051	1.102	1.157	1.208	1.275	1.314
$r(c_{12})$	иD	1.047	1.098	1.146	1.198	1.254	1.311
	$\sigma D$	1.049	1.108	1.153	1.210	1.284	1.316
$r(c_{13}^{E\mathrm{eff}})$	$u\varphi$	1.048	1.099	1.147	1.191	1.250	1.295

Table 1. Relative values of effective elastic stiffness moduli

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	$\sigma \varphi$	1.054	1.101	1.168	1.208	1.254	1.318
	иD	1.049	1.100	1.147	1.190	1.247	1.289
	$\sigma D$	1.051	1.098	1.157	1,197	1.245	1.297
	uφ	1.193	1.391	1.618	1.843	2.083	2.337
$r(e^{E \operatorname{eff}})$	$\sigma \varphi$	1.170	1.315	1.529	1.713	1.932	2.179
$(c_{33})$	иD	1.195	1.397	1.629	1.860	2.101	2.367
	$\sigma D$	1.176	1.335	1.556	1.759	1.984	2.259
	$u \varphi$	1.336	1.708	2.134	2.542	3.055	3.550
E  eff	$\sigma \varphi$	1.278	1.564	1.896	2.250	2.697	3.157
$r(c_{44})$	иD	1.341	1.725	2.159	2.580	3.106	3.608
	$\sigma D$	1.294	1.595	1.972	2.341	2.815	3.328

Tables 2, 3 and 4 present similar results for effective piezoelectric moduli (stress coefficients)  $e_{31}^{\text{eff}}$ ,  $e_{33}^{\text{eff}}$ , and  $e_{15}^{\text{eff}}$ , effective dielectric permittivity moduli  $\varepsilon_{11}^{S\text{eff}}$ ,  $\varepsilon_{33}^{S\text{eff}}$ , and effective piezoelectric moduli (charge coefficients)  $d_{31}^{\text{eff}}$ ,  $d_{33}^{\text{eff}}$ , and  $d_{15}^{\text{eff}}$ , respectively. Note that the values of piezoelectric charge coefficients have a significant influence on the performance of piezoelectric devices, especially for hydroacoustic applications.

Table 2. Rela	ative values	of effective	piezoelectric	moduli	(stress	coefficients)

Relative	Boundary	Percentage of inclusions					
moduli	problem	10	20	30	40	50	60
	uφ	0.956	0.907	0.830	0.727	0.620	0.509
$r(a^{\text{eff}})$	$\sigma \varphi$	0.977	0.936	0.909	0.814	0.693	0.624
$r(e_{31})$	иD	0.959	0.914	0.834	0.727	0.610	0.470
	$\sigma D$	0.968	0.909	0.863	0.758	0.626	0.520
	uφ	0.897	0.788	0.676	0.574	0.473	0.376
$r(a^{\text{eff}})$	$\sigma \varphi$	0.909	0.828	0.723	0.641	0.545	0.448
$r(e_{33})$	иD	0.892	0.778	0.659	0.547	0.444	0.324
	$\sigma D$	0.900	0.806	0.689	0.588	0.487	0.351
	uφ	0.898	0.787	0.660	0.572	0.468	0.347
$r(a^{\text{eff}})$	$\sigma \varphi$	0.912	0.822	0.719	0.639	0.527	0.433
$(e_{15})$	иD	0.893	0.772	0.638	0.541	0.425	0.298
	$\sigma D$	0.903	0.798	0.675	0.584	0.459	0.339

Table 3. Relative values of effective dielectric permittivity moduli

Relative	Boundary		Percentage of inclusions				
moduli	problem	10	20	30	40	50	60
	uφ	0.872	0.741	0.608	0.511	0.415	0.308
$r(c^{S \text{ eff}})$	$\sigma \varphi$	0.875	0.755	0.619	0.528	0.435	0.325
$(z_{11})$	иD	0.867	0.727	0.589	0.484	0.378	0.268
	$\sigma D$	0.870	0.736	0.600	0.497	0.389	0.279
	uφ	0.883	0.765	0.652	0.551	0.454	0.364
$r(c^{S \text{ eff}})$	$\sigma \varphi$	0.887	0.775	0.665	0.569	0.472	0.382
$(a_{33})$	иD	0.880	0.758	0.640	0.532	0.434	0.323
	$\sigma D$	0.882	0.765	0.647	0.543	0.443	0.329

Relative	Boundary	Percentage of inclusions					
moduli	problem	10	20	30	40	50	60
	uφ	0.645	0.444	0.304	0.210	0.146	0.100
$r(d^{\text{eff}})$	$\sigma \varphi$	0.690	0.517	0.374	0.271	0.188	0.137
$r(a_{31})$	иD	0.641	0.438	0.297	0.201	0.139	0.087
	$\sigma D$	0.675	0.488	0.344	0.239	0.161	0.104
	uφ	0.650	0.448	0.306	0.214	0.150	0.103
$r(d^{\text{eff}})$	$\sigma \varphi$	0.692	0.521	0.370	0.273	0.194	0.138
$(a_{33})$	иD	0.645	0.440	0.297	0.203	0.140	0.087
	$\sigma D$	0.676	0.492	0.340	0.240	0.166	0.103
	$u \varphi$	0.672	0.461	0.309	0.225	0.153	0.098
$r(d^{\rm eff})$	$\sigma \varphi$	0.714	0.526	0.379	0.284	0.195	0.137
$(a_{15})$	иD	0.666	0.447	0.295	0.210	0.137	0.083
	$\sigma D$	0.697	0.500	0.342	0.249	0.163	0.102

Table 4. Relative values of effective piezoelectric moduli (charge coefficients)

For piezocomposite with soft inclusions, we have obtained the following results. The models  $(u\varphi)$  and (uD), in which fixation conditions are pointed out, are more rigid than the models  $(\sigma\varphi)$  and  $(\sigma D)$ , in which mechanical stresses are fixed. Therefore, the effective stiffness moduli for models with specified displacements are greater than for models with specified stresses, i.e.  $(c_{\alpha\beta}^{E \text{ eff}})_{\sigma\xi} < (c_{\alpha\beta}^{E \text{ eff}})_{u\xi}, \quad \xi = \varphi, D$ . At the same time, the influence of electric boundary conditions on the stiffness moduli is extremely insignificant.

For effective dielectric permittivity moduli the following inequalities hold:  $(\varepsilon_{ii}^{S \text{ eff}})_{uD} < (\varepsilon_{ii}^{S \text{ eff}})_{u\varphi} < (\varepsilon_{ii}^{S \text{ eff}})_{u\varphi}$ . Thus, the dielectric constants are the highest for the model with specified stresses and electric potential. Note that the differences in the values of the effective dielectric permittivity moduli increase as the percentage of the non-piezoelectric phase increases.

The inequalities for effective piezoelectric stress coefficients somewhat differ from their inequalities for effective dielectric permittivity moduli:  $(e_{33}^{\text{eff}})_{uD} < (e_{33}^{\text{eff}})_{u\varphi} < (e_{33}^{\text{eff}})_{\sigma D} < (e_{33}^{\text{eff}})_{\sigma \varphi}$ ,  $(e_{15}^{\text{eff}})_{uQ} < (e_{15}^{\text{eff}})_{uQ} < (e_{15}^{\text{eff}})_{u\varphi} < (e_{15}^{\text{eff}})_{\sigma \varphi}$ ,  $(|e_{31}^{\text{eff}}|)_{u\varphi} < (|e_{31}^{\text{eff}}|)_{\sigma D} < (|e_{31}^{\text{eff}}|)_{\sigma \varphi}$ . It can be seen that both the values of the piezomoduli and the values of the dielectric constants are maximum for the  $\sigma \varphi$ -problem. The differences in the values of the effective piezoelectric stress coefficients also increase as the fraction of the elastic inclusions increases.

The inequalities for nonzero effective piezoelectric charge coefficients almost repeat the corresponding inequalities for effective piezoelectric stress coefficients:  $(|d_{i\alpha}^{\text{eff}}|)_{uD} < (|d_{i\alpha}^{\text{eff}}|)_{u\varphi} < (|d_{i\alpha}^{\text{eff}}|)_{\sigma D} < (|d_{i\alpha}^{\text{eff}}|)_{\sigma \varphi}$ . Note that the choice of boundary conditions has the greatest influence on the piezoelectric charge coefficients, and the relative differences between the values of these piezomoduli can reach 50 %.

#### **6.** Conclusions

Thus, in present paper we develop the effective moduli method and finite element technique in accordance with [20, 21]. To find the effective moduli of an inhomogeneous body, we set four static piezoelectric problems for a representative volume. These problems differ by the boundary conditions, which are set on the representative volume surfaces, and which guarantee the constant values of electric displacements, strains, stresses and electric fields for homogeneous material. Special formulas are derived to calculate the effective moduli of piezoelectric media with arbitrary anisotropy. Based on these formulas, we find the full set of Finite element modelling of ceramomatrix piezocomposites by using effective moduli method with...

effective moduli for ceramic polycrystalline piezocomposites using finite element method. The finite element computations were implemented using the computation package ANSYS, and specially developed computer programs were written in macrolanguage APDL ANSYS. At that, the generation of the granular structures for representative volumes was carried out using separate finite element software ACELAN-COMPOS.

As a representative volume, we consider a cube evenly divided into cubic piezoelectric finite elements. At the first stage, depending on the given percentage of inclusions the material properties, selected by special granular algorithm ACELAN-COMPOS finite elements, are modified to the properties of inclusions. Further from the solutions of homogenization problems, we determine the effective moduli of the piezocomposite made of piezoceramics and crystallites. To provide an example, we consider polycrystalline piezoceramics with sapphire ( $\alpha$ -corundum) crystallites Al<sub>2</sub>O<sub>3</sub> as inclusions. The effective moduli for inclusions are calculated as the average moduli of monophase polycrystallite of trigonal system. The results of calculations give the full set of effective moduli.

We note that the results obtained here differ from the results presented in [16,30,31]. In particular, we did not obtain a growth of the piezoelectric modulus  $d_{33}^{\text{eff}}$  in the range of 0–20 % of the inclusions. These differences are due to that the porous ceramomatrix composites were studied in [16,30,31]. Thus, the optical photomicrographs of the polished surface of these piezocomposites, obtained in the Research Institute of Physics from Southern Federal University [16,30], are shown in Fig. 3.





Fig. 3. Optical photomicrographs of porous ceramomatrix piezocomposites with different percentage of inclusion

From these figures, it can be seen that the pores in piezoceramics are ten times smaller than the sizes of crystallites. Therefore, for such complex three-phase material the homogenization can be carried out in two stages. At the first stage, the effective moduli of porous piezoceramics can be calculated, and at the second stage, the effective moduli of two-phase composite ceramic/crystallites can be determined. Then, for modelling the porous piezoceramics, one can use the models developed in [32–35], where pores were considered as voids, as well as the models of inhomogeneous polarization near the pore boundary [20]. We plan that these approaches will be the subject of further research.

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### GEOMETRY OF GaAs NANOWIRE SEEDS IN SiO<sub>x</sub>/Si (111) TEMPLATES

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Abstract. We present an energetic model to describe the initial stage of growth of GaAs nanowire seeds in  $SiO_x/Si$  (111) templates. The model explains the experimentally observed geometry of GaAs seed crystal emerging from Ga droplets in the holes, with either stepwise or ring geometry at the outer periphery of the holes and restricted by the steps that are much larger than monoatomic. Understanding and controlling this geometry is crucial for further growth of nanowires, improving their vertical yield and optimizing the morphology and crystal structure.

Keywords: GaAs nanowires, Ga droplet, elastic stress relaxation, surface energy, silicon templates

#### **1. Introduction**

Epitaxial growth of III-V nanowires [1] and other elongated structures [2] on silicon substrates may enable excellent crystal quality which is unattainable in thin films or even quantum dots [3]. Self-assisted, or self-catalyzed vapor-liquid-solid (VLS) growth of GaAs nanowires on Si (111) substrates, promoted by gallium droplets [4-8], has recently emerged as a gold-free alternative of a more traditional gold-catalyzed VLS growth [9-12], selective area epitaxy [13] or self-induced growth of nanowires [14]. During self-catalyzed growth of GaAs nanowires in lithographically defined templates in SiO<sub>x</sub>/Si (111) substrates, the liquid gallium droplets are pre-deposited and then GaAs nanowire seeds nucleate from thee droplets in the holes. This initial stage of GaAs nanowire arrays, such as the vertical yield, morphology and crystal structure [15-17]. In this work, we try to understand the unusual geometry of GaAs underneath gallium droplets in the holes, with either stepwise or ring geometry at the outer periphery of the holes and restricted by the steps that are much higher than monoatomic [17].

#### 2. Model

In the standard VLS growth of developed nanowires far away from the substrate, theoretical considerations [18-20] and *in situ* growth monitoring [21,22] reveal mononuclear formation of planar nanowire monolayers which proceeds layer-by-layer so that the flowing steps are always monoatomic. However, the VLS growth within the holes is different – first, GaAs crystal nucleates on the lattice mismatched silicon substrate and, second, the crystal has lateral solid-solid interface with the SiO<sub>x</sub> mask rather than free sidewalls in contact with vapor.



**Fig. 1.** Schematics of the geometry of GaAs growing from liquid gallium in a SiO<sub>x</sub>/Si (111) hole. The hole walls are SiO<sub>x</sub> and the bottom is silicon. The opening angle  $\varphi$  can vary from 0

to  $\pi$  depending on the gallium droplet and seed size. The GaAs crystal is a section of cylindrical ring (or the full ring at  $\varphi = \pi$ ) of height *h* and width *W*, with the aspect ratio w/h

Initially, the gallium droplet may occupy a part of the hole (for smaller gallium volumes) or completely fill the hole (for larger gallium volumes) as shown schematically in Fig. 1. In the former case, the gallium droplet should be positioned at the edge of the hole for surface energetic reasons [23]. The initial droplet volume can be characterized by the angle  $\varphi$  showing which portion of the hole bottom is covered with liquid gallium ( $\varphi < \pi$  for incomplete and  $\varphi = \pi$  for complete filling). Assuming cylindrical geometry, we consider free energy of forming a GaAs crystal at the outer periphery of the hole, with the opening angle  $2\varphi$  ( $\varphi < \pi$  corresponds to incomplete and  $\varphi = \pi$  to complete ring), width w and height z (see Fig. 1), at a fixed volume of GaAs. The latter is given by V = zS, where  $S = \varphi r^2 - \varphi (r - w)^2 = \varphi r^2 x (2 - x)$  is the surface area of the base and x = w/r is the width of the crystal divided to the hole radius r = d/2 (the case  $x \to 0$  corresponds to planar growth on the inner sidewalls of SiO<sub>x</sub> and x = 1 to planar growth on the silicon bottom. Disregarding the volume term with chemical potential (which is the same for any configuration of the GaAs crystal at a fixed V), we can write

$$\Delta G = \frac{\lambda \varepsilon_0^2 V}{1 + Az / w} + 2\varphi r z (\gamma_{GaAs-SiO_x}^* - \gamma_{SiO_x-Ga}^*) + 2w z \gamma_{GaAs-Ga}^* + 2\varphi (r - w) z \gamma_{GaAs-Ga}^*$$

$$+ S (\gamma_{GaAs-Si} + \gamma_{GaAs-Ga} - \gamma_{Si-Ga}).$$

$$(1)$$

Here, the first term describes the elastic energy contribution induced by the lattice mismatch between GaAs and Si [24-27], with  $\lambda = 1.4 \times 10^{11}$  J/m<sup>3</sup> as the effective elastic modulus of bulk GaAs,  $\varepsilon_0 = 0.04$  at the lattice mismatch, and  $A \cong 7.5$  as the relaxation coefficient [26]. Very importantly, coherent growth of GaAs on silicon requires the radius of the GaAs crystal to be smaller than the critical radius of 53 nm [27], which is fulfilled under the experimental conditions of Ref. [17] and hence all GaAs NWs should be free of dislocations at the base. The next three terms stand for the surface energies of vertical

sidewalls of GaAs, with  $\gamma^*$  representing the surface energies of the corresponding vertical interfaces as shown in Fig. 1 (the GaAs-SiO<sub>x</sub> and GaAs-Ga surfaces are created and the SiO<sub>x</sub>-Ga one is eliminated upon nucleation). The last term stands for the in-plane surface energy change, with  $\gamma$  representing the surface energies of the corresponding in-plane interfaces (the GaAs-Si and GaAs-Ga surfaces are created and the Si-Ga one is eliminated upon nucleation).

Introducing dimensionless free energy  $f = \Delta G / (\lambda \varepsilon_0^2 V)$ , after some simple manipulations we get

$$f(x) = \frac{\varphi x^2 (2-x)}{\varphi x^2 (2-x) + AV / r^3} + \frac{\varphi a + (1-\varphi)bx}{\varphi x (2-x)} + \frac{r^3}{V} c \varphi x (2-x),$$
(2)

with the control parameters

$$a = \frac{2\Delta\gamma_*}{\lambda\varepsilon_0^2 r}, b = \frac{2\gamma_{GaAs-Ga}}{\lambda\varepsilon_0^2 r}, c = \frac{\Delta\gamma}{\lambda\varepsilon_0^2 r},$$
(3)

 $\Delta \gamma_* = \gamma^*_{GaAs-SiO_x} + \gamma^*_{GaAs-Ga} - \gamma^*_{SiO_x-Ga}$  as the vertical and  $\Delta \gamma = \gamma_{GaAs-Si} + \gamma_{GaAs-Ga} - \gamma_{Si-Ga}$  as the in-plane surface energy change. When  $x \ll 2$ , Eq. (2) is simplified to

$$f(x) = \frac{\varphi x^2}{\varphi x^2 + Av} + \frac{a}{2x} + \frac{c\varphi x}{v},$$
(4)

where we do not write an unimportant *x*-independent constant. The parameter  $v = V/(2r^3) \cong \pi(V/V_{hole})$  is proportional to the ratio of the GaAs volume to the effective total volume of the hole  $V_{hole} = 2\pi r^3$  at the hole height h = 2r corresponding to the hole aspect ratio of 1. Clearly, the *x* dependence of the free energy given by Eq. (4) is controlled by five parameters, the volume coefficient  $v \ll 1$ , the elastic energy relaxation *A*, the opening angle  $\varphi$ , and the two surface energy coefficients *a* and *c* describing the changes of the vertical and in-plane surface energies upon nucleation of a GaAs crystal in the hole. The case  $c \ll 0$ , a > 0 corresponds to the situation where GaAs initially wets the Si substrate but not the SiO<sub>x</sub> walls of the hole [25], consistent with the fact that GaAs crystals grow in two-dimensional (2D) form on silicon and as irregular three-dimensional (3D) crystals on SiO<sub>x</sub> [15,16].

#### 3. Results and discussion

The energetically preferred configuration  $x_0$  is now determined by the minimum of f(x) in Eq. (4) for a given set of parameters. If we assume  $va/(2\varphi) \ll |c|$ , the minimum at intermediate x appears due to the elastic energy term in Eq. (4) for sufficiently large GaAs volumes when  $Av \gg \varphi x^2$  and corresponds to the ring width

$$w_0 \cong \frac{A|\Delta \gamma|}{\lambda \varepsilon_0^2}.$$
(5)

With the known A and  $\lambda \varepsilon_0^2$ , the experimentally observed ratio  $\omega_0 / r \cong 0.25$  for r=30 nm corresponds to a plausible  $\Delta \gamma = -0.225$  J/m<sup>2</sup>. Figure 2 shows the free energy as a function of x for the full ring geometry of GaAs ( $\varphi = \pi$ ) with these parameters and at  $\Delta \gamma_* = 0.05$  J/m<sup>2</sup>, corresponding to a/2 = 0.0074 and c = -0.033, for different values of  $V/V_{hole}$ .

These graphs show the following major properties. For very small GaAs volumes (the curve at  $V/V_{hole} = 0.02$ ), the energetically preferred configuration is 2D GaAs layer. As the GaAs volume increases, the free energy acquires the local minimum at  $x \approx 0.2$  for the

parameters considered, which becomes global at a slightly larger  $x_0 \cong 0.23$ , corresponding to the energetically preferred width  $w_0 \cong 0.23R$ , as observed in the experiments of Ref. [17]. Further increase of the GaAs volume does not affect the position of the energy minimum. According to Eq. (5), the width of the ring does not depend on the opening angle, yielding the same width for differently sized gallium droplets in the holes. The height of the rings  $h_0 = V/(\varphi R^2 x_0)$  increases linearly with the GaAs volume and becomes larger for smaller  $\varphi$ .



**Fig. 2**: Free energy versus relative width of full GaAs rings ( $\varphi = \pi$ ) for different  $V/V_{hole}$  values (lowest curve -  $V/V_{hole} = 0.02$ , highest curve -  $V/V_{hole} = 0.15$ ), showing the collapse to a volume-independent preferred configuration corresponding to the minimum free energy at  $x_0 \approx 0.23$ 

In conclusion, our analytic model correctly describes the experimentally observed shapes of GaAs nanowire seed crystals nucleating from gallium droplets in  $SiO_x/Si$  (111) templates. These results are also supported by a more detailed numerical modeling [17]. A combination of the elastic energy relaxation due to the lattice mismatch between GaAs and Si (111) substrate and the surface energy constrains leads to the unusual geometry of GaAs crystals in the form of either steps or rings whose heights are much larger than monoatomic. These results can further be used as the initial condition for the description of subsequent time evolution of the GaAs nanowire morphology starting from the holes.

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## NUMERICAL SIMULATION OF HYPERVELOCITY IMPACTS OF VARIOUSLY SHAPED PROJECTILES WITH THIN BUMPERS

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**Abstract.** The paper presents a numerical simulation of hypervelocity impacts of variously shaped projectiles with thin bumpers. A numerical model was verified using a full-scale experiment of hypervelocity impact of a sphere with thin aluminum-alloy bumper. Hypervelocity impacts of nonspherical projectiles of different spatial orientation with thin bumpers were also numerically investigated. The investigations show that a hypervelocity impact of a nonspherical projectile advancing with its sharp edge towards the bumper results in a denser debris cloud formation and, therefore, such an impact is more dangerous than any of other considered cases for the spaced protection.

**Keywords:** hypervelocity impact, space debris, non-spherical projectiles, debris clouds, Whipple shields

#### **1. Introduction**

A quantity of space debris in the near-Earth space is growing in geometric progression [1,2]. Such debris consists of used rocket stages, colliding fragments of spent satellites, etc. Fast and aggressive space development makes protection of space equipment, manned and unmanned space vehicles against hypervelocity impacts in the space very important.

Whipple shields, two or more rigid thin bumpers spaced at a certain distance from each other, are used for protection of the International Space Station against micrometeoroids and man-made debris. The main idea of such spaced multilayer protection is that a hypervelocity projectile breaks and disperses after the interaction with the first bumper. A debris cloud resulted from that impact expands and interacts with the next bumper at a larger area, thus the load intensity of the next bumper significantly decreases [4]. Front bumpers of Whipple shields used at the ISS (International Space Station), about 1-2 mm thickness, are made of heat-strengthened aluminum-alloy, the spaces between the bumpers are filled with layers of woven materials made of aramid and ceramic fibers; the back bumpers are made of aluminum-alloy of about 3-4 mm thickness [5].

For full-scale experimental studies of hypervelocity impacts, projectiles are accelerated mainly by multistage light gas guns. Such studies require many financial and labor expenditures; moreover, with that method of acceleration, it is very hard to achieve a projectile velocity higher than 11-12 km/s. However, velocities of space debris/micrometeoroids impacts can exceed 15 and 30 km/s correspondingly. Therefore, the quantity and quality of full-scale experiments are limited. From another hand, numerical simulations are free from the above-mentioned disadvantages; it is a cost-efficient, visual and

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descriptive method of hypervelocity impact investigations. The numerical simulation can result in new geometrical shapes and configurations of the bumpers allowing efficiently absorbing the energy of projectiles of a considerable range of velocities, shapes, and dimensions. Moreover, a shape of debris clouds and their energy, after passing the front bumper, can be studied with a high time resolution, which is very valuable from the scientific point of view. The numerical investigation of the debris cloud dynamics, its propulsion and expansion velocities, mass distribution of debris in the cloud can allow to formulate requirements to a multilayer shield protection more accurately.

# **2.** Verification of numerical simulation of hypervelocity impact of spherical projectile with thin bumper

The numerical simulation of a hypervelocity impact of spherical projectiles with a thin bumper was performed using smoothed particles hydrodynamics method [6]. This grid-free Lagrangian method is widely used for describing hypervelocity impact processes; numerical data obtained using this method are in good agreement with known full-scaled experiments [7,8]. Johnson-Cook plasticity and damage equations [9] were applied to describe a behavior of projectiles and bumpers made of aluminum alloys. In the plasticity equation von Mises flow stress Y depends on strain  $\varepsilon_p$ , strain rate  $\varepsilon_p^*$  and homologous temperature of the material  $T_g$  which depends on temperature T, initial temperature  $T_0$  and melting temperature  $T_m$ :

$$Y = \left[A + B\varepsilon_p^n\right] \left[1 + C\ln\varepsilon_p^*\right] \left[1 - T_g^m\right],\tag{1}$$

$$T_g = \frac{T - T_0}{T_m - T_0}.$$
 (2)

A failure criterion – critical strain  $\varepsilon^{f}$ , is a function of pressure, strain rate and homologous temperature  $(D_1, D_2, D_3, D_4, D_5, -$  empirical coefficients):

$$\varepsilon^{f} = \left[ D_{1} + D_{2} e^{D_{3}\sigma} \left[ 1 + D_{4} \ln \varepsilon_{p}^{*} \left[ 1 + D_{5} T_{g} \right] \right].$$

$$(3)$$

The material failure occurs when *D* is equal to 1:

$$D = \sum \frac{\Delta \mathcal{E}}{\mathcal{E}^f}.$$
(4)

For a projectile made of aluminum Al 1100, the equation of state has a form of the Mie–Gruneisen equation assuming linear dependence of pressure P on internal energy E. For the shock-compressed material, the pressure was found from:

$$P = \frac{\rho_0 c^2 \mu \left[ 1 + \left( 1 - \frac{\gamma_0}{2} \right) \mu \right]}{\left[ 1 - (S_1 - 1) \mu \right]^2} + \gamma_0 E,$$
(5)

where c – the sound velocity in the material,  $\gamma_0$  – the Gruneisen parameter of the material. For the expanding material the pressure was found from:

$$P = \rho_0 c^2 \mu + \gamma_0 E \,. \tag{6}$$

For an Al 6061-T6 heat-strengthen aluminum alloy bumper the equation of state was in the form of a linear polynomial ( $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$  - coefficients):

$$P = C_1 \mu + C_2 \mu^2 + C_3 \mu^3 + C_4 E.$$
(7)

Parameter  $\mu$  is the ratio of material density  $\rho$  to its initial density  $\rho_0$ :

$$\mu = \frac{\rho}{\rho_0} - 1. \tag{8}$$

The approach to plasticity and failure description was made in favor of Johnson-Cook equations because they allow taking into account strain rate and softening temperature including a phase transition. It is important to take into account those factors because at a hypervelocity impact materials of a projectile and a bumper can melt and evaporate. For example, at more than 3 km/s impact velocity interacting aluminum objects partially melt; at more than 7 km/s impact velocity the projectile fully melts [10].

Parameter	Unit	Al 1100	Al 6061-T6
Initial density, $\rho_0$	kg/m <sup>3</sup>	2770	2750
Yield stress, A	Pa	$4.1 \times 10^{7}$	$3.241 \times 10^{8}$
Strain hardening constant, B	Pa	$1.25 \times 10^{8}$	$1.138 \times 10^{8}$
Strain hardening coefficient, n		0.183	0.42
Strain rate constant, C		0.001	0.002
Thermal softening coefficient, m		0.859	1.34
Initial temperature, $T_0$	K	293	293
Melting temperature, $T_m$	K	893	893
Fracture coefficients, $D_1$		0.071	-0.77
$D_2$		1.248	1.45
$D_3$		-1.142	-0.47
D <sub>4</sub>		0.0097	0
$D_5$		0	1.6

Table 1. Parameters of materials in plasticity and failure equations

The projectile and the bumper melting and evaporating at a hypervelocity impact increase the protection efficiency. As it is shown in [11], at 7.4 km/s velocity of the copper projectile the copper bumpers are most weight efficient; they have 30% less surface density than the aluminum bumpers with similar protective characteristics. It happens because a copper projectile melts and evaporates most intensively when it interacts with a copper bumper. The chosen equations are widely used for numerical simulations of material impulse loading processes. Therefore, parameters of materials given in Tables 1, 2, 3 for calculations were taken from known sources [12,13].

Table 2. Coefficients in	the equation of state fo	r Al 6061-T6	
			Т

$C_1$ , GPa	C <sub>2</sub> , GPa	<i>C</i> <sub>3</sub> , GPa	$C_4$
74.2	60.5	36.5	1.96

#### Table 3. Coefficients in the equation of state for Al 1100

<i>c</i> , m/s	$S_I$	γo
3935	1.578	1.69

The numerical model used in the calculations in this work was verified using the known full-scale experiment. In the paper [14] the experiment of a hypervelocity impact between 5.01-mm ball and 1-mm thick bumper was described. The bumper was made of aluminum alloy Al 6061-T6, and the projectile was made of aluminum Al 1100. The mass of the projectile was 0.18 g. In the full-scale experiment, the impact was at the 90° angle to the bumper surface and the impact velocity was in the range of 4.17-4.33 km/s. The shadowgraphs of the debris cloud forming at the impact and expanding in time were taken at

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various moments of time – up to 40  $\mu$ s after the impact. Therefore, the model parameters were chosen so that the numerical calculation results were in the best agreement with the experimental data.

The hypervelocity impact between a 5.01-mm ball of 0.18g mass and made of Al 1100 and a plane bumper of 1 mm thickness made of Al 6061-T6 was numerically simulated. The impact was at 4.19 km/s velocity and perpendicular to the bumper surface. All simulations were performed in 3D formulation.



**Fig. 1.** Debris cloud formed 16 µs and 24 µs after the impact, side view. Spherical Al 1100 projectile with velocity of 4.19 km/s, Al 6061-T6 bumper with thickness of 1 mm

Figure 1 presents images (side views) of the debris clouds resulted from the impacts at 16  $\mu$ s and 24  $\mu$ s moments of time and initial state of the problem (0  $\mu$ s). The numerical calculation is in good agreement with the full-scale experimental data. The main mass of

debris is concentrated in a head part of the cloud. The images obtained in both the full-scale and numerical experiments show the characteristic "bulge" in the head part (vanguard) of the debris cloud. The numerical simulation allows distinctly distinguishing materials of the projectile and the bumper and track dynamics of the bulge generation and development frame-by-frame with  $10^{-8}$  s time resolution.



**Fig. 2.** "Bulge" development in the debris cloud vanguard. Positions of fragments, belonging to the back surface of the sphere are pointed out. Spherical Al 1100 projectile with mass of 0.18 g and velocity of 4.19 km/s, Al 6061-T6 bumper with thickness of 1 mm

The numerical calculations show that the bulge in the vanguard of the debris cloud consists of projectile particles gathered into a dense group and advancing along the impact trajectory. At 2.5 µs (Fig. 2) the projectile debris has formed rather a dense group of the shape reminding the initial shape of the projectile. That group has a mixed phase composition; the debris are in both liquid and solid phases there. In time, the solid fragments from the remote surface of the projectile are outrunning the main mass of the debris in the vanguard and forming the bulge in the head part of the cloud. It happens because these fragments are moving with higher longitudinal velocity than the bumper debris and other debris of the projectile. The similar bulge was observed in [15,16] under alike initial conditions - impact velocity, projectile diameter and bumper thickness, but the projectile and the bumper were made from a different grade of aluminum. By all appearance, for such a bulge formation the projectile material should have less density and ultimate strength than the bumper material. Under that condition, 4.19 km/s impact velocity is not enough for complete melting of the projectile and the remote part of it remains in the solid phase [17]. The evaporated and melted material is expanding rather evenly with the cloud advancement, whereas the solid particles remain on the impact axis. Exactly those particles are the biggest threat for the spaced multilayer bumper protection.

At 16  $\mu$ s moment of time the cloud length/diameter ratio in the widest part is 1.58 mm (the numerical calculation) and 1.53 mm (the full-scale experiment), the error is less than 3.5%. At 24  $\mu$ s moment the length/diameter ratio is 1.58 mm (numerical calculation) and 1.59 mm (the full-scale experiment), the error is less than 0.5%. With inaccuracy of the geometric dimensions measuring taken into the account, it is fair to conclude that the numerical calculation error in comparison with the full-scale experiment is less than 4%. From the equality of the cloud's geometric dimensions (length and diameter) at the same moments of time, we can conclude that relations of the expansion velocity in longitudinal and

transverse directions are equal in both full-scale and numerical experiments. The diameter values of the crater forming on the bumper are also in satisfactory agreement. In the numerical calculation, it is 11.3 mm, in the full-scale experiment -11 mm. The vanguard cloud velocity is 3.74 km/s in the calculation and 3.8 km/s in the full-scale experiment. In general, the numerical simulation has been performed with satisfactory accuracy, therefore, the selected approach and the material parameters can be used for investigation of hypervelocity impacts between projectiles and bumpers of other configuration.

#### 3. Simulation of non-spherical projectiles impact with thin bumper

A spherical shape of the projectile is a simplification, in real life space debris colliding with space vehicles can be of various shapes. Numerical calculations allow investigating hypervelocity impacts of projectiles of various shape and spatial orientation and comparing differences and characteristics of debris clouds formed in various cases. With the help of the verified model, a hypervelocity impact of a cylindrical projectile (its diameter is equal to its length) on a thin bumper has been simulated. The impact velocity, projectile material (Al 1100), bumper material (Al 6061-T6), bumper thickness (1 mm) and projectile mass (0.18 g) are identical to the verified case. Therefore, results of impacts of projectiles with the same kinetic energy but of various shapes can be compared; and it is possible to determine the distinctive features of debris clouds formed as a result of the impacts of various projectiles.



Fig. 3. The debris cloud formed after the impact of 0,18 g cylindrical Al 1100 projectile with 1mm thin Al 6061-T6 bumper at various moments of time. Side view. Projectile velocity – 4.19 km/s, projectile mass – 0.18 g, bumper thickness – 1 mm. (Note, that in the side view of three-dimensional problem cylinder with its diameter equal to length looks like a cube)

At the initial stage of the debris cloud formation, the symmetric outer cone of particles of rear bumper surface is formed on the impact axis (Fig. 3). In time, the outer cone is expanding and a dense debris group, rather evenly distributed on the cloud front surface, is

following it. The debris mass advancing along the impact axis is approximately 20% out of the initial projectile mass. The debris vanguard on the front surface is expanding evenly with the cloud advancement. The debris cluster on the impact axis following the cone is less subjected to the expansion and preserves practically all its mass during the simulated period (0-12  $\mu$ s). Thus, that cluster is the most dangerous part of the debris cloud for the spaced bumper protection against the cylindrical projectile impact.

Similar debris cloud characteristics – the cluster on the impact axis and the leading cone were obtained experimentally in [18]. In that hypervelocity impact experiment, cylindrical projectile was made of Al 2024-T4 and 2 mm thin bumper was made of Al 6061-T6. Most likely, the leading debris cone is formed due to the bumper material spallation. In that case, the initial stage of the bumper destruction has a shock-wave nature induced by shock waves generation in the bumper resulted from the plane shock and rarefaction waves following the shock wave front.

#### 4. Study of cubic projectile orientation effect on results of impact with thin bumper

Axial-symmetric projectiles (cylinders, balls) can be accelerated to space velocities (4-5 km/s and more) by light gas guns. It is simpler to study hypervelocity impacts of projectiles without axial symmetry (projectiles of arbitrary shapes that are closer to real life space debris) numerically. For the extreme case study 3D calculations of a cubic shape projectile with its face and edge orientated toward a thin bumper have been performed.

Initial conditions, mass and velocity of cubic projectiles, projectiles' and bumpers' materials, coincide with those used in the calculations of impacts between the spherical and cylindrical projectiles and the thin bumper. Two cases of hypervelocity impacts have been studied: in the first case, the cube face was parallel to the bumper surface; in the second case, the projectile edge was oriented to the bumper surface.

The development dynamics of the debris cloud in both simulated cases (Fig. 4) has been studied and compared. When the cube impacts by its face, a formed debris cloud is similar to the one resulted from a cylindrical projectile of the same mass and with a diameter equal to the length. Both clouds have similar characteristics– the leading cone and the dense group of the projectile particles with the 20% out of the initial projectile mass in the vanguard of the debris cloud. The characteristic cloud dimensions at 12  $\mu$ s moment of time, such as a length without the leading debris cone and a diameter in the widest part, are approximately equal. The cloud length without the bumper debris cone is 38.5 mm, which is approximately the same as the diameter in the widest part (38 mm).

We observe a different picture when the cube impacts by its edge (Fig. 4). In this case, most of the projectile fragments (more than 50% of the initial mass) are concentrated in the dense group on the impact axis. The diameter of the cloud in the widest part reduces to 24 mm at 12 µs moment of time. In case of the cube face impact, the angle of the debris dispersion is about 30 degrees to the impact trajectory; debris are evenly dispersed on the cloud front surface and form a small compaction on the impact axis. In the case of the cube edge impact, the resulted debris cloud is narrower and oblong. The angle of the debris dispersion is 20 degrees to the impact trajectory; the projectile debris forms a dense group in the center. In this case, the cloud vanguard velocity is 3,9 km/s, which is 7% higher than in the case of the face impact. Such reduction in the debris dispersion area and an increase of the debris velocity reduces the efficiency of spaced multilayer protection. The leading cone of debris is absent due to a constant applied load that prevents the spallation of the rear bumper surface.

The results of calculations show that at hypervelocity impacts of projectiles of nonspherical, cylindrical or cubic, shapes with a protective structure consisting of two spaced bumpers, the load intensity on the second bumper cannot be significantly reduced by increasing the distance between the bumpers. The best solution is to fill the space between the Numerical simulation of hypervelocity impacts of variously shaped projectiles with thin bumpers

bumpers with ballistic materials or with some liquid or gaseous medium [19]. In case of a spherical projectile, projectile and bumper debris are dispersed on the cloud vanguard rather evenly. Such a cloud is expanding to all directions uniformly, therefore increasing the gap between the bumpers we increase the load area. However, in the case of a nonspherical projectile, a dense debris group is formed on the impact axis; this group does not expand considerably in time, and it interacts with the second bumper on the same area independently on the distance between the bumpers. This phenomenon is visualized better in case of the cubic edge impact on the bumper; when more than a half of the initial projectile mass remains on the impact axis. It could be caused by a shorter lifetime of shock waves and fewer pressure values developing in nonspherical projectiles [20]. As a result, the projectile destruction is less intensive; larger fragments are formed that can be seen in the case of the cube sharp edge impact.



**Fig. 4.** Comparison of the debris clouds formed in various moments of time due after hypervelocity impacts of cube Al-1100 projectiles of different spatial orientations with thin Al 6061-T6 bumpers. Side view. Projectile velocity – 4.19 km/s, projectile mass – 0.18 g, bumper thickness – 1 mm. (Note, that in the side view of three-dimensional problem cube oriented with its edge towards the bumper looks like a hexagon)

Comparing images of the debris clouds formed in all cases considered, it is fair to conclude that at a hypervelocity impact of nonspherical particle by their sharp edge with a spaced bumper protection the penetration of the second bumper is most probable. Such a configuration, two bumpers at a certain distance from each other, is much less efficient in protection against space debris of nonspherical shape. Thus, the conclusion made in [21] is confirmed.

#### 6. Conclusions

In general, all results obtained by the calculations are in good agreement with known experimental data. Thus, the model used in this work can be applied to further studies on hypervelocity impacts. The numerical model describing a process of a hypervelocity impact of a spherical projectile on a thin bumper has been verified. Based on the similarity between know experimental results and obtained numerical data, we can conclude that the method applied, equations and material parameters are valid.

The performed calculations show that at a hypervelocity impact of an aluminum ball on a bumper made of a heat-strengthen aluminum alloy, a "bulge" is formed in the cloud vanguard on the impact axis. It consists of material of the remote surface of the projectile. At the hypervelocity face impact of a cylindrical or cubic projectile, a leading cone is formed due to the spallation of rear surface of the bumper.

The calculations of a nonspherical projectile orientation effect on the debris cloud formation have been performed. Two boundary cases – cubic face and cubic sharp edge impacts, have been considered. In case of the face impact, the angle of disperse is higher than in case of the edge impact, and the debris are rather evenly dispersed on the cloud vanguard with small thickness (bulge) on the impact axis. When the cube impacts by its edge, the cloud formed is much narrower, the disperse angle is only 75% of the angle in the face impact case. The debris are dispersed on the vanguard unevenly, more than 50% of the initial projectile mass is concentrated in the dense group on the impact axis, and the cloud vanguard advancement velocity is 10 % higher.

Reduction of the debris dispersion area and an increase of their velocity cause reduction of the bumper protection efficiency. The calculations of hypervelocity impacts of nonspherical projectiles using the verified model show that penetration of two spaced bumpers is most probable in the case when a cubic projectile impacts the bumper by its sharp angle, which is verified by know experimental data. At hypervelocity impact between a nonspherical, cylindrical or cubic projectile (with its sharp edge) and a two spaced bumper protection, the load intensity of the second bumper cannot be significantly reduced by increasing the distance between the bumpers, because the main part of fragments in the debris cloud is propagating along the impact axis.

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### FORMATION OF ORDERED ZnO STRUCTURES GROWN BY THE ALD METHOD ON HYBRID SiC/Si (100) SUBSTRATES

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**Abstract.** Crystalline structure and composition of the ZnO films grown by atomic layer deposition (ALD) on the n- and p-type Si (100) substrates with a SiC buffer layer were studied. The SiC buffer layers have been synthesized by a novel method of atomic substitution (partial chemical replacement) of Si atoms by carbon atoms in the subsurface layer of the Si substrate. A four-component epitaxial texture of ZnO in a direction close to [101] on the n- and p-type (100) Si vicinal substrates with a SiC buffer layer has been revealed and investigated with electron diffraction. Formation mechanism of the epitaxial textures of ZnO was found to depend on the conductivity type (n- or p-type) of the Si (100) substrates. A theoretical model explaining the effect of the texture formation and its dependence on the type of Si substrate conductivity has been proposed. The effect is associated with the transformation of the vicinal Si (100) surfaces into the SiC surfaces during its synthesis by the atomic substitution method. Significant differences have been found between the structures and between the growth mechanisms of the ZnO layers on the SiC/Si (111) and (100) substrates.

Keywords: zinc oxide films, ALD method, silicon carbide; epitaxy; thin film growth

#### **1. Introduction**

This work continues the previous studies [1] of the growth of the zinc oxide (ZnO) films by atomic layer deposition (ALD) on silicon (Si) substrates with silicon carbide (SiC) buffer layers grown by the method of topochemical substitution of atoms [2-4]. Zinc oxide, as is well known, crystallizes in a hexagonal lattice system with lattice parameters a = 0.325 nm and c = 0.521 nm. The Silicon carbide films on the silicon surfaces, which are the substrate for the ZnO layer, were synthesized by the atomic substitution method. Depending on the crystallographic orientation, the Si surfaces can consist of both layers of the cubic SiC phase and layers of the hexagonal phase [5]. On the Si (111) surface, essentially a cubic polytype of 3*C*-SiC is formed [5], on the Si (110) surface, mainly hexagonal polytypes grow, with the 6H-SiC polytype being basically formed and, to a lesser degree, the 4H-SiC polytype [5]. A film consisting of a mixture of various SiC polytypes grows on the (100) Si surface. In [6], it was found that the structure of the surface SiC layers synthesized on the vicinal surfaces of Si (100) substrates deviating from the basic orientation by  $2^{\circ} - 7^{\circ}$  substantially depends on the doping type of the initial silicon substrate. It turned out [6] that in the process of replacing silicon atoms with carbon atoms, singular (100) Si faces transform into a SiC face consisting
of an ensemble of facets resembling sawtooth structures, whose lateral surfaces are covered with (111) planes. These studies showed that on the vicinal p-type Si surface, deviated by  $4^{\circ}$ and more from the singular face (100) during the synthesis of SiC, an ordered phase of SiC is formed, with surface morphology in the form of facets (flakes) consisting of cubic and hexagonal layers. In this case, the planes of the hexagonal facets may have the orientation:  $[1\overline{1}0\overline{2}]; [1\overline{1}00]; [1\overline{1}0\overline{1}]$ . Cubic facets consist of (111) faces and are positioned at an angle of 54°44' to the (100) face. If initially the vicinal surface of the Si (100) substrate was prepared from Si cut at an angle of 4° to the surface (100), for example, towards [011], then after thermal annealing [3,6], such a surface will be covered with an ensemble of steps (011). After topochemical transformation of this surface into the SiC surface, it would be covered by an ensemble of facets with (111) planes (111) located at an angle of 54°44' to the (100) face. Moreover, all facets will be ordered along the [011] direction at an angle of  $\approx 35^{\circ}$  to the (001). Thus, during the synthesis of SiC, a modified SiC surface is formed, structured along the [011] direction. As shown by earlier studies [7], Si substrates with a SiC layer structured in a similar way are good templates for the growth of semi-polar hexagonal AlN and GaN crystals. Such a quasi-stepped surface of a silicon carbide layer stimulates the formation of nuclei of hexagonal semi-polar AlN, and the semi-polar layer of AlN, that in turn stimulates the formation of a semi-polar GaN layer, for example, the  $(1\overline{1}01)$  GaN plane is located at an angle of  $35-47^{\circ}$  with the "C" GaN axis and the (001) SiC plane.

On the vicinal n-type Si surface deviated by an angle of  $4^{\circ}$  or more from the singular (100) face, the process during the synthesis of SiC proceeds differently. On this surface, only the 3*C*-SiC cubic phase is formed, and the density of the (111) facets is not large, and they are very small. As a result, polycrystalline AlN and GaN films grow on vicinal n-type Si surfaces, as a rule, when grown by the method of chloride-hydride epitaxy (HVPE), because the substrate has very few orienting centers, and the differences between the SiC lattice parameters in the plane (100) and the lattice parameters of GaN along its semipolar planes, for example (1101), are rather large. It was shown in [8] that in order to grow semipolar AlN and GaN layers on the faceted the SiC/Si(100) surface, it is necessary to create an AlN nucleus, whose critical size would not exceed the size of the SiC facet. This requires a high growth rate of the AlN layer of the order of 1  $\mu$ m /hour. Otherwise, the polar AlN and GaN layers will grow, which on the SiC/Si (100) surface will have a polycrystalline structure.

In this connection, it is of great interest to find out the differences in the morphology and structure of ZnO layers grown on n and p type Si (100) substrates with a SiC buffer layer. Such a study is very important for finding out the mechanism of growth of the ZnO layer on SiC/Si (100). It should be noted that for comparison, we present some data on the formation of ZnO on SiC grown on Si (111). In this work, we do not consider growth on a pure silicon substrate in since as was shown in [1], ZnO films grown by the ALD method on Si have a polycrystalline structure.

Thus, the aim of the present work is to study the morphology and crystal structure of ZnO layers grown by the ALD method, depending on the orientation of the initial Si substrate and the type of its conductivity.

## 2. Experimental technique

The epitaxial SiC layer was grown on vicinal surfaces, with a deviation of  $4^{\circ}$  from the (100) plane, of the n- and p-type Si (100) substrates. Silicon substrates with a resistivity of 10  $\Omega$ ·cm were used for SiC growth. The growth of SiC was carried out using the new method of chemical substitution of atoms developed in [2–4]. To synthesize a SiC layer by this method, following to [2–4], a topochemical reaction between the single-crystal Si substrate and carbon monoxide CO gas was used.

$$2Si (crystal) + CO (gas) = SiC(crystal) + SiO(gas) \uparrow.$$
(1)

(2)

(3)

The analysis [2-4] showed that reaction (1) splits into two successive stages. Si  $(crystal) + CO(gas) = C + SiO(gas) \uparrow + V_{Si}$ , Si  $(crystal) + C + V_{Si} = SiC(crystal)$ .

Silicon vacancies  $V_{Si}$  play a key role at both stages of transformation [2–6]. In the first stage of reaction (2), they ensure not only the diffusion of the CO reagent to the reaction zone, but also the reaction product of SiO from the reaction zone. In addition, the C atom and the vacancy  $V_{Si}$ , which are formed in pairs in stage (2), have a strong interaction with each other, caused by the overlapping of elastic fields in a medium with cubic symmetry, to which silicon crystal belongs [2-5]. In particular, if these pairs align along the [111] direction, which corresponds to an energy minimum, they form a stable configuration, which we call dilatation dipoles by analogy with electric dipoles. In fact, silicon saturated with such dilatation dipoles (4 dipoles per Si cell) is an intermediate complex or an intermediate phase for almost barrierfree conversion into silicon carbide [9]. Since the SiC cell volume is two times smaller than the Si cell volume, the presence of vacancies here also plays a key role, providing a barrierfree displacement of large regions of the crystal.

Topochemical reaction (1) proceeded in a vacuum furnace at a temperature T = 1280 °C and a pressure of CO  $p_{CO} = 0.4$  Torr for 25 min. An epitaxial SiC film with a thickness of about 50 nm was formed from a mixture of predominantly hexagonal 4*H* and 6*H* polytypes [5]. Under the SiC film in the Si bulk, voids and cavities were formed, caused by the evolution of an ensemble of dilatation dipoles and merely silicon vacancies. They do not affect the SiC quality.

Then, ZnO films were deposited on the obtained Si templates with a buffer layer of SiC by the method of molecular layering. Zinc oxide, as in [1], was obtained by molecular layering [1,10,11] using diethyl zinc ( $Zn(C_2H_5)_2$ ) reagents and deionized water (H<sub>2</sub>O). These substances, having a sufficiently high vapor pressure, were alternately supplied in a stream of nitrogen, which served as the carrier gas. When a substrate was exposed to water vapor, an adsorbed phase of the corresponding OH groups forms on it. During subsequent exposure to diethyl zinc, ZnO structural units are formed on the substrate due to the interaction with OH groups. The sum of these two stages is described by the reaction  $Zn(C_2H_5)_2 + H_2O = ZnO + 2C_2H_6$ . (4)

At a given flow of reagents, the temperature is chosen so that the reagent excess, together with the reaction product  $C_2H_6$ , have time to leave the reactor. The substrate temperature was 250°C. Reactions occur on the substrate surface at high speed, so the film growth is determined mainly by the speed of delivery of the reagent molecules from the gas phase to the substrate surface. The substrate processing time in reagent vapors was  $10^{-2} - 5 \cdot 10^{-2}$ s, purge time was 4-5 s. Thus, the deposition time of one monolayer (one reaction cycle) was about 8–10 s. The thickness of the ZnO films was ~ 200 nm.

The grown ZnO films were studied by scanning electron microscopy, elemental microanalysis, X-ray diffraction and reflection high-energy electron diffraction (RHEED). Elemental analysis and scanning microscopy of the films were carried out on a Zeiss Merlin microscope with a thermopole-left cathode, equipped with an analytical attachment for energy dispersive elemental microanalysis of Oxford Instruments INCA X-Act. The accelerating voltage of the electron beam was 10 kV, and the beam current was 220 pA. An Everhart-Thornley detector and a semiconductor back-scattered electron detector were used to record the images. X-ray diffraction studies were performed with a D8 Discover high resolution diffractometer (Bruker AXS) using a parallel beam of filtered CuK<sub> $\alpha$ </sub> radiation with a point focus and a spot diameter of 0.5 mm. To obtain electron diffraction data, we used an EMR-100 electron diffractometer with an electron energy of 50 keV.

### 3. Research results

**Scanning electron microscopy and elemental analysis.** Figure 1 shows the image of the end sections of the ZnO/SiC /Si (100) samples grown on n-type and p-type Si obtained using a scanning electron microscope.





с

200 nm

Si

On a SiC/Si (100) n-type substrate, a ZnO layer with a thickness of about 170 nm has grown. The thickness of the ZnO layer on a SiC / Si(100) p-type substrate was about 230 nm. The thicknesses of the ZnO layers on SiC /Si(111) n-type and p-type substrates were of the order of 250 nm. The thickness of the SiC layer on n-type Si (100) was ~ 50 nm, the thickness of the SiC layer on p-type Si (100) was ~ 60 nm, the thickness of the SiC layers on n- and p-type Si (111) substrates were ~ 110 nm. Under the SiC layer there are pores in the bulk of the silicon substrate, which were formed as a result of the topochemical reaction (2) and (3). Figure 2 presents the results of X-ray fluorescent microanalysis of the ZnO film composition. X-ray fluorescence analysis was performed at various points of the ZnO film, namely: on its surface, in the middle part of the ZnO layer, at the interface of the ZnO film with the SiC film, in the middle part of the SiC layer, at the interface of the SiC layer with the Si substrate, and approximately at a distance of about 1 µm from the SiC-Si interface into the depth of the silicon substrate. The analysis showed that ZnO films grown on SiC/Si (100) substrates of both n-type and p-type are stoichiometric. The atomic content in the ZnO layer grown on an n-type substrate is the following: Zn = 26.5%, oxygen O = 17.2%, silicon Si = 19.3\%, carbon C = 37%. The content of the same atoms in the ZnO layer grown on an p-type substrate is Zn = 25.8%, oxygen O = 17.7\%, silicon Si = 19.3\%, carbon C = 37\%. ZnO films grown on SiC/Si(111) n-type and p-type substrates contained above given atoms in the following composition: Zn = 25.6%, O = 17.8%, Si = 18.7%, C = 37.9%. Note that the concentration of silicon and carbon in this case should not be taken into account, since during microanalysis, the electron beam penetrates to a depth exceeding the thickness of the ZnO films. The excess carbon concentration in comparison with silicon only means that there is a SiC layer between the ZnO layer and Si. The analysis carried out by us showed that the Zn/O ratio is higher for the ZnO sample on an n-type substrate, i.e. oxygen concentration is greater in samples grown on a p-type substrate. This means that the concentration of oxygen vacancies is somewhat higher in a ZnO film grown on an n-type substrate. As is known, oxygen vacancies are electron donors. However, this difference is comparable with the magnitude of the error of the method.



**Fig. 2.** X-ray fluorescence analysis spectra for  $K_{\alpha}$  and  $L_{\beta}$  lines showing the content of Zn, O, C, and Si in the center of the ZnO layer grown on SiC/Si (100) and SiC/Si (111) samples with n-and p- type silicon

**X-ray diffraction studies.** X-ray diffraction studies showed that on the SiC sublayers grown on n-type and p-type Si (100) and Si (111) substrates a uniaxial three-component ZnO texture along the [101], [001] and [hk0] directions was formed (in the latter case the [hk0] directions were oriented along the surface normal, and the [001] directions of crystallites were parallel to the surface and had random azimuthal orientations). A typical image of X-ray reflections of such a "background" uniaxial texture is shown in Fig.3.

An epitaxial texture along the direction close to [101] was superimposed on the background uniaxial zinc oxide texture. The  $2\theta$ - $\chi$  diagrams of the ZnO layers grown on the SiC/Si (100) substrates of the n- and p-type conductivity are shown in Fig.4.

Formation of ordered ZnO structures grown by the ALD method on hybrid SiC/Si (100) substrates



**Fig. 3.** A typical series of symmetrical  $\theta$ -2 $\theta$  scans for different tilt angles  $\chi$  of a ZnO layer grown on a SiC/Si(100) substrate with either n-type or p-type silicon. sample. The background texture maxima of ZnO are visible at  $\chi = 0$  (|| [101] + || [001]). A  $\chi$ -profile of such a diagram at a given Bragg angle (2 $\theta$ ) represents a meridional profile of the corresponding pole figure



**Fig. 4.** A series of symmetrical  $\theta$ -2 $\theta$  scans for various tilt angles  $\chi$  of ZnO samples grown on the SiC/Si (100) substrates; (a) Si (100) n-type; (b) Si (100) p-type. The epitaxial texture maxima are visible

The combined pole figure of the ZnO/SiC/Si (100) sample grown on n-type Si (100) is shown in Fig. 5.

Figure 5 clearly shows the relatively sharp texture maxima of SiC and ZnO, which are characteristic of epitaxial textures. For the ZnO/SiC /Si (100) sample grown on the p-type Si (100) the combined PF is similar.

Figure 6 shows the  $2\theta - \chi$  diagrams for the ZnO layer (texture || [101] + || 001]) grown on the SiC/Si(111) substrates with n- and p-type silicon.

For all samples, the profiles of the texture maxima for the main directions ( $\chi$  scans) were obtained, and the peaks were fitted with the Gaussian functions. Full widths of these curves at half maximum (FWHM) measured with a standard error of about 1% characterize the texture sharpness. The ZnO [101] texture maximum had FWHM  $\approx 5.4^{\circ}$  on the SiC/Si (100) substrate with the n-type conductivity. On a SiC/Si (100) substrate with the

p-type conductivity the same texture has a sharpness of  $4.9^{\circ}$ . On the other hand, the sharpness of the ZnO texture along the [001] direction on the SiC/Si (100) substrate with the n-type conductivity was  $5.10^{\circ}$ , which is similar to that on the p-type silicon ( $5.3^{\circ}$ ). On the n-type SiC/Si (111) substrates the ZnO texture had a sharpness of  $6.30^{\circ}$  and  $4.5^{\circ}$  along the [101] and [001] directions, correspondingly. On the p-type SiC/Si (111) substrate the texture sharpness was as large as  $7.2^{\circ}$  in the [101] direction and only  $4.5^{\circ}$  in the [001] direction.



Fig. 5. The combined pole figure for the ZnO/SiC/Si (100) sample grown on the n-type Si (100). The angle  $\chi$  varied from 0 to +70<sup>0</sup> in the process of measurement



**Fig. 6.** A series of symmetrical  $\theta$ -2 $\theta$  scans for various tilt angles  $\chi$  of ZnO samples with texture || [101] + || [001] grown on SiC/Si(111) substrates. (a) - n-type conductivity; (b) - p-type conductivity

**Electron diffraction studies.** Figure 7 shows the RHEED pattern obtained from the surface of ZnO samples formed on SiC grown on n- and p-type Si (100), obtained on an EMR-100 electron diffraction image at 50 keV electron energy. Diffraction patterns are

shown along two directions, namely, along the projection of the [001] axis and in the projection of the [011] axis. As is known, while registering a RHEED pattern, electrons with an energy of 50 keV penetrate into the film layer to a depth not exceeding 30-50 nm, while X-ray beams penetrate much deeper. Therefore, RHEED is appropriate to investigate the structure of the surface layers, which may differ from the structure averaged over the entire thickness of the layer, which was studied by X-ray diffraction. Above, we showed that the ZnO layer is textured, with some order along the [101] and [001] directions. As a rule, with an increase in the film thickness, if the substrate has ordering centers, the degree of film crystallinity may increase [12]. This is what we observe in Fig. 7. For the ZnO layer grown on a n-type Si (100) substrate as well as for the ZnO layer grown on a p-type Si (100) substrate, there is a gradual transformation from texture to epitaxial orientation. So, in Fig. 7a and Fig. 7c it is clearly seen that the ZnO epitaxial layer starts to form along the [001] axis at the surface of SiC samples grown on a n-type Si substrate as well as on a p-type Si substrate. The reflexes are still quite diffused, though there are reflexes indicating the presence of the twin phase. However, in general, an epitaxial structure has already been formed in this zone. Moreover, within the experimental error, this structure is more ordered for a sample grown on an n-type substrate. This result coincides with the result of our research of the FWHM of the texture profiles. Studies of electron diffraction patterns in the projection onto the axis of the [101] zone (Fig. 7b and Fig. 7d) show that the ZnO sample grown on an n-type substrate in this direction is only a slightly ordered texture. On the other hand, the structure of the ZnO layer grown on the p-type substrate along the [101] direction is more ordered than the structure of the ZnO layer on the n-type substrate. Despite the diffusion of reflexes, this surface is closer to the epitaxial one than to the textured surface. This result also coincides with the result of our research of the FWHM of the texture profiles.



Fig. 7. RHEED patterns from ZnO samples formed on SiC grown on n- and p-type Si (100) obtained in two directions; in the projections of the [001] and [101] and axes (a) – n-type Si (100) in the [001] direction; (b) – n-type Si (100) in the [011] direction; (c) – p-type Si (100) in the [101] direction

Figure 8 shows RHEED patterns for reflection from the surface of ZnO samples formed on SiC of SiC on n- and p-type Si (111).



**Fig. 8.** RHEED patterns from ZnO samples grown on SiC on n- and p-type Si (111) registered along two directions; in the projection of the [001] axis and in the projection of the [101] axis.

(a) – n-type Si (111) in the [001] direction; (b) – n-type Si (111) in the [011] direction;
(c) p-type Si (111) in the [001] direction; (d) – p-type Si (111) with p-type conductivity in the [101] direction

From the data shown in Fig. 8, it follows that the ZnO layers lying near the surface of the ZnO/SiC /Si (111) films are textured both in the direction of the [001] zone axis and in the direction of the [101] axis regardless of the type of the substrate conductivity. The appearance of a larger number of diffused point reflections in Fig. 8c and Fig. 8d as compared with the reflexes in Fig. 8a and Fig. 8b can be attributed, in our opinion, to the experimental error. It is important to note the following. The ZnO layers grown on SiC/Si (111) are much less ordered than the ZnO layers grown on SiC/Si (100) substrates. Averaging the FWHM profiles along the [001] and [101] directions also confirms this conclusion.

# 4. Conclusion

Thus, in the present work, it was proved that the surface of SiC films grown by replacing Si (100) atoms is covered by an ensemble of ordering centers, i.e. crystal facets. In this case, as was previously theoretically shown [6], the facets on the vicinal surface of p-type Si are ordered and consist of layers of both cubic and hexagonal phases. This structure of SiC layers affects a strong ordering effect on the growth of epitaxial layers of crystals crystallizing in hexagonal symmetry. Thus, in the present study, we unambiguously showed that SiC/Si (100) hybrid substrates synthesized by the method of topochemical substitution of atoms for p-type Si, have ordering effects not only on the AlN and GaN layers growing by the HVPE method at high synthesis temperatures, but also on ZnO layers synthesized by the ALD method at low synthesis temperatures (about 250°C). Thus, the facet formation on the surface of SiC films grown by the method of topochemical substitution of atoms on Si (100) leads to the removal of the degeneracy of the surface symmetry and the formation of growth centers of ZnO films along certain directions.

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# THE INFLUENCE OF AN ADHESIVE LAYER ON THE INTERACTION BETWEEN A PIEZO-ACTUATOR AND AN ELASTIC 3D-LAYER AND ON THE EXCITED WAVE FIELDS

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**Abstract.** Piezoceramic transducers are extensively used in nondestructive testing (NDT), structural health monitoring (SHM) and condition monitoring (CM) of various mechanical systems including wind turbines, aircraft structures, bridges and pipeline systems. Piezoelectric transducers are surface bonded on the host structure and are excited to produce structural responses. This article highlights the effect of the adhesive layer between the studied structure and the transducer on the contact characteristics and the structural wave fields. The research also focuses on the efficiency of the both methods used for calculation of the occuring wave fields: finite-element (FE) method and semi-analytical approach based on the Green's matrix representations and the Fourier transform.

**Keywords:** anisotropic infinite layer, Green's matrix, piezoelectric actuator, wave excitation, finite element model, Fourier transform

# **1. Introduction**

The condition monitoring (CM) of functional and safety-relevant components is an urgent requirement in different industrial sectors [1,2]. Condition monitoring allows one to mitigate risk, boost safety, and reduce maintenance costs for dynamically loaded components and systems. Compared to traditional non-destructive testing [3], where a more or less regular but timely inspection of the component takes place, in the CM the sensors remain permanently on or in the structure to be monitored and are polled on a permanent or periodic base. As a result, occurring damage can be detected by changes in the sensor signal almost immediately. Structural Health Monitoring [4–7] enables condition-based maintenance, increasing safety.

For integrated structural monitoring the ultrasonic waves in the form of Lamb waves represent a promising approach [8–12] since they appear merely in plate and shell structures, propagate over long distances and have a high sensitivity to detect damage. In order to use Lamb waves for damage detection in terms of active and integrated structural monitoring, special systems of sensors and actuators are required for excitation, reading and interpretation of the waves [11–18]. The actuators and sensors should be designed as surface transducers and are stated at the surface of the structure. Numerous studies assume an ideal contact between transducer and studied structure, however the effect of the bonding layer is described only in a few works [10,11,19–21]. This idealized assumption is not robust enough for structural monitoring since the transducers are always connected to the plate structure via an adhesive bonding layer. The adhesive layer transmits the forces between transducer and structure with losses. These losses are summarized in the literature under the

term shear lag. Giurgiutiu in [6] proposes a model of mode transfer behaviour, which takes into account the influence of the adhesive layer on the shear force. A few studies [16–19,21] have been devoted to the effects of adhesive layers between surface-mounted PZTs and host structures for very low excitation frequencies up to several kHz, which corresponds to much bigger wavelengths compared to the size of the PZT. The shear lag effect [16] becomes more dominant with a lower shear modulus and thicker adhesive layer, and shear transfer between the PZT and host structure becomes less effective. In [11] effects of the adhesive bond-line layer on the Lamb wave generation and reception were simulated and compared with the available test data. It has been experimentally demonstrated in this article that the signal increases in amplitude as the thickness of the adhesive layer increases from 10 to 40  $\mu$ m. It is explained by the fact that the resonance phenomenon of the PZT with a thicker and softer adhesive layer is less restricted, so that more energy could be generated from the PZT excitation. The study of the effect of adhesive layer remains a live issue and will be investigated.

The aim of this paper is to assess the need for using an adhesive layer between the host structure and piezoelectric element for modelling the wave propagation. With this purpose the dependence of the contact stresses and displacements on the characteristics of adhesive layer are analysed in the first part of the current study. Then the effect of taking into account this layer on the wave propagation in the isotropic and anisotropic layers is examined. These simulations are carried out using the FE-package Comsol Multiphysics at different vibration frequencies. The second part of the paper is devoted to comparing the results obtained for the FE- and the semi-analytical model, based on the Fourier transform, the Green's matrix representation [8,13] and the numerical contour integration.

#### 2. Problem formulation

An infinite layer of thickness *h* is considered, which occupies the volume  $D = \{(x, y, z) | -\infty < x < \infty; -\infty < y < \infty; -h \le z \le 0\}$ . *a* The oscillations of the layer are excited by a PZT-actuator of thickness  $h_{PZT}$  and radius *a*, mounted on the upper surface of the host structure as shown in the Fig. 1. The thickness of the adhesive layer between the structure and the piezoelectric tablet is  $h_b$ . Time dependency is assumed harmonic in the form  $e^{-i\omega t}$ , where  $\omega$  is the vibration frequency.



Fig. 1. Scheme of the loaded structure

Lame's equations for the steady-state harmonic vibrations of the layer are written in compact form:

$$L\mathbf{u} + \rho \omega^2 \mathbf{u} = 0, \tag{1}$$

where  $\rho$  is the mass density and **u** is the displacement field. The upper and bottom surfaces of the layer are free of stress. The displacements **u** are caused by harmonic vibrations of a piezoelectric patch driven by a harmonically oscillating potential applied to the upper and

lower surfaces of the piezoelectric actuator. The fundamental equations of the PZT-actuator are represented in strain-charge form:

$$\boldsymbol{\varepsilon} = \mathbf{s}^E \cdot \boldsymbol{\sigma} + \mathbf{d}^* \cdot \mathbf{E} \tag{2}$$

$$\mathbf{D} = \mathbf{d} \cdot \boldsymbol{\sigma} + \mathcal{E}_0 \boldsymbol{\varepsilon}_r^{\ o} \cdot \mathbf{E} \,, \tag{3}$$

where  $\boldsymbol{\sigma}$  is the stress tensor and  $\boldsymbol{\varepsilon}$  is the strain tensor,  $\mathbf{s}^{E}$  is the compliance tensor for constant electric field,  $\mathbf{d}$  is the piezoelectric charge coefficients matrix,  $\mathbf{E}$  is the electric-field vector,  $\mathbf{D}$  is the electric charge displacement density, and  $\boldsymbol{\varepsilon}_{r}^{\sigma}$  is the electric permittivity tensor, constant  $\varepsilon_{0}$  is the electric permittivity of free space and "\*" indicates transpose operation. The tensor  $\boldsymbol{\varepsilon}$  and the vector  $\mathbf{E}$  are expressed in terms of the displacements  $\mathbf{u}$  and the electric potential  $\varphi$  respectively

$$\boldsymbol{\varepsilon} = \frac{1}{2} \left( \nabla \mathbf{u} + \nabla \mathbf{u}^* \right), \tag{4}$$

 $\mathbf{E} = -\nabla \varphi \; .$ 

(5)

The first aim of this study is to determine the displacement fields  $\mathbf{u}$  occurring in isotropic and anisotropic infinite layers and to estimate the influence of the adhesive layer properties on the resulting contact characteristics calculated for the FE-model. This model is considered in detail in the next section.

# **3. Finite Element Model**

Let us consider two different finite-element models simulating the structures actuated by a circular piezoelectric wafer. In the first model an isotropic thin layer of thickness h=2 mm is actuated by a piezoelectric thin-film actuator of thickness  $h_{PZT}=0.2$  mm and radius a=10 mm made of PZT-5H with the piezoelectric constant  $d_{31}=-265$  mm/kV. Material properties of the host structure are taken as follows: mass density  $\rho=2500$  kg/m<sup>3</sup>, Poisson's ratio  $\nu=0.33$  and Young's modulus E=20 GPa.

According to the second model an anisotropic layer of thickness h=4 mm is made of carbon fibre reinforced plastic (CFRP) material T700 is driven by piezoelectric actuator of the thickness  $h_{PZT}=2.1$  mm and radius a=25 mm. The piezoelectric constant of the PZT-4 material used in the actuator is  $d_{31}=-140$  mm/kV. Mechanical properties of the host structure are given through the following engineering constants:  $E_1=127.6$  GPa,  $E_2=11.3$  GPa,  $E_3=11.3$  GPa,  $G_{12}=5.97$  GPa,  $G_{13}=5.97$  GPa,  $G_{23}=3.75$  GPa, Poisson's ratios  $v_{12}=v_{13}=0.3$ ,  $v_{23}=0.34$  and material density  $\rho=1578$  kg/m<sup>3</sup>.

In both FE-models the piezoelectric actuators are bonded to the host structure using an adhesive layer with the following properties: mass density  $\rho$ =910 kg/m<sup>3</sup>, Poisson's ratio v<sub>23</sub>=0.37 and Young's modulus *E*=1.02 GPa. Thickness of the bonding layer is taken to be  $h_b$ =50 µm.

In both considered models, an electric potential is applied on the top of the PZT actuator, while its bottom surface is grounded. The amplitude of the electric potential is taken U=100 V in case of the isotropic host structure, and U=400 V in the second model with anisotropic host structure. A perfectly matched layer (PML) simulates a reflectionless boundary condition. The outer edge of the PML is fixed. All other boundaries are assumed to be free.

Unknown wave-fields are obtained by the frequency response analysis in a wide frequency range. Calculations are performed for both models in case with and without a bonding layer.

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# 4. Numerical results for the finite element model

Comparison of the contact characteristics for the models with and without bonding layer. Below in Fig. 2, contact shear stresses for the isotropic structure are presented depending on the glue thickness. The vibration frequencies are taken equal to f=15 kHz (a) and f=145 kHz (b). One can see that a thicker bonding layer with the thickness  $h_b=50$  µm produces a weakened load transfer between the piezoelectric actuator and the host structure. In the model without bonding layer when  $h_b=0$  µm the shear stresses are concentrated at the edge of the circular contact zone. Fig. 3 demonstrates the amplitudes of the *r*- components of contact displacements distribution, while the *z*-components are present in Fig. 4 at the vibration frequencies f=15 kHz (a) and f=145 kHz (b). It should be noticed that the use of a bonding layer leads to a smoother distribution of the displacements near the end of the contact zone. It is apparent that in the case of lower frequencies, the contact displacements can be approximated by a linear function. With the growth of the frequency, the distribution of contact characteristics has a more complicated character and cannot be approximated by well-known simple functions.

In Fig. 5, contact shear stresses for the anisotropic layer are present depending on the glue thickness and the angle  $\gamma$ . It is obvious that the influences of a bonding layer on the contact shear stresses and displacement fields are the same as for the isotropic structure. It should be noticed that the contact characteristics calculated for  $\gamma = 0^{\circ}$ , along the fibers, have significantly higher amplitudes than the characteristics obtained at  $\gamma = 90^{\circ}$ . Contact *r*-displacements presented in Fig. 6 have approximately three times higher amplitudes at  $\gamma = 0^{\circ}$  (a) than at  $\gamma = 90^{\circ}$  (b).



Fig. 2. Absolute values of contact shear stresses in an isotropic structure depending on the thickness of the bonding layer at f=15 kHz (a) and f=145 kHz (b)



Fig. 3. Absolute values of r -components of contact displacements in an isotropic structure depending on the thickness of the bonding layer at f=15 kHz (a) and f=145 kHz (b)



**Fig. 4.** Absolute values of *z*-components of contact displacements in an isotropic structure depending on the thickness of the bonding layer at f=15 kHz (a) and f=145 kHz (b)

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Fig. 5. Absolute values of contact shear stresses in an anisotropic structure depending on the bond thickness and angle  $\gamma$  at f=15 kHz



**Fig. 6**. Absolute values of contact *r*-displacements in an anisotropic structure depending on the thickness of the bonding layer at  $\gamma = 0^{\circ}$  (a) and  $\gamma = 90^{\circ}$  (b) at f=15 kHz

# Dependency of wave propagation on the adhesive layer characteristics.

Below the surface r- (a) and z- (b) displacements of the isotropic layer are presented at vibration frequency f=15 kHz (Fig.7) and f=145 kHz (Fig. 8). The results obtained for two models with and without bonding layer between the host structure and the PZT-actuator are compared. One can see that the bonding layer influences mostly the r-components of the surface displacements near the vibration source. The difference of displacement amplitudes in a far field is insignificant for both r- and z-components.



**Fig. 7.** Real and imaginary parts of surface r- (a) and z- (b) displacements for an isotropic plate depending on the bond thickness at f=15 kHz

Similar calculations were simulated for an anisotropic CFRP-plate. The comparison was performed at different directions: along the fibre direction at  $\gamma = 0^{\circ}$  and at  $\gamma = 90^{\circ}$  across the fibres. The surface *r*-displacements distribution of the anisotropic plate is present in Fig. 9, and Fig. 10 demonstrates *z*-displacements. In both figures wave fields are calculated at a vibration frequency f=10 kHz and the angles  $\gamma = 0^{\circ}$  (a) and  $\gamma = 90^{\circ}$  (b). It is obvious that similar to the isotropic structure case the influence of the bonding layer on the surface displacements is negligible in the far field. The amplitudes obtained for the model without bonding layer take higher values near the vibration source compared to the model with an adhesive layer.

It is apparent from the Fig. 9 that the amplitudes of surface *r*-displacements calculated along the fibers direction (a) take more than ten times higher values than the displacements in perpendicular direction (b). One can see from Fig. 10 that the *z*-components of displacements calculated across the fibers (a) have approximately five times lower values than the displacements along the composite fibers. This effect is clearly visible in Fig. 11, where the surface plot of the *z*-displacements at vibration frequency f=10 kHz is shown. In this figure the highest amplitudes are present in red color and it is visible that the oscillations propagate along the composite fibers from the vibration source placed in the middle of the host structure. They slightly attenuate along the host structure and approach zero values in the area of a perfectly matched layer.

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Fig. 8. Real and imaginary parts of surface r- (a) and z- (b) displacements for an isotropic plate depending on the bond thickness at f=145 kHz



**Fig. 9.** Real and imaginary parts of surface *r*-displacement depending on the bond thickness at  $\gamma = 0^{\circ}$  (a) and  $\gamma = 90^{\circ}$  (b) at f = 10 kHz



**Fig. 10.** Real and imaginary parts of surface *z*-displacement depending on the bond thickness at  $\gamma = 0^{\circ}$  (a) and  $\gamma = 90^{\circ}$  (b) at f=10 kHz



**Fig. 11.** Surface plots of *z*-displacement  $[\mu m]$  distribution in a carbon fiber plate at different vibration frequencies: f=10 kHz (a) and f=50 kHz (b)

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### 5. Simulation of the wave field using Fourier transform

The second semi-analytical approach for the determination of wave fields appearing in isotropic or anisotropic infinite layers is based on an application of the Fourier transform and Green's matrix formulation. The Fourier transform with respect to the coordinates x, y is applied to the equation (1) and boundary conditions. The solution of the considered problem can be represented in the Fourier domain as follows [8]:

$$U_i(\alpha_1, \alpha_2, z) = K_{ij}(\alpha_1, \alpha_2, z)Q_j(\alpha_1, \alpha_2), \ i, j = 1, 2, 3,$$
(6)

where  $K_{ij}(\alpha_1, \alpha_2, z)$  is the Fourier transform of the elements of Green's matrix **K** of the considered structure, and vector **Q** with the components  $Q_j(\alpha_1, \alpha_2)$  is the Fourier transform of the load vector  $\mathbf{q}(x, y)$ . An algorithm to evaluate Green's matrix in the frequency-wavenumber domain is described in detail in [8]. In order to obtain the displacement vector **u**, the inverse Fourier transform to the vector **U** was applied:

$$\mathbf{u}(x, y, z) = \frac{1}{4\pi^2} \iint_{\Gamma_1 \Gamma_2} \mathbf{K}(\alpha_1, \alpha_2, z) \mathbf{Q}(\alpha_1, \alpha_2) e^{-i(\alpha_1 x + \alpha_2 y)} d\alpha_1 d\alpha_2 , \qquad (7)$$

or in cylindrical coordinates

$$\mathbf{u}(r,\varphi,z) = \frac{1}{4\pi^2} \int_{0}^{2\pi} \int_{\Gamma^+(\gamma)}^{2\pi} \mathbf{K}(\alpha,\gamma,z) \mathbf{Q}(\alpha,\gamma) e^{-i\alpha r \cos(\gamma-\varphi)} \alpha d\alpha d\gamma , \qquad (8)$$

where  $x = r \cos \varphi$ ,  $y = r \sin \varphi$ , z = z,  $r = \sqrt{x^2 + y^2}$ ,  $\alpha_1 = \alpha \cos \gamma$ ,  $\alpha_2 = \alpha \sin \gamma$  and  $\alpha = \sqrt{\alpha_1^2 + \alpha_2^2}$ . Here  $\gamma \in [0, 2\pi]$  and  $\varphi \in [0, 2\pi]$  are assumed to be real,  $\Gamma_1$ ,  $\Gamma_2$ ,  $\Gamma^+(\gamma)$  denote the integration contours, which partially deviate from the real axis while bypassing the real poles of the Green's functions in accordance with the principle of limiting absorption [22]. According to this principle, the integration contour  $\Gamma^+$  bypasses positive real poles of the matrix **K** from below in case without backward waves (see Fig. 12).

In this work a computation of the displacements in an anisotropic plate caused by a circular PZT-actuator of radius  $r_0$  using a semi-analytical procedure is present. The action of a circular source can be represented as follows

$$\tau_{xz} = \tau_0 \delta(r - r_0) \cos \varphi, \ \tau_{yz} = \tau_0 \delta(r - r_0) \sin \varphi, \ \sigma_z = 0 \ \text{for } z = 0.$$
(9)

The application of the double Fourier transform leads to  $Q(\alpha, y) = 2\pi i \pi r L(r \alpha) \cos y$ 

$$Q_{1}(\alpha,\gamma) = 2\pi i \tau_{0} r_{0} J_{1}(r_{0}\alpha) \cos \gamma ,$$

$$Q_{2}(\alpha,\gamma) = 2\pi i \tau_{0} r_{0} J_{1}(r_{0}\alpha) \sin \gamma ,$$

$$Q_{3}(\alpha,\gamma) = 0 ,$$
(10)

where  $J_1(r_0\alpha)$  is the Bessel function of the first kind. Surface displacements (8) are computed using the integral approach based on the Fourier transform after finding the solution of the problem in Fourier domain [8]. This requires the computation of the inverse Fourier transform, which means the computation of the two-dimensional improper contour integral and consecutive evaluation of the integral with respect to the frequency  $\omega$ .



Fig. 12. Integration contour

The computation of the double integral (8) over wavenumbers causes such difficulties as integral singularity near real poles of Green's matrix, strong oscillations of the integrand and significant time expenses. The following sequence of double integrals can be considered:

$$\mathbf{u}_{R_n}(r,\varphi,z) = \frac{1}{4\pi^2} \int_{0}^{2\pi} \int_{\Gamma_{R_n}^+(\gamma)}^{K} \mathbf{K}(\alpha,\gamma,z) \mathbf{Q}(\alpha,\gamma) e^{-i\alpha r \cos(\gamma-\varphi)} \alpha d\alpha d\gamma , \qquad (11)$$

where  $\Gamma_{R_n}^+ \to \Gamma^+$ ,  $n \to \infty$ . The sequence (11) converges to the initial 2D-integral, i.e.  $\forall \varepsilon > 0$ ,  $\forall \omega, \varphi, z$ ,  $\forall r > 0$ ,  $\exists n > 0$ :

$$\left|u_{j}(r,\varphi,z)-u_{j,R_{n}}(r,\varphi,z)\right|<\varepsilon, \quad j=1,2,3.$$

$$(12)$$

Thus instead of the improper double integral (8) the double integral over the bounded domain (11) can be considered, i.e. for a given value  $\varepsilon$  such  $R = R_n$  exists that  $\mathbf{u}(r, \varphi, z) \approx \mathbf{u}_n(r, \varphi, z)$ . (13)

and (11) is satisfied. An example of a contour 
$$\Gamma_R^+$$
 in the case when all the real poles except

and (11) is satisfied. An example of a contour  $\Gamma_R$  in the case when all the real poles except the only one irregular pole  $k_1(\gamma)$  are regular, is present in Fig.13.



**Fig. 13.** Finite integration contour  $\Gamma_{R_n}^+$ 

Here  $d = \text{Im} k_{nc}(\gamma)/2$  is the value of the deviation of the integration contour from the real axis into the complex plane,  $k_{nc}$  is the complex pole nearest to the real axis,  $M = \max_{m} k_m(\gamma)$ ,  $k_m$  are real poles, and the value *R* is taken so that  $M < \text{Re}\alpha \le R$ . For the evaluation of the 2D-wavenumber integral (8) as an iterated integral (11), the integration with adaptive quadratures [23] is applied in this work.

# 6. Comparison of surface displacements for FE- and semi-analytical models

An example of the calculation of displacement fields for the CFRP-panel of the thickness h=1 mm and material properties described in Section 3, is illustrated below. The harmonic wave propagation is excited by a load (9), distributed in a circle of radius R=2.5 mm at vibration frequencies f=10 kHz and f=40 kHz. The real and imaginary amplitudes of z-displacements are evaluated in direction  $\gamma = 0^{\circ}$  using the semi-analytical and the FE-approaches. The results obtained for f=10 kHz are present in Fig. 14, and Fig. 15 corresponds to the vibration frequency f=40 kHz. It is obvious that both approaches give comparable results. The slight difference in the ampitudes is visible near the excitation source, whereas the results obtained in a far field agree well for both considered approaches. The best results agreement corresponds to the lower vibration frequency (Fig. 14). It should be noted that the higher frequency (Fig. 15) needs a sufficient computational cost due to the FE-mesh refinement and the consequently significant time costs, since the axial-symmetry model cannot be applied for an anistropic plate and the 3D-model is requiered. Thereby the required computation time for the FE-model increases with increasing frequency, whereas the semi-analytical approach works equally fast for any properties of a host-structure and at any vibration frequency.



**Fig. 14.** Surface *z*-displacement of anisotropic plate at  $\gamma = 0^{\circ}$  and f = 10 kHz



**Fig. 15.** Surface *z*-displacement of anisotropic plate at  $\gamma = 0^{\circ}$  and f = 40 kHz

#### 7. Conclusions

In this paper, an effect of an adhesive layer between an infinite 3D-layer and a piezoelectric actuator is analysed. Vibrations of the two host structures made of isotropic material and of carbon fibre plate excited by a circular piezoelectric actuator were investigated. A significant effect of the bonding layer on the resulting contact shear stresses was shown. A thicker adhesive layer produces the dumped load transfer between the PZT-element and the host structure. In the case when the bonding layer thickness is equal to zero, shear stresses concentrate near the end points of the contact area. It was shown that both *r*- and *z*- surface displacements are not strongly influenced by the thickness of the adhesive layer especially far from the contact zone. At the same time, the angle  $\gamma$  effects the distribution of the displacement fields in case of a composite plate. It is obvious that the *r*-components of displacements along the composite fibres take approximately ten times higher amplitudes than the displacements.

Two approaches are used to simulate the excitation of the host structure: finite-element method and the semi-analytical approach based on the use of the Fourier transform. The resulting displacement fields, caused by a circular surface load, are compared for both approaches for anisotropic host structure at different vibration frequencies. Both applied methods showed a good agreement especially in a far field. The analysis of the obtained wave fields showed that both approaches can be effectively used for isotropic and composite structures at lower frequencies. For a growing vibration frequency, the FE-model of anisotropic plate needs a significant FE-mesh refinement and leads to considerable calculation times. It can be concluded that at higher frequencies the semi-analytical approach is preferable especially in case of composite host structures.

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# **ON SOME FEATURES OF IDENTIFICATION OF INHOMOGENEOUS** PRESTRESSED STATE OF THERMOELASTIC HOLLOW CYLINDER WITH COATING

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Abstract. An inverse thermoelasticity problem of identification of inhomogeneous prestressed state of an infinitely long hollow cylinder with a coating is formulated. The characteristics of cylinder's material are described by piecewise continuous functions. A direct thermoelasticity problem is solved on the basis of the shooting method and inversion of solutions based on the Durbin method after applying the Laplace transform. The nonlinear inverse problem is solved by constructing an iterative process, at each stage of which the operator equations of the first kind are solved. The most informative time intervals for gaining the additional information are determined. The influence of prestress level, coupling parameter and coating thickness on the results of prestress reconstruciton is analyzed.

**Keywords:** thermoelasticity, prestress, coating, cylinder, identification, inverse problem

#### **1. Introduction**

Protection of structural elements (like turbine blades, combustion chambers, piping systems and nozzle guide vanes), operating under conditions of combined thermomechanical loading, is usually provided by applying a thermal protective coating on their surfaces [1]. The main characteristic of thermal protective coatings is low thermal conductivity coefficient, due to which the temperature on the metal substrate surface is reduced down to 100-300°C. The production of materials with thermal protective coatings is a complex technological process. Due to the multi-stage technological operations, inhomogeneous residual stresses often occur in the final product and can lead to coating delamination.

The first results of investigations of dynamic thermoelasticity problems in the presence of homogeneous prestresses were given in [2]. For rigorous description of thermomechanical processes in prestressed bodies, it was necessary to involve an apparatus of nonlinear thermoelasticity. However, for a wide range of problems for prestressed thermoelastic bodies a simplified linearized theory is widely used [3], which based on the A.N. Guz model [4].

Since the main structural elements are often not available for direct observation and control, there is a need to develop a non-destructive method of identification of the prestressed state. Because of the considerable interest in the problem of prestressed state identification, the number of publications on this issue is steadily growing [5-11]. However, most diagnostic methods are aimed at investigating homogeneous prestressed state. Mathematically inhomogeneous prestressed state is manifested in the dependence of the differential thermoelasticity operators coefficients on the coordinates. The determination of the inhomogeneous prestressed state is only possible by use of the apparatus of coefficient inverse problems (CIP) of thermoelasticity [12,13] and requires some additional information. The research in the field of thermoelasticity CIP is mainly limited by slightly inhomogeneous materials [14].

Two types of mechanics inverse problems statements are widespread in practical applications. For the first type the additional information is assumed to be known at internal points of a body at some moment of time; for the second type the additional information is known only on the part of the boundary on certain time interval.

If additional information is only known on the body's boundary, the inverse problem is essentially nonlinear. As a rule, the solution of CIP is reduced to the solution of the corresponding extremal problems by use of gradient methods [13,15]. The use of gradient methods for minimization requires significant computation time and has a number of other drawbacks. As an alternative to gradient methods, an approach based on constructing an iterative process, assuming solving a linearized operator equation of the first kind at each iteration, has been used in recent years [16]. It should be noted that the problems of reconstructing material characteristics and inhomogeneous prestressed states in elastic and thermoelastic bodies were solved in [17-21]. However, an issue of identifying prestresses in bodies with coatings remained unexplored in these studies.

In this paper we present the equations of thermoelasticity for a prestressed cylinder based on the approach proposed in [12]. The coated cylinder is modeled as a thermoelastic cylinder with thermomechanical characteristics that are described by piecewise continuous functions of radial coordinate. After applying the Laplace transform, the direct problem of thermoelasticity is solved on the basis of the shooting method and inversion of transformants based on the Durbin method. In the inverse problem, on the basis of the algorithm developed in [12], we restore the functions with a first-kind discontinuity point on the interface of the coating with the cylinder. The analysis of the effect of the prestress level, the coupling parameter and the coating thickness on the results of the reconstruction of inhomogeneous prestresses is made. The developed approach allows recovering arbitrary functions characterizing prestressed states of cylinders.

# 2. Problem of identification of the inhomogeneous prestressed state of a thermoelastic cylinder

Consider an infinitely long hollow thermoelastic cylinder with an inner surface r = a. On the outer surface of the cylinder r = b there is a coating of a thickness h. The coated cylinder is subjected to a prestressed state which is characterized by the components of the prestress tensor  $\sigma_{rr}^{0}$  and  $\sigma_{\phi\phi}^{0}$ , which are related to each other by the equilibrium equation  $\frac{d\sigma_{rr}^{0}}{dr} + \frac{\sigma_{rr}^{0} - \sigma_{\phi\phi}^{0}}{r} = 0$ . The inner surface of the cylinder is thermally insulated and free of mechanical stresses. The uniformly distributed mechanical  $p_{0}$  and thermal load  $q_{0}$  act on the outer surface of the coated cylinder (r = b + h). The cylinder's material is characterized by the density  $\rho_{s}$ , the Lame coefficients  $\lambda_{s}$  and  $\mu_{s}$ , the thermal conductivity coefficient  $k_{s}$ , the specific heat capacity  $c_{s}$ , the thermal stress coefficient  $\gamma_{s}$ , and the prestress  $\sigma_{rr}^{0s}$  and  $\sigma_{\phi\phi}^{0s}$  (s-

substrate); the coating's material is described by the characteristics  $\rho_c$ ,  $\lambda_c$ ,  $\mu_c$ ,  $k_c$ ,  $c_c$ ,  $\gamma_c$ ,  $\sigma_r^{0c}$  and  $\sigma_{\phi\phi}^{0c}$  and (c-coating). Consider the material characteristics of the cylinder-coating system in the form of piecewise continuous functions of the form:

$$F(r) = \begin{cases} F_s(r), & \text{при } r \in [a,b]; \\ F_c(r), & \text{при } r \in [b,b+h] \end{cases}$$
(1)

where F(r) conditionally denotes any of the material parameters  $\rho(r)$ ,  $\lambda(r)$ ,  $\mu(r)$ , k(r), c(r),  $\sigma_{rr}^0(r)$ ,  $\sigma_{\phi\phi}^0(r)$ . We denote any of the material characteristics of the cylinder by  $F_s$ , and any of the coating ones by  $F_c$ .

Similarly, we introduce the notation for physical fields:

$$Q(r,t) = \begin{cases} Q^{s}(r,t), & \text{при } r \in [a,b]; \\ Q^{c}(r,t), & \text{при } r \in [b,b+h] \end{cases}$$
(2)

Here, Q(r,t) is any of the functions describing the thermo-elastic process:  $u_r(r,t)$  radial displacement,  $\theta(r,t)$  - temperature increment,  $T_{rr}(r,t)$ ,  $T_{\varphi\varphi}(r,t)$  - components of the Piola incremental stress tensor.

In accordance with the model proposed by A.N. Guz [4], the equations of coupled thermoelasticity for a prestressed cylinder under conditions of plane deformation  $(u_r = u_r(r,t), u_0 = 0, u_z = const)$  have the following form [12]:

$$\frac{\partial T_{rr}}{\partial r} + \frac{T_{rr} - T_{\varphi\varphi}}{r} = \rho \frac{\partial^2 u_r}{\partial t^2},\tag{3}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(k(r)r\frac{\partial\theta}{\partial r}) = c(r)\frac{\partial\theta}{\partial t} + T_0\gamma(r)(1 + \frac{\sigma_{rr}^0}{\lambda + 2\mu})(\frac{\partial^2 u_r}{\partial r\partial t} + \frac{1}{r}\frac{\partial u_r}{\partial t}), \qquad (4)$$

$$T_{rr} = (\lambda + 2\mu)\frac{\partial u_r}{\partial r} + \lambda \frac{u_r}{r} + \sigma_{rr}^0 \frac{\partial u_r}{\partial r} - \gamma \theta, \qquad (5)$$

$$T_{\varphi\varphi} = \lambda \frac{\partial u_r}{\partial r} + (\lambda + 2\mu) \frac{u_r}{r} + \sigma^0_{\varphi\varphi} \frac{u_r}{r} - \gamma \theta, \qquad (6)$$

$$\frac{\partial \Theta}{\partial r}(a,t) = 0, \ -k(b+h)\frac{\partial \Theta}{\partial r}(b+h,t) = q_0, \tag{7}$$

$$T_{rr}(a,t) = 0, \ T_{rr}(b+h,t) = p_0,$$
(8)

$$\theta(r,0) = u_r(r,0) = \frac{\partial u_r}{\partial t}(r,0) = 0.$$
(9)

Similarly, we can write the thermoelasticity initial-boundary problem for the case when the coating is set on the inner side of the cylinder.

At the interface boundary between the coating and the cylinder r = b, by virtue of continuity, the following coupling conditions for radial stresses, temperature and heat flow must be met:

$$u_r^s(b,t) = u_r^c(b,t), \ T_{rr}^s(b,t) = T_{rr}^c(b,t),$$
  

$$\theta^s(b,t) = \theta^c(b,t), \ k_s(b) \frac{\partial \theta^s}{\partial r}(b,t) = k_c(b) \frac{\partial \theta^c}{\partial r}(b,t).$$
(10)

Let us introduce dimensionless parameters and variables into (3)-(10):

$$h_{0} = b + h - a, \quad z = \frac{r - a}{h_{0}}, \quad z_{0} = \frac{a}{h_{0}}, \quad h_{1} = \frac{h}{h_{0}}, \quad H = 1 - h_{1}, \quad \overline{s}(z) = \frac{\lambda + 2\mu}{\mu_{0}}, \quad \overline{\lambda}(z) = \frac{\lambda(r)}{\mu_{0}}, \\ \overline{k}(z) = \frac{k(r)}{k_{0}}, \quad \overline{c}(z) = \frac{c(r)}{c_{0}}, \quad \overline{\gamma}(z) = \frac{\gamma(r)}{\gamma_{0}}, \quad \overline{\rho}(z) = \frac{\rho(r)}{\rho_{0}}, \quad \nu = \sqrt{\frac{\mu_{0}}{\rho_{0}}}, \quad t_{1} = \frac{h_{0}}{\nu}, \quad t_{2} = \frac{h_{0}^{2}c_{0}}{k_{0}}, \quad \tau = \frac{t}{t_{2}}, \\ W(z,\tau) = \frac{\gamma_{0}\theta}{\mu_{0}}, \quad U(z,\tau) = \frac{u_{r}}{h_{0}}, \quad \Omega_{r}(z,\tau) = \frac{T_{rr}}{\mu_{0}}, \quad \Omega_{\phi}(z,\tau) = \frac{T_{\phi\phi\phi}}{\mu_{0}}, \quad \Omega_{r}^{0}(z) = \frac{\sigma_{\phi\phi}^{0}}{\mu_{0}}, \quad \Omega_{\phi}^{0}(z) = \frac{\sigma_{\phi\phi\phi}^{0}}{\mu_{0}},$$

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$$\delta_{0} = \frac{\gamma_{0}^{2} T_{0}}{\mu_{0} c_{0}}, \qquad \varepsilon = \frac{t_{1}}{t_{2}}, \qquad p^{*} = \frac{p_{0}}{\mu_{0}}, \qquad q^{*} = \frac{q h_{0} \gamma_{0}}{k_{0} \mu_{0}}, \qquad \mu_{0} = \frac{1}{h_{0}} \int_{a}^{b+h} \mu(r) dr, \qquad k_{0} = \frac{1}{h_{0}} \int_{a}^{b+h} k(r) dr,$$

$$c_{0} = \frac{1}{h_{0}} \int_{a}^{b+h} c(r) dr, \qquad \gamma_{0} = \frac{1}{h_{0}} \int_{a}^{b+h} \gamma(r) dr, \qquad \rho_{0} = \frac{1}{h_{0}} \int_{a}^{b+h} \rho(r) dr, \qquad \lambda_{0} = \frac{1}{h_{0}} \int_{a}^{b+h} \lambda(r) dr.$$

After the transformation of (3)-(10) into dimensionless form, taking into account the conjugation conditions, the initial-boundary problem, takes the form:

$$\frac{\partial \Omega_r}{\partial z} + \frac{\Omega_r - \Omega_{\varphi}}{z + z_0} = \varepsilon^2 \overline{\rho} \frac{\partial^2 U}{\partial \tau^2}, \qquad (11)$$

$$\Omega_r = (\overline{s} + \Omega_r^0) \frac{\partial U}{\partial z} + \frac{\overline{\lambda}}{z + z_0} U - \overline{\gamma} W , \qquad (12)$$

$$\Omega_{\varphi} = \overline{\lambda} \frac{\partial U}{\partial z} + (\overline{s} + \Omega_r^0 + (z + z_0) \frac{d\Omega_r^0}{dz}) \frac{U}{z + z_0} - \overline{\gamma} W, \qquad (13)$$

$$\frac{1}{z+z_0}\frac{\partial}{\partial z}(\overline{k}(z+z_0)\frac{\partial W}{\partial z}) = \overline{c}\frac{\partial W}{\partial \tau} + \delta\overline{\gamma}(1+\frac{\Omega_r^0}{\overline{s}})(\frac{\partial^2 U}{\partial z\partial \tau} + \frac{1}{z+z_0}\frac{\partial U}{\partial \tau}),$$
(14)

$$\frac{\partial W}{\partial z}(0,\tau) = 0, \ -\overline{k}(1)\frac{\partial W}{\partial z}(1,\tau) = q^*,$$
(15)

$$\Omega_r(0,\tau) = 0, \ \Omega_r(1,\tau) = p^*,$$
(16)

$$W(z,0) = U(z,0) = \frac{\partial U}{\partial \tau}(z,0) = 0,$$
 (17)

$$U^{s}(H,\tau) = U^{c}(H,\tau), \ \Omega^{s}_{r}(H,\tau) = \Omega^{c}_{r}(H,\tau),$$
  
$$\partial W^{s} \qquad \partial W^{c}$$

$$W^{s}(H,\tau) = W^{c}(H,\tau), \ \overline{k_{s}}(H)\frac{\partial W^{s}}{\partial z}(H,\tau) = \overline{k_{c}}(H)\frac{\partial W^{c}}{\partial z}(H,\tau).$$
(18)

The direct problem of thermoelasticity consists in determining the functions  $U(z,\tau)$ ,  $W(z,\tau)$  from (11)-(18) for known thermomechanical characteristics  $\overline{s}(z)$ ,  $\overline{\lambda}(z)$ ,  $\overline{k}(z)$ ,  $\overline{c}(z)$ ,  $\overline{\gamma}(z)$ ,  $\overline{\rho}(z)$  and prestresses  $\Omega_r^0(z)$ ,  $\Omega_{\varphi}^0(z)$ .

For arbitrary laws of variation of thermomechanical characteristics and prestresses, the problem (11)-(18), after applying the Laplace transform, can be solved only numerically. Proceeding in a similar way to [12], in order to solve the obtained system of differential equations in transforms, we use the shooting method modified for the case of piecewise continuous functions. To find the actual space of solutions, we used the Durbin method [22].

In the inverse problem, it is required to determine the functions  $\Omega_r^0(z)$ ,  $\Omega_{\varphi}^0(z)$  from (11)-(18) with known thermomechanical characteristics  $\overline{s}(z)$ ,  $\overline{\lambda}(z)$ ,  $\overline{k}(z)$ ,  $\overline{c}(z)$ ,  $\overline{\gamma}(z)$ ,  $\overline{\rho}(z)$  for some additional information.

$$W(\mathbf{l}, \tau) = f_1(\tau), \ \tau \in [a_1, b_1].$$
(19)  
b) Displacement data

$$U(1,\tau) = f_2(\tau), \ \tau \in [a_2, b_2], \tag{20}$$

measured on the outer surface of the cylinder with the coating z = 1 on time intervals  $[a_1, b_1]$ and  $[a_2, b_2]$  that are informative in terms of identifying and close to the reference point. With the known  $\Omega_r^0(z)$ , the prestresses  $\Omega_{\omega}^0(z)$  can be easily found from the equilibrium

equation 
$$\frac{d\Omega_r^0}{dz} + \frac{\Omega_r^0 - \Omega_{\phi}^0}{z + z_0} = 0.$$

The inverse problem (11)-(20) is a nonlinear problem that can be solved on the basis of an iterative process, as in [12]. It should be noted that problems of reconstruction of thermomechanical characteristics and prestresses characterized by continuous functions were solved on the basis of such approach. In this paper we restore functions that have a point of discontinuity of the first kind on the interface between the coating and the cylinder on the basis of the algorithm developed in [12].

# 3. A scheme for solving the inverse problem

Consider a procedure for restoring the prestress  $\Omega_r^0(z)$  of a cylinder-coating system. The function  $\Omega_r^0(z)$ , similarly to [12,19], is represented in the form  $\Omega_r^0(z) = \beta \overline{g}(z)$ , where

 $\beta = \frac{\max \sigma_{rr}^{0}}{\cdots}$  is the prestress level,  $\overline{g}(z)$  is the law of inhomogeneity distribution which must

be restored.

The iterative process of restoring a piecewise continuous function  $\overline{g}(z)$  consists of two stages.

At the first stage, the initial approximation is determined in the form of a piecewise constant function based on minimization of the residual functional. In case of the additional information (19), the residual functional has the form:

$$J_{1} = \int_{a_{1}}^{a_{1}} (f_{1}(\tau) - W(1,\tau))d\tau, \qquad (21)$$

and in case of the additional information (20), it will be represented as

$$J_2 = \int_{a_2}^{b_2} (f_2(\tau) - U(1,\tau)) d\tau.$$
(22)

Using the initial approximation  $\overline{g}^{(0)}(z)$ , the corresponding displacement  $U^{(0)}(z,\tau)$  and temperature  $W^{(0)}(z,\tau)$  are found from the solution of the direct problem (11)-(18).

In the second step, the corrections are found from the solution of the Fredholm integral equations of the first kind.

Thus, in the case of thermal loading ( $p^* = 0$ ,  $q^* = 1$ ), to find the correction  $\delta \overline{g}^{(n-1)}$ , it is necessary to solve the following equation:

$$\int_{0}^{1} \delta \overline{g}^{(n-1)} R_{1}(z,\tau) dz = G(\tau), \quad \tau \in [a_{1}, b_{1}].$$
(23)

In the case of mechanical loading ( $p^* = 1, q^* = 0$ ), it is necessary to solve the equation:

$$\delta_0 \int_0^1 \delta \overline{g}^{(n-1)} R_2(z,\tau) dz = P(\tau), \ \tau \in [a_2, b_2].$$
(24)

Here, the kernels and the right-hand sides of equations (23), (24) have the form:  $R_1(z,\tau) = \int_0^{\tau} \left(\frac{\partial^2 U^{(n-1)}}{\partial z \partial \tau_1}(z,\tau_1) + \frac{1}{z+z_0} \frac{\partial U^{(n-1)}}{\partial \tau_1}(z,\tau_1)\right) W^{(n-1)}(z,\tau-\tau_1) d\tau_1,$  On some features of identification of inhomogeneous prestressed state of thermoelastic hollow cylinder with coating 59

$$R_{2}(z,\tau) = \int_{0}^{\tau} \left(\frac{\partial U^{(n-1)}}{\partial z}(z,\tau_{1})\left(\frac{\partial U^{(n-1)}}{\partial z}(z,\tau-\tau_{1}) - U^{(n-1)}(z,\tau-\tau_{1})\right) + \frac{U^{(n-1)}(z,\tau_{1})}{z+z_{0}}U^{(n-1)}(z,\tau-\tau_{1})\right)d\tau_{1}$$

$$G(\tau) = \int_{0}^{\tau} q^{*}(\tau-\tau_{1})(f_{1}(\tau_{1}) - W^{(n-1)}(1,\tau_{1}))d\tau_{1}, P(\tau) = \int_{0}^{\tau} p^{*}(\tau-\tau_{1})(f_{2}(\tau_{1}) - U^{(n-1)}(1,\tau_{1}))d\tau_{1}.$$

The equations (23), (24) for the determination of corrections represent the Fredholm equations of the first kind with completely continuous operators; for their inversion we used the A.N. Tikhonov regularization method [23].

After finding the corrections, we obtain the corrected functions  $\overline{g}^{(n)} = \overline{g}^{(n-1)}(z) + \delta \overline{g}^{(n-1)}(z)$  that give an approximate solution of the inverse problem (11)-(20) when the exit conditions are satisfied.

The following inequalities serve as the exit conditions:

$$J_1 \le \eta, \tag{25}$$

$$J_2 \le \eta. \tag{26}$$

## 4. Results of computational experiments

In the present work, the internal radius of the cylinder was assumed to be equal a = 0.5 cm; the external one was assumed b = 1 cm, the coating thickness in various computational experiments varied within 0.088 < h < 0.214 (cm), which in dimensionless form correspond to the interval  $0.15 < h_1 < 0.3$ . A copper was used as a cylinder material and  $Al_2O_3$  as a coating, as it has a low thermal conductivity.

Following the above scheme, computational restoration experiments were conducted. The exit from the iterative process in all the experiments was done according to the conditions (25) or (26) for  $\eta = 10^{-4}$ .

As it is well known, the results of solving an inverse problem strongly depend on the choice of the most informative time periods for retrieving additional information. The most informative are the time intervals close to the reference point, in which the additional information changes most strongly. In thermoelastic processes, due to the energy dissipation, the temperature and displacements come to a steady state over time. Therefore, measurements of the additional information in this mode are not very informative. The time required to reach such a mode depends both on the loading method and on the thermomechanical characteristics of the coating and cylinder'

s materials. In the course of analyzing the additional information, the most informative time intervals were revealed both for the thermal and in the mechanical methods of loading. It was found out that the measurement of temperature is the most informative on the interval  $[a_1, b_1] = [0, 6]$  at 4 observation points inside it, and measurement of displacement on the interval  $[a_2, b_2] = [0, 1.2]$  is the most informative at 6 observation points inside it.

When solving inverse problems, it is important to investigate the sensitivity of the input information. Calculations showed that the changes in additional information, i.e. temperature and displacement, measured on the outer surface of the cylinder, are greatly influenced only by prestresses with  $\beta \ge 8 \cdot 10^{-4}$ . In subsequent calculations it was accepted  $\beta = 10^{-3}$ .

Following the above scheme, we carried out computational experiments to restore the function  $\overline{g}(z)$ . The figures below show the results of reconstruction of the dimensionless function; while the solid line depicts the graph of the original function, the dots show the restored one.

Firstly, computational experiments were performed with the thermal method of loading  $(p^* = 0, q^* = 1)$ . The results of the function  $\overline{g}(z)$  reconstruction for the  $Al_2O_3/Cu$  system

turned out to be unsatisfactory – the reconstruction error at some points exceeded 20%. That was found out to be caused by the small thermomechanical coupling parameter of these materials –  $\delta_0 = 0.03$ . At the same time, with a large coupling parameter  $\delta_0 = 0.4$ , which is true only to a small number of materials, the reconstruction error did not exceed 7%, and no more than 14 iterations were required to fulfill the exit condition (25).

Figures 1-2 show the result of restoring  $\overline{g}(z)$  with the coupling parameter  $\delta_0 = 0.4$ . Figure 1 presents the result of reconstruction of  $\overline{g}_1(z) = \begin{cases} 1, & 0 \le z \le H; \\ 1.25 \cos(z), & H < z \le 1 \end{cases}$  (H = 0.7) in the case when the outer surface of the cylinder is coated. Figure 2 shows the result of restoration of  $\overline{g}_2(z) = \begin{cases} z+1, & 0 \le z \le H; \\ 0.56+e^{-z}, & H < z \le 1 \end{cases}$  (H = 0.3) in case when the inner surface of the cylinder is coated.

From Figs. 1,2, it can be seen that the largest reconstruction error (7%) occurred in the vicinity of the interface between the coating and the cylinder at  $H - \xi < z < H + \xi$  ( $\xi = 0.06$ ), which is caused by the features of the computational scheme.

Then experiments were carried out to reconstruct the function  $\overline{g}(z)$  under the mechanical loading method ( $p^* = 1$ ,  $q^* = 0$ ). In this case, the reconstruction error decreased significantly and did not exceed 9%. Also, no more than 12 iterations were required to fulfill the exit condition (26).

In Figs 3,4 we present the result of  $\overline{g}_3(z)$  recovery, which has the form of an increasing function  $0.15+3z^3$  for the coating, and a constant equal to 0.15 for the cylinder. The influence of the relative thickness  $h_1 = 0.3$  (Fig. 3),  $h_1 = 0.15$  (Fig. 4) of the coating on the results of reconstruction was investigated. From Figs. 3,4 it follows that the reconstruction error increases significantly with the decrease of  $h_1$ . For  $h_1 \le 0.06$  the reconstruction of  $\overline{g}(z)$  becomes impossible due to a large error.



**Fig. 1.** The result of recovery of  $\overline{g}_1(z)$ ; thermal loading type



**Fig. 2.** The result of reconstruction of  $\overline{g}_2(z)$ ; thermal loading type

In Figs. 5,6 we present the results of  $\overline{g}(z)$  recovery for the case when the coating is deposited on the inner surface of the cylinder. Figure 5 shows the result of the reconstruction of the piecewise continuous functions  $\overline{g}_4(z) = \begin{cases} -0.5 \ln(0.1+2z), & 0 \le z \le 0.3; \\ 0.1, & 0.3 < z \le 1 \end{cases}$ . In Fig. 6 we show the result of the restoration of the piecewise constant function  $\overline{g}_5(z) = \begin{cases} 0.2, & 0 \le z \le 0.3; \\ 1, & 0.3 < z \le 1 \end{cases}$ . The maximum reconstruction error is observed in the vicinity of the coating-cylinder interface 0.24 < z < 0.36 and does not exceed 6%.



Fig. 3. The result of restoration of  $\overline{g}_3(z)$  with a coating thickness equal to  $h_1 = 0.3$ ; mechanical loading type



**Fig. 4.** The result of restoration of  $\overline{g}_3(z)$  with a coating thickness equal to  $h_1 = 0.15$ ; mechanical loading type



**Fig. 5.** The result of restoration of  $\overline{g}_4(z)$ ; mechanical loading type



**Fig. 6.** The result of restoration of  $\overline{g}_5(z)$ ; mechanical loading type

# 5. Conclusions

The method for determining inhomogeneous prestressed state of an infinitely long hollow thermoelastic coated cylinder is presented. The solution of the inverse problem is constructed on the basis of an iterative process, at each step of which the corrections are determined by solving the Fredholm integral equations of the first kind. The computational experiments of reconstruction of the inhomogeneous prestressed state of the coated cylinder are carried out. It is found out that the maximum reconstruction error occurs in the vicinity of the coatingcylinder connection. The reconstruction results for the thermal cylinder loading depend on the coupling parameter value. With a small coupling parameter, a large error arises in the prestressed state reconstruction. For any loading type, the results of reconstruction of the prestressed state depend on the coating thickness. With a decrease in the coating thickness, the reconstruction error considerably increases.

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# APPLIED THEORY OF BENDING VIBRATIONS OF A PIEZOELECTRIC BIMORPH WITH A QUADRATIC ELECTRIC POTENTIAL DISTRIBUTION

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**Abstract.** An applied theory of cylindrical bending vibrations of a bimorph plate is developed, which takes into account the nonlinear distribution of the electric potential in piezoelectric layers. Finite-element analysis of this problem showed that such distribution arises when solving the problems of finding the resonant frequencies and modes of vibration or in the case of forced oscillations during their mechanical excitation, when the electric potential adopted in the work showed good consistency of the results with finite-element calculations for natural oscillations and steady-state oscillations for a given potential difference when the electric potential distribution is close to linear.

Keywords: plate, cylindrical bending, electro elasticity, nonuniform potential distribution

# **1. Introduction**

It is known that piezoelectric materials are widely used as actuators, sensors and generators in the engineering and aerospace industry for the monitoring of structures, monitoring forms, active suppression of parasitic vibrations, noise reduction, etc. Such a wide apply is achieved due to its good electromechanical properties, flexibility in the design process, ease of production and high efficiency transformation, as electric energy into mechanical energy, and in the opposite direction. When using piezoelectric materials as actuators, deformations can be controlled by changing the magnitude of the applied electrical potential. In sensors, the measurement of deformation occurs due to the measurement of the induced potential. In the field of energy storage with the help of piezoelectric materials there is a transformation of free mechanical energy present in the structures into electrical energy and its subsequent transformation into low-power devices suitable for power supply. A detailed review is given in [1-3].

Typical actuators, sensors and generators, working on a bend, represent a multilayer structure consisting of several layers with different mechanical and electrical properties. The traditional design, consisting of two piezoelectric layers glued to the substrate or to each other – is called a bimorph. More complex multilayer structures are already referred to functionally graded materials.

Various mathematical models were proposed for modeling layered structures working as a sensor, actuator and generator. Thus, in the early works [4, 5] were presented analytical solutions three-dimensional equations of the theory of electroelasticity in static cylindrical bending and free vibrations. Nevertheless, the derivation and obtaining analytical solutions of such equations in the case of arbitrary geometry is a complex problem. Another approach is the use of models with induced deformation to simulate the response of the actuator, which were used in [6, 7]. But there the electric potential was not considered as a variable describing the state. That, in turn, did not allow to obtain related electromechanical responses, but only allowed to simulate the response of the actuator. Finite element models have been proposed in many papers, for example in [8-12]. Nevertheless, they also have their drawbacks. For example, the need for large computational power when using three-dimensional elements in problems where the thickness of one layer is much smaller than the other dimensions of the structure.

When modeling piezoelectric structures, the hypothesis of the linear distribution of the electric potential over the thickness is widely used. This means that the induced potential is considered. This is useful for modeling actuators [13] and piezoelectric generators [14]. However, in some materials with polarization in thickness, when an electric field is applied, shear strains and stresses may occur [12]. In addition, shear stresses and deformations occur in multilayer piezoelectric composites [15]. In this connection, taking into account the nonlinear part of the potential is of some interest.

The paper [16] considered a sandwich model of the third order. The authors have shown that such a model gives an additional contribution to the stiffness due to the quadratic deformation of the shear and the cubic term of the electric potential. This fact was confirmed by higher natural frequencies. A number of papers [17, 18] are devoted to the development of a related refined layer-by-layer theory for finite element analysis of multilayer functionally graded piezoelectric materials. The authors used both quadratic and cubic electric potential and took into account the longitudinal potential distribution. This allowed to take into account the shear stresses and strains. Forced and free oscillations with good convergence with analytical solutions and commercial FE packages were considered. However, no graphs of the longitudinal distribution of potential were presented. In [19], a refined bound global-local theory for finite element analysis of thick piezoelectric composites operating on the shear mode was presented. The authors used a quadratic potential distribution over the thickness. Applied theories of oscillations of multilayer piezoelectric plates, taking into account the specific distribution of the electrical potential along the thickness of the structure, were developed in [20,21]. In [22] an applied theory of oscillations of piezoelectric transducers with inhomogeneous polarization was developed.

A brief review showed that the use of the nonlinear distribution of the electric potential, along with the longitudinal distribution is of some interest in the problems of calculation of multilayer actuators, as it allows more accurate modeling of shear stresses and strains arising in such structures. Nevertheless, the behavior of the nonlinear electric potential in the vicinity of resonances is not sufficiently studied. In this connection, we have developed an applied theory of cylindrical bending of bimorph piezoelectric structures, taking into account the quadratic distribution of the potential thickness along with its longitudinal change.

# 2. Formulation of the problem

In this paper, the plane problem of the steady bending vibrations of a plate having an infinite width in the direction  $x_2$  is considered. The plate consists of three layers. The outer two layers are two identical layers of piezoactive material polarized in the direction of the axis  $x_3$ . Between them is a purely elastic layer. We assume that all the functions considered are independent of the variable  $x_2$ . We choose the origin of coordinates on the middle plane.


Fig. 1. The plate under study

Assume that the piezoelectric layers are deposited on the electrodes on both sides  $x_3 = \pm (H/2 + h)$  and  $x_3 = \pm H/2$  (bold lines in Fig 1.). The external and internal electrodes are interconnected, respectively. The plate oscillations are excited by the distributed harmonic load  $p_i$  with circular frequency  $\omega$ .

The oscillations of the plate are described by the following equations:

$$\sigma_{ij,j} + \rho \omega^2 u_i = p_i, \qquad D_{i,i} = 0,$$
 (1)  
where  $\sigma_{ij}$  - components of the stress tensor;  $\rho$  is the density of the material;  $u_i$  are the

components of the displacement vector;  $D_i$  are the components of the electric induction vector. We assume that the side surface of the plate is stress-free:  $\sigma_{11} = \sigma_{13} = 0$  for  $x_1 = \pm a$ . There are no external loads  $\sigma_{13} = \sigma_{33} = 0$  on the faces  $x_3 = \pm (H/2 + h)$  of the plate. The external medium is air, so  $D_1 = 0$  for  $x_1 = \pm a$ .

In this case, the constitutive relations for electroelastic medium polarized in the direction of the axis  $x_3$  are of the form:

$$\begin{aligned}
\sigma_{11} &= c_{11}^{E} \varepsilon_{11} + c_{13}^{E} \varepsilon_{33} + e_{31} \varphi_{,3}, \\
\sigma_{33} &= c_{13}^{E} \varepsilon_{11} + c_{33}^{E} \varepsilon_{33} + e_{33} \varphi_{,3}, \\
\sigma_{13} &= 2 c_{44}^{E} \varepsilon_{13} + e_{31} \varphi_{,1}, \\
D_{3} &= e_{31} \varepsilon_{11} + e_{33} \varepsilon_{33} - \epsilon_{33}^{S} \varphi_{,3},
\end{aligned}$$
(2)

where  $c_{ij}^{E}$  are the elastic moduli measured with a constant electric field,  $\varepsilon_{ij}$  are the strain tensor components,  $e_{ij}$  is the piezoelectric constant,  $\varphi$  is the electric potential, and  $\epsilon_{ij}^{S}$  is the permittivity measured at constant deformations.

For a purely elastic inner layer, the constitutive relations have the following form:

$$\hat{\sigma}_{11} = c_{11} \varepsilon_{11} + c_{13} \varepsilon_{33}, 
\hat{\sigma}_{33} = c_{13} \varepsilon_{11} + c_{33} \varepsilon_{33}, 
\hat{\sigma}_{13} = 2 c_{44} \varepsilon_{13}.$$
(3)

Further, to construct an applied theory of oscillations, we adopt the Kirchhoff hypotheses. In accordance with them, the distribution of displacements along the thickness has the following form

$$u_1(x_1, x_3) = -x_3 w_{,1}, u_3(x_1, x_3) = w(x_1),$$
(4)

where  $w(x_1)$  is the deflection function of the middle surface of the plate.

In addition, the hypotheses assumed suggest that the normal stress is equal  $\sigma_{33} = 0$  everywhere in the plate region. Using this condition, we exclude the deformation  $\varepsilon_{33}$  from the constitutive relations for the electric (2) and elastic (3) media:

 $\begin{aligned}
\sigma_{11} &= c_{11}^* u_{1,1} + e_{31}^* \varphi_{,3}, \\
D_3 &= e_{31}^* u_{1,1} - \epsilon_{33}^* \varphi_{,3}, \\
\hat{\sigma}_{11} &= \tilde{c}_{11}^* u_{1,1},
\end{aligned} \tag{5}$ 

$$c_{11}^{*} = c_{11}^{E} - \frac{c_{13}^{E2}}{c_{33}^{E}}, \qquad e_{31}^{*} = e_{31} - \frac{c_{13}^{E}e_{33}}{c_{33}^{E}}, \epsilon_{33}^{*} = \epsilon_{33}^{S} + \frac{e_{33}^{2}}{c_{33}^{E}}, \qquad \tilde{c}_{11} = c_{11} - \frac{c_{13}^{2}}{c_{33}}.$$
(6)

Expressions for  $\sigma_{13}$ ,  $\hat{\sigma}_{13}$  and  $D_1$  remain unchanged.

We assume that the electric potential for the upper piezoelectric layer has the following distribution:

$$\varphi(x_1, \tilde{x}_3) = V_1(x_1) \frac{\tilde{x}_3}{h} \left(\frac{2\tilde{x}_3}{h} - 1\right) + V_2(x_1) \left(1 - \frac{4\tilde{x}_3^2}{h^2}\right) + V_3(x_1) \frac{\tilde{x}_3}{h} \left(\frac{2\tilde{x}_3}{h} + 1\right).$$
(7)

Here, for the convenience of the description, the relative coordinate  $\tilde{x}_3 = x_3 - (H/2 + h/2)$  is introduced. In the lower layer we assume an analogous distribution for  $\tilde{x}_3 = x_3 + (H/2 + h/2)$ .

Using the electric potential in the form (7) allows to take into account the electric boundary conditions on  $x_3 = \pm (H/2+h)$  and  $x_3 = \pm H/2$ , as well as the value in the middle of the piezoactive layers  $x_3 = \pm (H/2+h/2)$ . In the framework of the problem under study, let us consider the following case:

$$V_{1}(x_{1}) = V_{1} = const, V_{2}(x_{1}) = \Phi(x_{1}), V_{3}(x_{1}) = V_{3} = const.$$
(8)

Here  $\Phi(x_1)$  is the unknown distribution function of the potential in the middle of the piezoactive layer in the direction of the  $x_1$  axis.

Next, we use the variational equation for the case of steady oscillations, which generalizes the Hamilton principle in the theory of electroelasticity. For the case of plane deformation in the absence of surface loads and surface charges, the variational equation has the form:

$$\int_{-a-h}^{a} \int_{-a-h}^{h} \delta \breve{H} dx_3 dx_1 - \rho \omega^2 \int_{-a-h}^{a} \int_{-a-h}^{h} u_i \delta u_i dx_3 dx_1 + \int_{-a-h}^{a} \int_{-a-h}^{h} p_i \delta u_i dx_3 dx_1 = 0,$$
(9)

where  $H = U - E_i D_i$  is the electric enthalpy whose variation is equal to  $\delta H = \sigma_{ij} \delta \varepsilon_{ij} - D_i \delta E_i$ .

Taking into account the accepted hypotheses (4), the enthalpy variation takes the following form:

 $\delta \vec{H} = \sigma_{11} \delta \varepsilon_{11} - D_1 \delta E_1 - D_3 \delta E_3. \tag{10}$ 

We assume that the components of the vector of distributed load are  $\mathbf{p} = \{0, p\}^T$ . We vary (10) and substitute it in (9). After integration over the thickness, we equate the coefficients for independent variations of  $\delta w$  and  $\delta \Phi$ . Thus, we obtain a system of differential equations

Applied theory of bending vibrations of a piezoelectric bimorph with a quadratic electric potential distribution

$$\frac{4}{3}e_{31}^{*}h\frac{d^{2}\Phi}{dx_{1}^{2}} + \left(\frac{1}{12}\tilde{c}_{11}^{*}H^{3} + \frac{1}{2}c_{11}^{*}H^{2}h + c_{11}^{*}Hh^{2} + \frac{2}{3}c_{11}^{*}h^{3}\right)\frac{d^{4}w}{dx_{1}^{4}} \\ + \left(\frac{1}{12}\tilde{\rho}\omega^{2}H^{3} + \frac{1}{2}\rho\omega^{2}H^{2}h + \rho\omega^{2}Hh^{2} + \frac{2}{3}\rho\omega^{2}h^{3}\right)\frac{d^{2}w}{dx_{1}^{2}} \\ - \left(H\omega^{2}\tilde{\rho} + 2h\omega^{2}\rho\right)w - p = 0,$$

$$\frac{16}{15}h\epsilon_{11}^{s}\frac{d^{2}\Phi}{dx_{1}^{2}} + \frac{4}{3}he_{31}^{*}\frac{d^{2}w}{dx_{1}^{2}} - \frac{32}{3}\frac{\epsilon_{33}^{*}}{h}\Phi + \frac{16}{3}\frac{\epsilon_{33}^{*}}{h}V_{1} + \frac{16}{3}\frac{\epsilon_{33}^{*}}{h}V_{3} = 0.$$

$$(11)$$

Equating the coefficients of independent variations of the nonintegral terms to zero, we obtain the boundary conditions:

$$\frac{4}{3}e_{31}^{*}h\frac{d\Phi}{dx_{1}} + \left(\frac{1}{12}\tilde{c}_{11}^{*}H^{3} + \frac{1}{2}c_{11}^{*}H^{2}h + c_{11}^{*}Hh^{2} + \frac{2}{3}c_{11}^{*}h^{3}\right)\frac{d^{3}w}{dx_{1}^{3}} \\
+ \left(\frac{1}{12}\tilde{\rho}\omega^{2}H^{3} + \frac{1}{2}\rho\omega^{2}H^{2}h + \rho\omega^{2}Hh^{2} + \frac{2}{3}\rho\omega^{2}h^{3}\right)\frac{dw}{dx_{1}} = 0, \\
- \left(e_{31}^{*}H + \frac{5}{3}e_{31}^{*}h\right)V_{3} + \left(e_{31}^{*}H + \frac{1}{3}e_{31}^{*}h\right)V_{1} + \frac{4}{3}e_{31}^{*}h\Phi \\
+ \left(\frac{1}{12}\tilde{c}_{11}^{*}H^{3} + \frac{1}{2}c_{11}^{*}H^{2}h + c_{11}^{*}Hh^{2} + \frac{2}{3}c_{11}^{*}h^{3}\right)\frac{d^{2}w}{dx_{1}^{2}} = 0, \\
- \frac{16}{15}h\epsilon_{11}^{*}\frac{d\Phi}{dx_{1}} = 0.$$
(12)

## 3. Numerical experiment

Using the obtained model, we investigate a plate made of piezoceramics PZT-4 fixed with hinges at points  $x_1 = \pm a$ . The inner layer is made of the same material, but does not have piezoactive properties. In view of the foregoing, the basic physical and geometric parameters of the model were given in the table.

Parameter	Value		Dimension
Linear dimensions	$H = 2 \times 10^{-3}, h = 5 \times 10^{-3}, a = 0.1,$		m
Density	$\rho = \tilde{\rho} = 7.5 \times 10^3$		kg/m <sup>3</sup>
Modules of	$c_{11}^E = c_{11} = 13.9 \times 10^{10}$ ,	$c_{13}^E = c_{13} = 7.43 \times 10^{10}$ ,	GPa
elasticity	$c_{33}^E = c_{33} = 11.5 \times 10^{10}$		
Piezoelectric	$e_{15} = 12.7$ , $e_{31} = -5.2$ , $e_{33} = 15.1$ ,		$C/m^2$
modules			
Permittivity	$\epsilon_{11}^{S} = 64.6 \times 10^{-10}, \ \epsilon_{33}^{S} = 56.2 \times 10^{-10}$		F/m

Table 1. Geometrical parameters and physical properties

We will compare the results of the proposed model with the results of the finite element (FE) analysis of a similar problem in the FE package ACELAN [23].

At the first stage, we find the first two modes of oscillation, under the condition  $V_1 = V_3 = 0$ :

 Table 2. Resonance frequencies

Mode of oscillation	Applied theory (Hz)	FE (Hz)	Error (%)
First	473.8	481.1	1.51
Second	1895.3	1881.8	0.71

Comparison of the results between applied theory and FE modelling showed a small spread between the results obtained

Next, consider the oscillations of the plate at a frequency of 1890 Hz, with the condition  $V_1 = V_3 = 0$  and p = 1.



**Fig. 2.** Deflection of the plate obtained on the basis of applied theory (plot in the upper part of figure) and FE method

Figure 2 demonstrates a good agreement between applied theory and finite element calculation.





The analysis of Fig. 3 demonstrates the nonlinear character of the distribution of the electrical potential along the thickness and length of the piezoactive layer, as well as the similarity of the results of applied theory and finite element analysis.

Figure 4 illustrates the distribution of the electrical potential along the length and thickness of the upper layer. Near the plate fixing points, local maxima of the electric potential values are observed, and in the middle - a minimum.



**Fig. 4.** Electrical potential distribution for the upper piezoactive layer, obtained on the basis of applied theory

Next, consider the case when the electric potential is V = -7.65 V on internal electrodes, and the potential on external electrodes is V = 0. The oscillations are excited by the action of a distributed force with an amplitude of 1000 N and a frequency of 1890 Hz.



**Fig. 5.** Distribution of the electrical potential along the length in the middle of the upper piezoactive layer, obtained on the basis of the applied theory (plot in the lower part of figure), and for the entire plate, obtained by the FE method

It can be seen from Fig. 5 that the values of distribution the electric potential, obtained on the basis of applied theory, are rather close to those obtained on the basis of finite element analysis. In addition, the distribution has a nonlinear form.

Figure 6 shows the distribution of the electrical potential along the length and thickness of the upper piezoactive layer.

Analysis of Fig. 5 and 6 allows us to conclude that in the case when an electric potential different from zero is specified on one of the electrodes, the form of the electric potential distribution along the thickness is close to linear. However, the distribution of the electrical

potential along the length of the piezoceramic layer is nonlinear, with a difference of 22% in the middle of the plate.



Fig. 6. Distribution of electrical potential for the upper piezoactive layer, obtained on the basis of applied theory

# 4. Conclusions

An applied theory of oscillations of a bimorph plate is developed, which takes into account the nonlinear distribution of the electric potential in piezoelectric layers. Such a distribution arises when solving the problems of finding the resonant frequencies and modes of vibration or in the case of forced oscillations during their mechanical excitation, when the electric potentials on the electrodes are zero. The quadratic distribution of the electric potential adopted in the work showed good consistency of the results with finite-element calculations for natural oscillations and steady-state oscillations for a given potential difference when the electric potential distribution is close to linear

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# MATHEMATICAL 3D MODELS OF IRREVERSIBLE POLARIZATION PROCESSES OF A FERROELECTRICS AND FERROELASTICS POLYCRYSTAL

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Abstract. A review of three-dimensional mathematical models describing the irreversible processes of polarization of polycrystalline ferroelectrics is given. Experimental works and most frequently used models for describing hysteresis properties are considered. These include well-known phenomenological and micromechanical models. Some of them allow describing the nonlinear response under the action of electrical and mechanical loads. For each of the models, physical and mathematical features, basic formulas and calculating algorithms are presented. The main advantages and disadvantages of each of the presented models are noted. Large and small loops of dielectric and deformation hysteresis are shown. A conclusion is drawn about the unresolved problems in the field of modeling of polycrystalline ferroelectrics - ferroelastics. The list of works on the review topic is given. Keywords: mathematical models, ferroelectrics, ferroelastics, hysteresis loops, phenomenological models, micromechanical models

## **1. Introduction**

Since the discovery of the phenomenon of ferroelectricity by Valašek in 1921, almost a century has passed, but the practical significance of this discovery is so great that it is not possible to talk about the completeness of research in this field at the moment. Many ferroelectric materials have been discovered, their structures have been studied, ferroelectric ceramic technologies have been developed, ferroelectrics-relaxors have been discovered, the technologies for creating porous ceramics and composite elements with piezoelectric and magnetic properties have been developed, but the questions of mathematical modeling of nonlinear response to electric fields and mechanical stresses remain relevant, and are far from their completion. Technologies of microminiaturization of working elements and thin-film structures put forward new requirements in the field of mathematical modeling of volumetric properties of materials. Indeed, small forces, as well as a small potential difference in such elements, can lead to large mechanical stresses and electric fields that can change the structure of the material due to partial or complete depolarization of the element. And if in the simplest cases it was sufficient to use one-dimensional models that explain the nonlinear hysteresis response of uniaxial (longitudinal) effects, now this is clearly not enough. Models are needed that describe both the longitudinal and transverse response under all possible influences.

The main focus of this review is on polycrystalline ferroelectric materials or ceramics, which are active materials and which, by virtue of their internal structure, have the ability to convert mechanical energy into electrical energy, and *vice versa*. By affecting the sample with

an electric field or mechanical stress, we observe a response both in the form of electric displacement and in the form of deformation [1].

At small external influences, deformations caused by them and electric displacements are small. Such processes are called reversible. Their modeling is reduced to the construction of constitutive relations in the form of linear algebraic relations connecting external and internal parameters like Hooke's generalized law. In other words, the mathematical model is described by linear algebraic operators, in which the elements of tensors of elastic, piezoelectric and dielectric constants are found experimentally. The calculation of the physical characteristics of the transducers, in which the piezoceramic elements are polarized before saturation, is performed within the framework of these linear models. They are sufficiently studied and include the equations of motion, the equations of electrostatics, geometric relationships and constitutive relationships; to which the initial and boundary conditions are added. In the simplest cases, the equations can be solved analytically, for more complex problems it is convenient to use numerical methods, for example, the finite element method.

The situation changes dramatically as soon as the external loads reach thresholds, and their intensity continues to increase. In this case, irreversible processes start with nonlinear response. And besides with increasing loads, we have someone nonlinear equation, while for decreasing ones we have other. The constitutive relations become not only non-linear but nonsingle valued. In mathematical terms, they are described by operator relations of hysteresis type. In addition to intense external loads, other parameters, in particular temperature, also affect the irreversibility of the process. For cooling or heat processes, when a temperature changes near a threshold value, called the Curie temperature, a solid phase transition occurs from a low symmetry phase to a high symmetry phase or vice versa. However, in this review we present models of irreversible processes of polarization and depolarization by an electric field and mechanical stresses under isothermal processes. Irreversible processes associated with relaxation properties, with the influence of temperature, with the influence of the size of the ferroelectric granules, the dynamics of processes and other features will not be considered here. The main circle of questions will be connected with the analysis of existing mathematical models describing the response of the material to external influences of high intensity for the isothermal process. In other words, the principles of constructing the constitutive relations for irreversible processes of deformation and polarization will be considered, their analysis carried out, and some conclusions formulated.

It is interesting to note that many irreversible processes have a similar response: the relationships between external and internal parameters are mathematically described by similar relationships. In plastic media, the stresses cause elastic and residual strains; in ferromagnetism, the magnetic field leads to induced and remnant magnetization; in ferroelectrics, the electric field generates induced and residual polarization, etc. For cyclic processes, the response is described by hysteresis relationships, as shown in Fig. 1.



**Fig. 1.** Hysteresis: a - plastically; b - magnetically; c – dielectrically

Therefore, it happens that the mathematical models developed for someone processes are often used to describe another processes. The closer the observed phenomena in the physical plane, the more accurately the mathematical apparatus works. Modeling of processes of polarization and depolarization, i.e. the construction of hysteresis-type operators plays an important role in the use of numerical methods for calculating the physical characteristics of the working elements of devices [2]. In particular, in the finite element method, such operators are the constitutive relations closing the system of equations obtained from the laws of continuum mechanics. An important role in modeling is played by experimental data.

#### 2. The main experimental data characterizing the response of the material

The criterion for the correctness and adequacy of the work of any model is a good coincidence of the predicted phenomena with experimental data. A qualitative experiment is a very complex study, so most of them reflect only certain properties with simple effects. The most significant experiments in static tests are those that reflect the complex response of a material due to the action of an electric field and mechanical stresses. Basically, these are the works where the properties of ferroelectric ceramics of the perovskite type are investigated: for example, BaTiO<sub>3</sub>, or a ceramics containing lead: PZT, PLZT 8/65/35. Interesting results on the response of PLZT 8/65/35 in the complex effect of electric and mechanical fields [3] are shown in Fig. 2.



**Fig. 2.** Full loops of dielectric and deformation type "butterfly" hysteresis for different values of compressive stresses: A -  $\sigma = 0$  MPa; B -  $\sigma = -6$  MPa; C -  $\sigma = -30$  MPa; D -  $\sigma = -60$  MPa

Large loops of dielectric and deformation hysteresis in uniaxial tests and fixed compressive stresses for both lead and lead-free ceramics give similar results [4 - 8] and are shown in Figs. 3, 4.

*Conclusion*: the loops of the dielectric and deformation hysteresis essentially depend on the intensity of the operating fields. Uniaxial mechanical compressive stresses along the electric field axis affect the ability of domains to rotate. The more intense the mechanical compressive stresses along the field, the less domains the electric field can turn along the line of its action.

As a rule, the mentioned above types of ceramic are the full ferroelectrics-ferroelastics. This means that the strain response to mechanical stresses is also non-linear. The distinctive ferroelastic properties of such materials [6, 8] can be seen in Figs. 5, 6.



**Fig. 3.** The effect of compressive stresses on the loop of dielectric hysteresis





*Conclusion*: for purely mechanical effects, the solid-solid phase transition takes place, the material from isotropic becomes anisotropic, the elastic moduli of the material (tangents to the curves) are changed, and residual deformations appeared that satisfy the condition of incompressibility of material. The last statement can be easily verified if we compare the values of longitudinal and transverse strains.

Dynamic tests, as a rule, are carried out for harmonic impacts. For example, the cyclic effects of an electric field and mechanical stresses can take place both in phase and in antiphase. The dielectric and deformation loops of such tests [9] are shown in Figs. 7, 8.



**Fig. 7.** Dielectric hysteresis for transverse compressive stresses: a – in phase; b – anti-phase



Fig. 8. Strain hysteresis for transverse compressive stresses: a - in phase; b - anti-phase

*Conclusion*: dielectric and deformation responses at transverse compressive stresses in the phase lead to a decrease in the horizontal slope and a decrease in the area of the loop. Dielectric and deformation responses at transverse compressive stresses in anti-phase lead to an increase in the horizontal slope and increase in the area of the loop.

Along with large loops, small loops of dielectric and deformation hysteresis are often investigated [9]. Such loops of the dielectric and strain hysteresis due to the action of the electric field are shown in Figs. 9, 10. Small loops of strain hysteresis due to the action of mechanical stresses are shown in Figs. 11, 12. Moreover, Fig. 18 reflects the expansion-contraction process, and Fig. 19 – pure compression followed by an increase in intensity.



*Conclusion*: according to small hysteresis loops, one can judge the changing elastic, dielectric and piezoelectric modules of the material.

Summing up, we can say that the main task of mathematical modeling of irreversible processes is the construction of hysteresis operators taking into account the changing anisotropy of material properties.

#### **3.** The simplest one-dimensional models

The most common one-dimensional models were numerically investigated in [2]. In the same place, algorithms are described and the results of calculations in the form of plots of dielectric and strain hysteresis loops are presented. Here we briefly mention the basic mathematical principles of models.

**The Rayleigh model.** This model describes hysteresis by simple parabolic functions. The Rayleigh model [10] was one of the first, in which hysteresis dependences for the magnetization processes of iron are described. In order to apply it to the polarization processes of polycrystalline ferroelectrics, the magnetic field must be replaced by an electric field, and the magnetization by polarization. Mathematically, the branches of the dielectric hysteresis are described by parabolic relationships, as shown in Fig. 13:

 $P = \begin{cases} \alpha E^2, & \text{initial polarization curve,} \\ \alpha E_{\max} E \pm \frac{\alpha}{2} (E_{\max}^2 - E^2), & \text{descending and ascending branches,} \end{cases}$ 

where  $\alpha = p_s / E_{\text{max}}^2$ ,  $p_s$  is the spontaneous polarization,  $E_{\text{max}}$  is the maximum value of the electric field.



**Fig. 13.** The Rayleigh model

Obviously, such dependence only approximately describes the hysteresis.

**Evolutionary models.** This model describes hysteresis phenomena with the help of evolutionary laws leading to hereditary operators. It was developed on the assumption that macroscopic electrical properties are described by a system of electric dipoles, the magnitude and orientation of which can be changed by external loads, and the material in the macroscopic plan is uniform. Dipole dynamics is regulated by an atomic lattice, for which typical times of electronic response are less than 10<sup>-11</sup> seconds. In [11] it is assumed that the dipole moment  $\mu$  depends on strain *S*, absolute temperature  $\theta$ , electric field *E* and the number of switching dipoles *N* in the form of a functional dependence  $\mu = \hat{\mu}(S, \theta, E, N)$ . And since the process of domain switching has a time scale of the order of 10<sup>-8</sup> to 10<sup>-5</sup> seconds, it is considered that the parameter *N* obeys the evolutionary law. Mechanical stress *T* and electrical displacement *D* can be represented by time-independent relationships:

 $T=T^*(S,\theta,E,N); \quad D=D^*(S,\theta,E,N); \quad \dot{N}=h(S,\theta,E,N)\,.$ 

Further assumptions are related to the type of introduced functions. In the case when they can be taken as linear, we obtain a hereditary theory of ferroelectricity:

$$T = C(0)(S - S_r) + \int_0^t \frac{d}{dt} C(t - \tau)(S(\tau) - S_r) d\tau + \Theta(0)(\theta - \theta_r) +$$
  
$$\int_0^t \frac{d}{dt} \Theta(t - \tau)(\theta(\tau) - \theta_r) d\tau + \eta(0)E + \int_0^t \frac{d}{dt} \eta(t - \tau)E(\tau) d\tau;$$
  
$$D = D_r + L(0)(S - S_r) + \int_0^t \frac{d}{dt} L(t - \tau)(S(\tau) - S_r) d\tau + \kappa(0)(\theta - \theta_r) -$$
  
$$\int_0^t \frac{d}{dt} \kappa(t - \tau)(\theta(\tau) - \theta_r) d\tau + \varepsilon(0) + \int_0^t \frac{d}{dt} \varepsilon(t - \tau)E(\tau) d\tau.$$

The creep functions entering here are not written out due to the cumbersome nature.

To determine the physical properties of polarized ceramic PZT 65/35, in onedimensional case [12], the temperature influence is neglected and, under certain conditions, instead of operator relations of the hereditary theory, linear relations are used containing additional terms in elastic, piezoelectric and dielectric modules. A connection was established between the velocities of elastic waves with elastic modules for polarized and unpolarized states, and was added experimentally founded value of the dielectric constant. After that, all parameters are determined. Similar studies can be found in [13–17].

**Models of the theory of plasticity.** These models qualitatively describe the polarizing effects; they are based on the similarity of the phenomena plasticity and polarization and were constructed using rheological models. The analogy of mechanical and electrical quantities is stated on the base of similar phenomena description: the generalized coordinate – the electric charge; generalized speed – current; coefficient of elastic compliance – capacity; the generalized force – the electromotive force. In the transition to continuous media, forces are replaced by mechanical stresses, displacements by strains, etc. As a result, one can write the following correspondence:  $\sigma \leftrightarrow E$ ,  $\varepsilon \leftrightarrow P$ , where *E* is the electric field; *P* is the polarization or electrical displacement;  $\sigma$  is the mechanical stress;  $\varepsilon$  is the deformation. The elastic element of Hooke is associated with a condenser, the element of Saint-Venant dry friction is a bipolar zener diode (Fig. 14).

Fig. 14. Condenser and bipolar zener diode



**Fig. 15.** Connection of elements: a – in series; b – in parallel

In the theory of plasticity, rheological formulas for elastic and plastic deformations are conveniently described by differential inclusions [18]. Therefore, it is natural to extend this apparatus to the theory of polarization. Then for the condenser and zener diode it is convenient to use the expressions:

$$E_e = \frac{1}{c} P_e; \quad E_0 \in rS(\dot{P}_0) \quad (c, r > 0 - const),$$

where the indices "e" and "0" indicate the induced and residual components, respectively, and S(v) is a sets function determined by the rule:

$$S(v) := \begin{cases} \{-1\}, \quad v < 0; \\ [-1,+1], \quad v = 0; \\ \{+1\}, \quad v > 0. \end{cases}$$

The generalization of the model is associated with various compounds of the elements, for example, in series (Fig. 15 a), or in parallel (Fig. 15 b). In the first case, we obtain a

differential inclusion that defines the "play" operator. In the second case, we obtain a differential inclusion, which defines the operator "stop" [19,20]. Next, we can determine the Prager polarization models by adding capacitors to the chains considered, as shown in Fig. 16.



Fig. 16. Polarizing models of Prager: a - capacitor in parallel; b - capacitor in series

Without dwelling on a detailed description of the Prager model, we note only the second case, shown in Fig. 16 b, which is described by the rheological formula [2]:

$$\left(1 + \frac{c_1}{c_2}\right) \dot{P} - c_1 \dot{E} \in S^{-1} \left(\frac{E - (1/c_2)P}{r}\right)$$

Without dwelling on a detailed description of the Prager model, we note only the second case, shown in Fig. 16 b, which is described by the rheological formula [2]:





Fig. 17. Generalized model of Prager



Varying the parameters of the model, it is possible to substantially change the shape of the hysteresis loop. The main drawback of this model is that with its help it is difficult to describe the saturation state.

**The Preisach model.** This model uses the rheological model "hysteron" [21,22], which describes the switching of a 180° domain with an increasing and decreasing electric field exceeding the coercive value. In fact, "hysteron" is a generalization of the sets function to the processes of switching a simple 180° domain. The model was proposed in 1935 by F. Preisach [23]. In the simulation of polarization, a set of 180° domains is introduced and the inhomogeneity of the structure is taken into account, according to which there is a large scatter of domains along coercive and internal fields. The switching of each domain is described by a rectangular hysteresis loop with its coercive ( $E_c$ ) and internal ( $E_i$ ) fields (Fig. 18).



0 E E E E E E E E E E E

Fig. 19. Diagram Preisach of depolarized ceramics

**Fig. 20.** Diagram Preisach at dE > 0





**Fig. 21.** Diagram Preisach at dE < 0

Fig. 22. Relay operator

The presence of a huge number of domains in ceramics allows us to talk about their probability distribution, with a probability density function  $\mu(x, y)$  defined on the plane  $\{|x| \le \infty, y > \infty\}$ :

$$\iint_{x \ge 0} \mu(x, y) dx dy = 1, \quad (x = E_i, y = E_c).$$

For each state in the half-plane there is a boundary separating the domains of two opposite directions. For an unpolarized state, it is the abscissa (Fig. 19). When an electric field of one or another sign is applied these boundary moves due to the involvement of new hysterons in the switching process (Fig. 20). If the electric field changes the direction of growth, then the direction of movement of the boundary also changes (Fig. 21).

The distribution function in the locality of coercive fields has a pronounced peak, which allows us to approximate it using known distributions, with subsequent determination of the parameters entering into it. There are also distribution functions in the form of polynomials in intense and coercive fields [24 - 27].

For a mathematical representation, we introduce the concept of an elementary dipole hysteresis operator (Fig. 22), or the relay operator [20]  $\gamma_{\alpha\beta}$  :  $C^0[o,T] \times \{-1,+1\} \rightarrow \{-1,+1\}$ , which is a rate independent one. The parameters  $\alpha$  and  $\beta$  for the relay operator and the parameters x and y for the hysteron are related by linear relations:  $\alpha = y - x$ ;  $\beta = y + x$ , so  $\gamma_{y-x,x+y} = \hat{\gamma}_{\alpha\beta}$ . The irreversible polarization is determined by the integral

$$P(t) = p_s^* \iiint_{x\geq 0} \mu(x, y) (\hat{\gamma}_{\alpha\beta} E)(t) dx dy,$$

where  $p_s^*$  is the maximum polarization value achievable in the process of ceramic polarization by a homogeneous electric field. It is noteworthy that if we choose a uniform distribution function

$$\mu(x, y) = \begin{cases} 1/E_{\max}^2, & \text{if} \quad (x, y) \in S_{\Delta}; \\ 0, & \text{if} \quad (x, y) \notin S_{\Delta}; \end{cases}$$

where  $S_{\Delta}$  is the region on the half-plane of the variables x and y, indicated in Fig. 19 by a triangle with hysterons, then by simple calculations of the integrals we easily find hysteresis dependences of the Rayleigh method.

The various shapes of the dielectric hysteresis loops, calculated using the Preisach model, can be found in [2]. The shape and slope of the loops depend strongly on the Gaussian distribution parameters. So for the case

$$\mu(x, y) = \frac{1}{\sqrt{2\pi}\sigma_1} \exp\left[\frac{-(x-a_1)^2}{2\sigma_1^2}\right] \frac{1}{\sqrt{2\pi}\sigma_2} \exp\left(\frac{-y^2}{2\sigma_2^2}\right),$$

where  $E_{\text{max}} = 2 \cdot 10^6 V/m$ ;  $\sigma_1 = \sigma_2 = 2 \cdot 10^2$  (the dimensions of  $\sigma_1, \sigma_2$  coincide with the dimensions of x, y), one can investigate the influence of the parameter  $a_1$  (dimensionality x). Assuming successively  $a_1 = 0, a_1 = 1 \cdot 10^6, a_1 = 2 \cdot 10^6, a_1 = 5 \cdot 10^6, a_1 = 7 \cdot 10^6$ , we obtain the loops shown in Fig. 23.

The Preisach model has become widespread not only in the description of magnetic and ferroelectric hysteresis, but it is intensively used in calculating the damping coefficients of many dynamical systems [28–52], including taking into account the dipole switching dynamics [53–60].



Fig. 23. Preisach model: the effect of increasing the parameter  $a_1$  on the shape of the hysteresis loop

#### 4. Three-dimensional models of polarization

Some three-dimensional models are a simple generalization of one-dimensional models to the 3D-case. These include evolutionary models, plasticity models and the Preysach model. But there are also those that differ fundamentally from those presented earlier. Some of them were described in [2], the other part will be presented below.

**Evolutionary model.** This model [61] describes hysteresis phenomena with the help of evolutionary laws leading to hereditary operators. In contrast to one-dimensional models, here the dipole moment is a vector quantity and is divided into instantaneous and transient parts:  $\boldsymbol{\mu} = \boldsymbol{\mu}_i + \boldsymbol{\mu}_i$ . The instant part depends functionally on strain, absolute temperature and electric field  $\boldsymbol{\mu}_i = \boldsymbol{\mu}_i (\mathbf{S}, \theta, \mathbf{E})$ , and the transition part is related to these parameters and to the vector **N** characterizing the number of domains by the evolutionary law. The vector parameter **N** also satisfies the evolutionary law:

 $\dot{\boldsymbol{\mu}}_{t} = \boldsymbol{f}_{u} (\boldsymbol{S}, \boldsymbol{\theta}, \boldsymbol{E}, \boldsymbol{N}), \quad \dot{\boldsymbol{N}} = \boldsymbol{f}_{N} (\boldsymbol{S}, \boldsymbol{\theta}, \boldsymbol{E}, \boldsymbol{N}).$ 

The constitutive relations for the stress tensor and the electric displacement vector are written in the form of functional relationships:

 $\mathbf{T} = \mathbf{T}^* \left( \mathbf{S}, \boldsymbol{\theta}, \mathbf{E}, \mathbf{N} \right); \quad \mathbf{D} = \mathbf{D}^* \left( \mathbf{S}, \boldsymbol{\theta}, \mathbf{E}, \mathbf{N} \right).$ 

The totality of these equations represents a general evolutionary model. The subsequent simplifications are related to the fact that only the isothermal process is considered, instead of the vector  $\mathbf{N}$ , only its projection to the axis of the electric field direction is considered, the evolutionary law for the transition part of the dipole moment is divided into two parts separately for strain and the electric field. Then the constitutive relations can be written in the form of a system of linear equations for the components of the corresponding tensors and vectors. In this case elastic, piezoelectric and dielectric constants for polarized ceramics get additional terms, but to avoid cumbersome expressions, they are not given here.

Another approach, based on the analogy between elastic and viscoelastic materials, was proposed in [62]. It is an extension of the Tiersten nonlinear response model [63] to the case of time dependence, for which the constitutive relations are written in the form of viscoelasticity operators.

**Models of the theory of plasticity.** Because of the similarity of the processes of polarization and plasticity, plasticity models are often used in describing irreversible processes of polarization and deformation, although they are phenomenological and are not related to the microstructure of the material. The polarization vector and the strain tensor consist of an induced (elastic) and a residual (plastic) part  $\mathbf{P} = \mathbf{P}_e + \mathbf{P}_0$ ,  $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_0$ . The induced components are related to mechanical stresses and electric field by linear relations, generalized to the three-dimensional case:

 $\boldsymbol{\epsilon}_{_{e}}=\boldsymbol{S}(\boldsymbol{\epsilon}_{_{0}},\boldsymbol{P}_{_{0}}):\!\boldsymbol{\sigma}\!-\!\boldsymbol{d}^{^{\mathrm{T}}}(\boldsymbol{\epsilon}_{_{0}},\boldsymbol{P}_{_{0}})\cdot\boldsymbol{E}; \qquad \boldsymbol{P}_{_{e}}=\boldsymbol{d}(\boldsymbol{\epsilon}_{_{0}},\boldsymbol{P}_{_{0}}):\!\boldsymbol{\sigma}\!+\!\kappa(\boldsymbol{\epsilon}_{_{0}},\boldsymbol{P}_{_{0}})\cdot\boldsymbol{E}\,.$ 

The physical characteristics  $\mathbf{S}, \mathbf{d}, \mathbf{\kappa}$  depend on the residual parameters. To determine the residual parts, a generalization is carried out from one-dimensional theory to three-dimensional by means of sets functions in the following way. For one hysteron in the one-dimensional case, the boundary  $\{E = -E_c, E = +E_c\}$  defines an interval within which  $E \in (-E_c, +E_c)$  there is no switching, and only after its attainment it is possible occurring the switching. In the three-dimensional case, the electric field is a vector quantity  $\mathbf{E} = \{E_1, E_2, E_3\}$ . The boundary of the segment is turning into the sphere  $f \equiv E_1^2 + E_2^2 - E_c^2 = 0$ ,

at achieving which a switch can occur. This description is well suited for single crystals when the field varies along one of the crystallographic axes. However, for polycrystalline ferroelectrics, with increase of the electric field, more and more domains are included in the switching process. To describe this phenomenon, a theory of plasticity with isotropic hardening is used. The surface of polarization changes its dimensions due to the introduction of a function of some parameter, remaining convex. If the increment of the field leads to the movement of the depicting point inside the surface or along a tangent to it, then there is no switching. But if the increment of the field leads to the motion of the depicting point along the normal to the surface, then the switching will occur and, as a consequence, the residual polarization changes. In the one-dimensional theory, a differential inclusion connecting the electric field and the rate of residual polarization was used to determine the rate of residual polarization. In the three-dimensional case, instead, an associated law is formulated, according to which the increment of the residual polarization is directed along the normal to

the surface  $d\mathbf{P}_0 = d\lambda \frac{\partial f}{\partial \mathbf{E}} = 2d\lambda (E_1\mathbf{i} + E_2\mathbf{j} + E_3\mathbf{k})$ . From here  $d\lambda = dP_0/2E$ , where

 $dP_0 = |d\mathbf{P}_0|$ ,  $E = |\mathbf{E}|$ . The increment  $\Delta P_0 = dP_0$  can be determined from a relationship  $P_0 = g(E)$  that is easily obtained from experimental data. Really, if  $\mathbf{E} = \{0, 0, E\}$ , and the hysteresis function  $P = \varphi(E)$  is gotten, then from  $P = P_e + P_0$ , and  $P_e = \kappa E$ , we easily obtain  $P_0 = g(E) \equiv \varphi(E) - \kappa E$ . For quasi-static processes, a sequence of values of the electric field is chosen  $\{E_m\}_{m=0}^M : E_m = E(t_m)$ , whence  $dP_{0,m} = g(E_m) - g(E_{m-1})$ . The presented scheme was realized in [64] in a slightly different interpretation of the unknown and determining parameters in [65].

In order to take into account the anisotropic hardening associated with changes in the physical characteristics of the material, plasticity models with both isotropic and kinematic hardening are used [66, 67]. The surface of polarization is modified

$$f \equiv (\mathbf{E} - \mathbf{E}^{\mathbf{B}}) \cdot (\mathbf{E} - \mathbf{E}^{\mathbf{B}}) - E_{c}^{2}(P_{0 \max}) = 0 ,$$

where  $\mathbf{E}^{\mathbf{B}} = \alpha \mathbf{P}_{\mathbf{0}}$  is the back field,  $E_c(P_0)$  is the hardening field. The parameter  $\alpha$  is a material characteristic which will be determined in the future, and the function  $E_c(P_0)$  is determined by experimentally. The increment of the residual polarization is determined by the associated law:  $d\mathbf{P}_0 = d\lambda \frac{\partial f}{\partial \mathbf{E}}$ , but the coefficient entering here is found by differentiating the equation of the polarization surface, and can be represented as

$$d\lambda = \frac{(\mathbf{E} - \mathbf{E}_{\mathbf{B}}) \cdot d\mathbf{E}}{(\mathbf{E} - \mathbf{E}_{\mathbf{B}}) \cdot \frac{\partial \mathbf{E}_{\mathbf{B}}}{\partial \mathbf{P}_{\mathbf{0}}} \cdot (\mathbf{E} - \mathbf{E}_{\mathbf{B}}) + 2E_{c} \frac{\partial E_{c}}{\partial \mathbf{P}_{\mathbf{0}}} \cdot (\mathbf{E} - \mathbf{E}_{\mathbf{B}})}.$$

The first term in the denominator is responsible for the kinematic hardening, and the second term is for isotropic hardening.

Mathematical 3D models of irreversible polarization processes of a ferroelectrics and ferroelastics polycrystal

In order to take into account the anisotropic hardening associated with changes in the physical characteristics of the material, both mechanical stresses, strains and polarization surface are constructed taking into account not only electrical but also mechanical parameters. The expressions for such a surface include the modified values of the electric field and mechanical stresses, and the surface itself is displaced in space [2, 68]:

$$f \equiv \frac{(\hat{\mathbf{E}} - \alpha \mathbf{P}_{0}) \cdot (\hat{\mathbf{E}} - \alpha \mathbf{P}_{0})}{E_{c}^{2}} - \frac{3}{2} \frac{(\hat{\mathbf{\sigma}} - \beta \boldsymbol{\varepsilon}_{0}) : (\hat{\mathbf{\sigma}} - \beta \boldsymbol{\varepsilon}_{0})}{\sigma_{c}^{2}} + \gamma \frac{(\hat{\mathbf{E}} - \alpha \mathbf{P}_{0}) \cdot (\hat{\mathbf{\sigma}} - \beta \boldsymbol{\varepsilon}_{0}) \cdot (\hat{\mathbf{E}} - \alpha \mathbf{P}_{0})}{E_{c}^{2} \sigma_{c}} + \eta \frac{\mathbf{P}_{0} \cdot (\hat{\mathbf{\sigma}} - \beta \boldsymbol{\varepsilon}_{0}) \cdot \mathbf{P}_{0}}{p_{sat} E_{c} \sigma_{c}} - 1 = 0$$

The constants  $\gamma$ ,  $\eta$ ,  $\mu$  entering here must ensure the convexity of the loading function. The parameters  $\alpha$ , $\beta$  are the functions of the intensity of the plastic deformation tensor and the residual polarization vector. Some authors use empirical formulas for their description, choosing parameters to satisfy the experimental data [68 – 73]. The increment of the residual  $\partial f$ 

parameters is determined by means of an associated law:  $d\mathbf{P}_0 = d\lambda \frac{\partial f}{\partial \hat{\mathbf{E}}}, \quad d\varepsilon_0 = d\lambda \frac{\partial f}{\partial \hat{\boldsymbol{\sigma}}}$  with

the same coefficient. This coefficient is determined after differentiating the equation of the polarization surface, but because of the bulky of the formulas, it is not given here. If we take in the previous expression  $\gamma$ ,= 0,  $\mu$  = 0, we obtain an expression for the loading function [70]. An example of loops of dielectric and deformation type "butterfly" hysteresis calculated from the described model from [70] for a certain set of parameters is given in Fig. 24.

The authors of [74] proposed to consider the related problems of polarization and deformation by introducing unconnected two loading functions for the electrical and mechanical parts with the subsequent determination of the two coefficients entering into the associated laws. It was noted in [75 - 80] that, in contrast to plasticity phenomena, where dislocations move for a long time, it is necessary to take into account the saturation state i.e. the state when all domains were switched and the switching process stopped. Therefore, it was suggested to consider four functions, two of which are loading surfaces, and the other two are criteria for the saturation state:

$$f^{f}(\mathbf{E}, \mathbf{P}_{0}) \equiv ||\mathbf{E} - c^{r} \mathbf{P}_{0}|| - E_{c},$$

$$h^{P}(\mathbf{\sigma}, \mathbf{E}, \mathbf{P}_{0}) = ||\mathbf{P}_{0}|| - \hat{P}_{sat}(\mathbf{\sigma}, \mathbf{E}, \mathbf{P}_{0}),$$

$$f^{f}(\mathbf{\sigma}, \mathbf{E}, \mathbf{P}_{0}, dev \boldsymbol{\varepsilon}_{0}^{f}) \equiv \sqrt{3/2} ||\mathbf{\sigma} - c^{f} dev \boldsymbol{\varepsilon}_{0}^{f}|| - \hat{\sigma}_{c}(\mathbf{E}, \mathbf{P}_{0}),$$

$$h^{f}(\mathbf{P}_{0}, dev \boldsymbol{\varepsilon}_{0}^{f}) = \sqrt{2/3} || dev \boldsymbol{\varepsilon}_{0}^{f}|| - (\varepsilon_{sat} - \sqrt{2/3} || dev \boldsymbol{\varepsilon}_{0}^{P} ||).$$



**Fig. 24.** a –  $D \leftrightarrow E$  hysteresis loop; b –  $\varepsilon \leftrightarrow E$  butterfly loop

It is assumed that  $dev\varepsilon_0$  is the deviator of residual strain tensor, and the residual strain consists of two parts:  $\varepsilon_0 = \varepsilon_0^f + \varepsilon_0^P$ . The first term corresponds to the strain due to the action of

the electric field, and the second term is the strain from the action of mechanical stresses. Associated laws lead to the appearance of four constants, which are found from the equations  $df^{P} = 0$ ,  $dh^{P} = 0$ ,  $df^{f} = 0$ ,  $dh^{f} = 0$ , but because of the cumbersomeness here are not given.

An example of hysteresis curves of the dielectric and deformation type "butterfly" hysteresis according to [77] can be seen in Fig. 25.



**Fig. 25.** a –  $D \leftrightarrow E$  hysteresis loop; b –  $\varepsilon \leftrightarrow E$  butterfly loop

Note that for the generally accepted plasticity models, empirically selected functions  $E_c(P_0)$  and others are provided in the calculation of the output of the hysteresis loop to the saturation state. The use of four functions to describe polarization processes lead to the fact that with increasing loads some conditions are replaced by others, and as a consequence, the smoothness of the loops is violated, sharply pronounced angles can appear on the hysteresis curves.

**The Preisach model.** Generalized Vector Preisach models have developed significantly for magnetization processes, while for polarization processes they are almost not used. The foundations of a simple generalization of the scalar model to the three-dimensional case are laid down in the works of I.D. Mayergoyz [82 – 85], and the main mathematical aspects are presented in [86]. The vector hysteresis model of Preisach is designed as a superposition of scalar models that are continuously distributed along all possible directions, and can be mathematically represented as:

$$\mathbf{f}(t) = \int_0^{2\pi} \int_0^{\pi/2} \mathbf{e}_{\theta\varphi} \left( \iint_{\alpha \geq \beta} v(\alpha, \beta, \theta, \varphi) \hat{\gamma}_{\alpha\beta} u_{\theta,\varphi}(t) d\alpha d\beta \right) \sin\theta d\theta d\varphi,$$

where  $\mathbf{f}(t)$  is the vector output value;  $\mathbf{e}_{\theta\varphi}$  is the unit vector along the direction defined by the spherical coordinates  $\theta, \varphi$ ;  $u_{\theta,\varphi}(t)$  is the projection of the input vector on the direction  $\mathbf{e}_{\theta\varphi}$ ;  $\hat{\gamma}_{\alpha\beta}$  is the hysteresis operator described in Section 3. For magnetic (ferroelectric) applications, we have  $\mathbf{u}(t)$  as the strength of the magnetic (electric) field;  $\mathbf{f}(t)$  is the residual magnetization (polarization) vector. The main idea of the method is that the total magnetization over all planes passing through the vectors of the magnetic field and the chosen direction is counted, and in each switching plane only 180° domains are approximated. It should be noted that for ferroelectric phenomena this model cannot be perceived by a simple analogy between electric and magnetic phenomena, because in ferroelectrics the position of domains is regulated by crystallographic axes. And if the rotation of the magnetization vector is possible for any position of the magnetic field, then for ferroelectrics there is no such possibility.

Models of plastic deformation of crystals (micromechanical models). The description of the model and the results of calculations can be found in [87–98]. Assuming that in the ferroelectric crystal the strain tensor and the polarization vector can be decomposed as a sum of linear (reversible)  $\varepsilon_{e}$ ,  $P_{e}$  and residual (analogous to plastic)  $\varepsilon_{0}$ ,  $P_{0}$  components:

 $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_{e} + \boldsymbol{\varepsilon}_{0}, \mathbf{P} = \mathbf{P}_{e} + \mathbf{P}_{0}$ , and, taking into account that  $\mathbf{D} \equiv \varepsilon_{0}\mathbf{E} + \mathbf{P}_{e} + \mathbf{P}_{0}$ , one can write down the determining equations of the linear piezoelectric response in the form:  $\boldsymbol{\varepsilon} = \mathbf{S}^{E} : \boldsymbol{\sigma} + \mathbf{d}^{T} \cdot \mathbf{E} + \boldsymbol{\varepsilon}_{0};$ 

$$\mathbf{D} = \mathbf{d} : \boldsymbol{\sigma} + \boldsymbol{\kappa}^{\boldsymbol{\sigma}} \cdot \mathbf{E} + \mathbf{P}_{\mathbf{0}}.$$

Here  $\sigma$ , **E**, **S**<sup>E</sup>, **d**,  $\kappa^{\sigma}$  are the stress tensor, the electric field strength vector, the elastic modulus tensor of the crystal, the tensor of the piezoelectric modules of the crystal, and the dielectric constants tensor of the crystal, respectively. In a tetragonal single crystal, six spontaneous polarization orientations are realized (along the positive and negative directions of the three crystallographic axes) therefore in the absence of external loads, the residual components are zero. When external loads are applied ( $\sigma$ , **E**), different domain switches are possible, with the possible implementation of 3D switching systems.

The residual deformation and polarization can be written as the sum of the contributions of individual domains:

$$\boldsymbol{\varepsilon}_{\mathbf{0}} = \sum_{I=1}^{6} c_{I} \boldsymbol{\varepsilon}_{SI}; \qquad \mathbf{P}_{\mathbf{0}} = \sum_{I=1}^{6} c_{I} \mathbf{p}_{SI},$$

where  $c_i$  is the concentration (volume fraction) of the I domain in a single crystal that satisfies the constraints:  $0 \le c_i \le 1$ ,  $\sum_{I=1}^{6} c_I = 1$ . Modules  $\mathbf{S}^{\mathbf{E}}, \mathbf{d}, \mathbf{\kappa}^{\sigma}$  of a single crystal are determined on the base of the modules of individual domains  $\mathbf{S}_{\mathbf{I}}^{\mathbf{E}}, \mathbf{d}_{\mathbf{I}}, \mathbf{\kappa}_{\mathbf{I}}^{\sigma}$  by relationships that take into account the volume fraction of each domain:

 $\mathbf{S}^{\mathbf{E}} = \sum_{I=1}^{6} c_{I} \mathbf{S}_{\mathbf{I}}^{\mathbf{E}}, \quad \mathbf{d} = \sum_{I=1}^{6} c_{I} \mathbf{d}_{\mathbf{I}}, \quad \mathbf{\kappa}^{\sigma} = \sum_{I=1}^{6} c_{I} \mathbf{\kappa}_{\mathbf{I}}^{\sigma}.$ 

The change in the concentration of the single I - domain of a single crystal is expressed in terms of the rate of switching from a state with an orientation I to a state with orientation J:

$$c_{I} = \sum_{\alpha=1}^{30} A^{I\alpha} \dot{f}^{\alpha} ,$$

where  $A^{I\alpha} = 1$ , if *I* - domain is the recipient  $\alpha$  of the switching system  $(\alpha : J \to I)$ ;  $A^{I\alpha} = -1$ , if *I* - domain is a donor  $\alpha$  switching system  $(\alpha : I \to J)$ ;  $A^{I\alpha} = 0$  in other cases. The rates of residual strains and polarization can be represented as

$$\dot{\boldsymbol{\varepsilon}}_{\boldsymbol{0}} = \sum_{I=1}^{6} \dot{c}_{I} \boldsymbol{\varepsilon}_{SI} = \sum_{\alpha=1}^{30} \dot{f}^{\alpha} \boldsymbol{\mu}_{\alpha} \boldsymbol{\gamma}_{\alpha}; \qquad \dot{\boldsymbol{P}}_{\boldsymbol{0}} = \sum_{I=1}^{6} \dot{c}_{I} \boldsymbol{p}_{SI} = \sum_{\alpha=1}^{30} \dot{f}^{\alpha} \boldsymbol{s}_{\alpha} \boldsymbol{P}_{\alpha},$$

where  $\boldsymbol{\mu}_{\alpha} = \frac{1}{2} (\mathbf{s}_{\alpha} \mathbf{n}_{\alpha} + \mathbf{n}_{\alpha} \mathbf{s}_{\alpha})$  is the Schmid orientation tensor;  $\mathbf{s}_{\alpha}$  is a unit vector in the direction of the polarization change;  $\mathbf{n}_{\alpha}$  is a unit vector associated with the axes of the cell;  $\gamma_{\alpha}$ ,  $P_{\alpha}$  are material constants.

To determine the kinematic variables  $\dot{f}^{\alpha}$  that play a fundamental role in describing the switching processes, the conditions of thermodynamic constraints are introduced *a priori*. Using the expression for the dissipation power

$$\delta = \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}}_0 + \mathbf{E} \cdot \dot{\mathbf{P}}_0 - \frac{1}{2} (\boldsymbol{\sigma} : \dot{\mathbf{S}}_{\mathbf{I}}^{\mathbf{E}} : \boldsymbol{\sigma} + 2\boldsymbol{\sigma} : \dot{\mathbf{d}}_{\mathbf{I}} \cdot \mathbf{E} + \mathbf{E} \cdot \dot{\mathbf{k}}_{\mathbf{I}}^{\boldsymbol{\sigma}} \cdot \mathbf{E}) = \sum_{\alpha=1}^{30} G^{\alpha} \dot{f}^{\alpha} ,$$

and taking into account all previous relationships, the driving force is calculated  $G^{\alpha}$ :

$$G^{\alpha} = \left[ \boldsymbol{\mu}_{\alpha} \boldsymbol{\gamma}_{\alpha} + \frac{1}{2} \sum_{I=1}^{6} A^{I\alpha} \left( \boldsymbol{\sigma} : \mathbf{S}_{\mathbf{I}}^{\mathbf{E}} + \mathbf{E} \cdot \mathbf{d}_{\mathbf{I}} \right) \right] : \boldsymbol{\sigma} + \mathbf{E} \cdot \left[ \mathbf{s}_{\alpha} P_{\alpha} + \frac{1}{2} \sum_{I=1}^{6} A^{I\alpha} \left( \mathbf{d}_{\mathbf{I}} : \boldsymbol{\sigma} + \boldsymbol{\kappa}_{\mathbf{I}}^{\boldsymbol{\sigma}} \cdot \mathbf{E} \right) \right].$$

After this, the evolution equations for finding the kinematic variables  $\dot{f}^{\alpha}$  are taken in the form:

$$\dot{f}^{\alpha} = B^{\alpha} \frac{G^{\alpha}}{G^{\alpha}_{c}} \left| \frac{G^{\alpha}}{G^{\alpha}_{c}} \right|^{n-1} \left( \frac{c_{I}^{donor(\alpha)}}{C_{0}} \right)^{m},$$

but in such a way the condition of non-negativity of dissipation is satisfied  $\delta \ge 0$ . Here  $G_c^{\alpha} > 0, B^{\alpha} > 0, n > 0, m > 0, C_0 > 0$  are material constants that determine the shape of the hysteresis curves;  $c_I^{donor(\alpha)}$  is the concentration of the *I* - domain (the donor  $\alpha$  switching system).

To describe the scleronomic behavior, one should choose  $n \gg 1$ , as usual, when analyzing the plasticity of crystals. The introduction of the last factor in the evolution equation allows us to describe the saturation effect and to satisfy the inequalities imposed on the volume fraction of domains. Assuming the uniformity of the mechanical stresses and the electric field at any time  $\sigma(t)$ ,  $\mathbf{E}(t)$ , it is possible to determine the driving forces  $G^{\alpha}$  for any switching system, and then directly the kinematic variables  $\dot{f}^{\alpha}$ . This model includes 7 parameters  $\gamma_{\alpha}$ ,  $P_{\alpha}$ ,  $G_{c}^{\alpha}$ ,  $B^{\alpha}$ ,  $n, m, C_{0}$ , which must be chosen from the condition of coincidence of calculated and experimental data.

In [99] generalizations were obtained, in the case when effects of the influence of grain boundaries of a polycrystalline material are taken into account.

For the transition from single crystals to polycrystals, the considered plasticity model of crystals must be supplemented by elements that take into account the mutual influence of the single crystals on each other. To this end, a finite-element (FE) approach was realized in [100] for a representative volume of a polycrystalline material. The set of single crystals for which the previously considered model is valid was described by a system of finite elements. Thus, the interaction of single crystals in the process of loading was accomplished by the interaction of one finite element with another, which is the base of the FE method. Such an approach does not take into account the influence of the grain boundaries, but allows us to operate with a huge number of domains taking account of their mutual influence on each other during switching process. This made it possible to describe in detail both the mutual influence of the crystallites on each other and take into account the micro-stresses under inhomogeneous and cyclic loading, and to find the reduced modules of polarized ceramics.

To evaluate the results of the described model, large dielectric hysteresis loops are given in Fig. 26 and Fig. 27, respectively, from [87] and [100].



Although a somewhat simplified model is presented in [87], it all the same belongs to this class of models, since it operates with the concentration of domains in the crystal.

Comparing these figures, one can draw an important conclusion: in Fig. 26 the loops have almost vertical walls, which are always observed in the polarization of ferroelectric crystals; in Fig. 27 the lateral walls of the loops have a pronounced slope and a smooth transition to the saturation curves, which is inherent in polycrystalline materials.

**Model of orientational switching.** In this model, a representative volume is considered, which includes a set of domains oriented in space in an arbitrary manner [101]. Not only 180°, but also 90° switching are considered, and the residual polarization vector and the residual strain tensor are determined by simple averaging:

$$\mathbf{P}_{\mathbf{0}} \equiv \langle \mathbf{p}_{s} \rangle = \frac{p_{s}}{N} \sum_{k} (\mathbf{c})_{k}; \qquad \mathbf{\varepsilon}_{\mathbf{0}} \equiv \langle \mathbf{\varepsilon}_{s} \rangle = \frac{\varepsilon_{s}}{N} \sum_{k} (\mathbf{c} \otimes \mathbf{c} - \frac{1}{2} \mathbf{a} \otimes \mathbf{a} - \frac{1}{2} \mathbf{b} \otimes \mathbf{b})_{k}.$$

The orientation of each domain is characterized by crystallographic axes  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  (Fig. 28). Let the vector of tenseness of the applied electric field is  $\mathbf{E}$ . We denote the plane, passing through the origin (the point of reduction) perpendicularity to the axis  $\mathbf{c}$  of the domain, as B, and the plane, passing through the vectors  $\mathbf{c}$  and  $\mathbf{E}$ , as A.



Fig. 28. Determination of angles in the model of orientational switching

The line of intersection of these planes will be a straight line OK. Let us denote  $\gamma_k$  is the smallest of the angles between **E** and the line of intersection of the planes. From the four possible directions of the vector **a** we choose the one at which it makes the angle closest to the field. We introduce the following angles:  $\gamma_c$  is the angle between the direction of the field and **c**-axis;  $\gamma_a$  is the angle between the vector **a** and the field **E**;  $\omega$  is the angle between **a**-axis and the line of intersection OK. It is obvious that the introduced angles are within  $0 \le \gamma_c \le \pi$ ;  $0 \le \omega \le \pi/4$ ;  $\omega \le \gamma_a \le \pi/2$ 

Let  $E_{cc}$ ,  $E_{ca}$  are the coercive fields of 180° and 90° switching, respectively. The main conditions are switching (rotations) of domains, which are written in the form of a system of inequalities of 180° rotations:

$$E\cos\gamma_c \ge E_{cc}; \quad \frac{E\cos\gamma_c}{E_{cc}} - \frac{E\cos\gamma_a}{E_{ca}} \ge 0.$$

For 90° rotations, we have  $\frac{E\cos\gamma_a}{E_{ca}} - \frac{E\cos\gamma_c}{E_{cc}} \ge 1$ , if the domain axis **c** is in the upper part of the sphere and  $E\cos\gamma_a \ge E_{ca}$ ;  $\frac{E\cos\gamma_a}{E_{ca}} - \frac{E\cos\gamma_c}{E_{cc}} \ge 0$ , if the domain axis **c** is in the lower part of the sphere. Dielectric hysteresis loops are constructed for quasi-static processes, i.e. for a sequence of equilibrium states  $\{E_i\}$ . For this purpose, the process of loading by an electric field E = E(t) is replaced by a sequence of its values  $E \in \{E_i\}$ :  $E_i = E(t_i)$ . For each state  $E = E_i$ , the domain switching conditions are checked, after which the residual polarization and the residual deformation are calculated. Then we have determined the arrangement of the spontaneous polarization vectors for a given vector **E**, we find the resultant polarization and strain. The dielectric hysteresis loop calculated from this model [2] can be seen in Fig. 29. Taking into account some point as a bringing point, we can assign to each vector of spontaneous polarization a unit vector. The distributions of the spontaneous polarization vectors before and after polarization are shown in Fig. 30.



For the calculations, the following values of the parameters included in the model were adopted: N = 1273248;  $E_{cc} = 2 \cdot 10^6 V/m$ ;  $E_{ca} = 3 \cdot 10^6 V/m$ ;  $E_{max} = 6 \cdot 10^6 V/m$ , where N is the number of spontaneous polarization vectors,  $E_{cc}$ ,  $E_{ca}$  are the coercive fields of 180° and 90° switching,  $E_{max}$  is the maximum value of the electric field. It should be noted that this model allows us to determine the magnitude of the cone angle  $\alpha$  in which the directions of the spontaneous polarization vectors are distributed after the removal of the electric field. With the specifying above numerical values of the parameters, we obtained:

 $\alpha = 129^{\circ}; P_{01} = -0.18 \cdot 10^{-4} p_s; P_{02} = -0.79 \cdot 10^{-5} p_s; P_{03} = 0.81 p_s.$ 

At physical terms, this model closely adjoins the physics of the phenomenon of polarization of polycrystalline ferroelectrics, but since it does not take into account the mutual influence of domains on each other, it has a "rectangular" loop like at single crystal.

**Model of energy switching.** This model also considers the representative volume, which includes a set of domains oriented in space in an arbitrary manner [2] and similar to the previous averaging method, the residual polarization vector is determined. The main difference infers in the description of the domain orientation and in the formulation of the domain switching criterion. For ferroelectrics of the perovskite type, the axes of the local system **a**, **b**, **c** are coaxial with the axes of the crystallographic system, as shown in Fig. 31 and with respect to a fixed system  $Ox_1x_2x_3$  are determined by means of three angles  $\varphi, \psi, \omega$ .



Fig. 31. Assignment the angles of the local coordinate system



**Fig. 32.** Possible positions of spontaneous vector. Polarization and deformation of a unit cell

Electric fields and mechanical stresses of high intensity cause a process of domain switching that are compatible with the crystallographic axes of the ferroelectrics, as shown in Fig. 32. With increasing external loads, the energy of each domain varies, but cannot exceed threshold values; switching occurs. If the domain is switched, then only to a position where its energy is minimal, and the switching moment occurs when the difference between the energies of the current state and the state with minimum energy exceeds the threshold value [1, 102, 103]. These conditions form the base of the criterion of energy switching:

 $-\mathbf{p}_{\mathbf{S}} \cdot \mathbf{E} + \mathbf{p}_{\mathbf{S}}^{\min} \cdot \mathbf{E} - \boldsymbol{\varepsilon}_{\mathbf{S}} : \boldsymbol{\sigma} + \boldsymbol{\varepsilon}_{\mathbf{S}}^{\min} : \boldsymbol{\sigma} \geq \boldsymbol{U}_{c} \,.$ 

Here **E** is the electric field vector;  $\boldsymbol{\sigma}$  is the tensor of mechanical stresses;  $U_c$  is the threshold value of energy.

Dielectric hysteresis loops are also constructed for quasistatic processes. Calculations showed that the form of the loop of dielectric hysteresis exactly coincides with the previous case; therefore, it is not given here. This is to be expected, since only domain switching conditions have changed.

Nevertheless, the energy model of switching has got its application after the appropriate generalization, which consists in taking into account the mutual influence of domains on each other. In [104, 105] it was done by applying the finite element method. The representative volume was divided into a lot of sub regions, taken for domains, and coinciding with finite elements. In each domain, the direction of the crystallographic axes was chosen by the random number sensor, and the direction of spontaneous polarization was set (for ferroelastics, the location of the spontaneous strain tensor was chosen). In a quasistatic process, the energy conditions are checked for each state in each finite element. If they are fulfilled, the domain is switched. After checking all the elements, the transition to the next state is made. The iterative process continues to the last state, which corresponds to the end of the load-unload process. The influence of domains on each other is realized by the mutual influence of finite elements on each other by the mechanical and electric fields. In [104,105] the energy criterion is presented somewhat in a different form, but the mathematical meaning of this has not changed. The results of calculations by the model [105] using the FE method can be seen in Fig. 33, where presented the large dielectric and strain loops of hysteresis.



**The Giles-Atherton model.** The model is based on the so-called "limit" (or anhysteretic) curve, derived analytically on the base of Weiss theory and Boltzmann statistics [106 - 113]. If there were no mechanisms for locking (or pinning) the domain walls in the ferroelectric, then after the removal of the electric field the polarization would be zero. This situation is observed in polar liquids, but in polycrystalline ferroelectrics there is a very different mechanism for switching domains. Nevertheless, the basic idea of modeling the polarization process is borrowed from there.

From the mathematical viewpoint, the limiting dependence can be explained and obtained by the methods of mechanics of a multilevel continuum. Let a transition be made from the unpolarized state at zero electric field to the current state with  $\mathbf{E} \neq 0$ . At the first stage, the micro-level is considered, for which it is supposed that the rotation of domains obeys statistical laws, therefore for a given electric field it is possible to find the distribution of all domains of representative volume. Then averaging is performed (the transition to the macro-level is carried out) and for a representative volume the polarization is obtained. Let assign to each vector of the electric field strength the resulting polarization vector. Since the correspondence is constructed for each transition from the unpolarized state to the current state, we obtain a single-valued dependence, which determines the "limiting" (maximum possible) polarization for a given electric field vector. The implementation of this approach was carried out by Tamm I.E. [106], and briefly it is as follows. Let the unit volume of the dielectric contains N domains with a constant density of the electric moment  $\mathbf{p}_{i}$ . Let for each vector of spontaneous polarization one established in compliance the collinear unit vector with beginning in some adducing point in space. The resulting polarization vector is found by determining the area of the unit sphere onto which the ends of the unit vectors exit. In an unpolarized state, all unit vectors are distributed uniformly over the entire surface, so that the resultant polarization is zero.

At the micro-level according to Weiss theory, it is considered that the field of forces acting on the dielectric domain is reduced to the sum of the electric field **E** and some "molecular field" proportional to the polarization of the representative volume:  $\mathbf{E}^{ef} = \mathbf{E} + \alpha \mathbf{P}_0$ , where  $\alpha$  is a certain constant that accepts for ferroelectrics large values in comparison with conventional dielectrics.

The fraction of the energy density of a domain that is similar to a dipole depends on the direction of its polarization vector and is expressed by the formula:  $U = -\mathbf{p}_s \cdot \mathbf{E}^{ef}$ .

According to the theorem of statistical mechanics, the Boltzmann theorem, under the conditions of thermodynamic equilibrium, the law of distribution of domains in the presence of a conservative force field (in this case the electrostatic field) differs from the law of their distribution in the absence of this field by a factor  $\exp(-U/k_*T)$ , where U is the density of the potential energy of the dipole in the electric field under consideration, T is the absolute

temperature,  $k_* = 1.38 \cdot 10^{-16}$  erg/deg is a Boltzmann constant. Therefore, the averaging operation yields the maximum possible polarization:

$$\mathbf{P}_{\infty} = \frac{p_s \int_{0}^{2\pi} d\varphi \int_{0}^{\pi} \exp\left(\frac{\mathbf{E}^{e_f} \cdot \mathbf{n}_s}{a}\right) \mathbf{n}_s \sin\psi d\psi}{\int_{0}^{2\pi} d\varphi \int_{0}^{\pi} \exp\left(\frac{\mathbf{E}^{e_f} \cdot \mathbf{n}_s}{a}\right) \sin\psi d\psi}, \quad \mathbf{p}_s = p_s \mathbf{n}_s, \quad a = \frac{kT}{p_s}.$$

Further actions are carried out at the macro-level for characteristics of a representative volume. As usual, the total polarization consists of two parts: reversible (induced)  $\mathbf{P}_{e}$ , and irreversible (residual)  $\mathbf{P}_{e}$ :

$$\mathbf{P} = \mathbf{P}_{e} + \mathbf{P}_{0}$$

The reversible part is a state parameter, and it can be defined as some part of the difference from the maximum and residual parts of the polarization:

 $\mathbf{P}_{\mathbf{e}} = c(\mathbf{P}_{\infty} - \mathbf{P}_{\mathbf{0}}),$ 

where c is still an indeterminate factor. The irreversible part of the polarization is the parameter of the process. To determine it, we estimate the energy necessary for breaking the mechanisms pinning the walls of the domain; calculate the work of the electric field in the ideal (limiting) case and count the work of the electric field in the real process of polarization. Further, the energy balance is derived, which can be formulated as follows: the real losses in the process of polarization are formed from losses in the ideal (limiting) case and the energy costs required to break the mechanisms of pinning the walls of the domains. This immediately yields the equation in the differentials for the residual polarization vector:

$$\mathbf{P}_{\infty} - \mathbf{P}_{\mathbf{0}} = k \frac{d\mathbf{P}_{\mathbf{0}}}{|d\mathbf{E}^{\mathrm{ef}}|},$$

where k is a positive constant to be determined. In a quasi-static process, the increment of the residual polarization vector is found numerically for each equilibrium state, after which the total polarization is determined. As a numerical approach the method of Runge-Kutta of the 4th-order gives good results [2]. You can also use the method of successive approximations with an invariable starting point. The latter circumstance is important, because at the same value of the electric field, the increment of the residual polarization vector depends on the direction of the process: as the field increases, we have one monotonic curve, while decreasing, another. When the electric field varies according to the harmonic law, we obtain dielectric hysteresis loops.

The model includes at oneself the 5 parameters:  $p_s$ ,  $\alpha$ , c, a, k, which are selected from the condition of coincidence of calculated and experimental data. In [2], in the onedimensional case, a lot of numerical experiments were carried out and the effect of the model parameters on the loop shape was investigated. It is shown that the coefficient  $\alpha$  is responsible for the amplitude of the loop, the coefficient a for its slope, the coefficient k for the loop area, the coefficient c for the flatness of the loop. Varying the values of the coefficients, one can achieve not only a qualitative but also a quantitative coincidence with the experimental data. For illustration, Fig. 34 shows the effect of the coefficient value on the form of dielectric loops. As the coefficient increases, the slope of the loop increases and its area increases.



Fig. 34. Giles-Atherton model: (a)  $k = 5.1 \cdot 10^5 V / m$ ; (b)  $k = 1.1 \cdot 10^6 V / m$ ; (c)  $k = 2.1 \cdot 10^6 V / m$ 

This model describes well the large hysteresis loops.

It was shown in [2,114] that the Giles-Atherton model can be generalized to the case of ferroelastics. In [114,115], changes were made to the Giles-Atherton model so to obtain not only large but also small hysteresis loops well coordinated with practice. Without dwelling on the subtleties of the additions, we present only the results of small loops of the dielectric and strain hysteresis in Figs. 35, 36. They agree well with the experimental data shown in Figs. 9, 12, not only qualitatively, but also quantitatively.



In [116,117] one is made a comparison between the Preisach and Giles-Atherton methods, including for the case where models include mechanical stresses.

The considered model of Giles-Atherton by its nature refers to micromechanical models. It uses statistical laws and approaches of a two-level continuum.

### **5.** Discussions

Each of the presented models performs the basic function related to the description of hysteresis dependencies. However, each of them is based on different prerequisites. Therefore, the results of the work of a particular model differ from the corresponding experimental data. Let us evaluate the positive and negative aspects of the models considered.

*Phenomenological models*: they are models in which functional nonlinearities are formulated for a representative volume. They include the Rayleigh model, evolutionary models and models of the theory of plasticity.

In the Rayleigh model, the nonlinear dependence between the electric field and polarization only approximately describes the dielectric hysteresis, and only for small and

medium values of electric field intensity. In evolutionary models, irreversible parameters were introduced in implicit form, for the disclosure of which evolutionary laws were used. Constitutive equations are obtained in the form of integral relations of the theory of viscoelasticity. The creep functions included in the integral relations are constructed for linear functions entering into the evolution equations, the formulation of increasing and falling hysteresis branches being based on inequalities in the functions describing the load and the response of the material. In the models of the theory of plasticity, the main role is played by the surface of polarization (loading), which includes itself a set of input parameters that make it possible to substantially change the shape of the hysteresis loop. Usually, these parameters are chosen so that the results of numerical calculations coincided with the experimental data, as accurately as possible.

*Micromechanical models*: they are models in which a two-level medium is used to construct the constitutive relationships in a representative volume. Initially the micro-level is considered at the first stage, where threshold loads are taken into account, leading to irreversibility of the proceeding process. Then, in the second stage, by means of averaging, the residual parameters are determined and the constitutive relations for the representative volume are built. The Preisach model, as well as the models plasticity of crystals, energy switching and Giles-Atherton all of them are included in the range of micromechanical models. For each of them, first, at the micro-level, the domain switching conditions are considered, and remaining parameters of the representative volume are found by averaging. In these models, a domain structure is considered in one or another extent.

The Preisach model operates with only 180° domains, and the hysteresis behavior of the functions is based on this. In mathematical terms, the approximation of a real loop is accomplished by elementary rectangular hysteresis loops. The model is intended only for finding the residual polarization, and does not operate with the induced part. In addition, this model does not include mechanical stresses, which significantly reduces its practical application in three-dimensional cases.

The remaining models consider more complete systems of domains. In the models of orientation and energy switching for each domain, a local coordinate system is introduced and the switching conditions are determined, which allows one to move step by step in the direction of irreversibility of the process and obtain an additive picture of the development of the residual parameters.

According to the model of orientational switching, the following conclusions can be drawn. In its essence, it is closer to the physics of the phenomenon of polarization of polycrystalline ferroelectrics, but does not take into account the influence of neighboring domains on each other during the polarization process. Because of this, the loop acquires angular shapes and is not suitable for describing the differential properties of the material. On the other hand, it allows us to find a solution of the angle in which the directions of all the spontaneous polarization vectors are located after reaching the saturation polarization. Another drawback of the model is that it does not include mechanical stresses, which does not allow it to investigate ferroelastic phenomena.

The energy model of switching by physical essence takes into account the physical phenomena of polarization of polycrystalline ferroelectrics, but also does not take into account the effect of neighboring domains on each other during the switching process. The dielectric hysteresis loop has angular shapes. In addition, this model operates only with the residual parameters of polarization and deformation and does not include induced components. However, it has an undeniable advantage, because it includes mechanical stresses, which makes it possible to describe ferroelectric and ferroelastic phenomena. Essential progress in terms of generalization of the model was achieved after applying the finite element method. As soon as each domain was matched with the final element, the effect

of the domains on each other was taken into account. This made it possible to obtain good results with satisfactory loops of dielectric and strain hysteresis.

In the Giles-Atherton model, statistical methods are used instead of switching criteria. Analytical expressions were obtained for determining the maximum possible polarization in the form of surface integrals in which the density of the domain distribution is described by functions of exponential type. The integrands were obtained on the base of the energy rotations of the domains as a function of the intensity of the electric field. In this model, the induced component is introduced along with the residual polarization, and the mutual influence of the domains on each other is taken into account twice. Firstly, by means Weiss field, and secondly, for the averaged characteristics in a representative volume, when been take into account the energy costs for breaking the mechanisms pinning the walls of the domain and calculating the work of the electric field in the ideal and real process of polarization. The model contains a set of 5 parameters, by appointing which it is possible to obtain a good coincidence of large hysteresis loops with experimental data. The drawbacks of the model include a very coarse approximation in the description of domain rotations in ferroelectrics, where this process is replaced by the process of rotation of dipoles as in polar liquids in the construction of limiting polarization. This immediately affects when trying to build small hysteresis loops, where the results of calculations lead to large discrepancies. It is noted that the modeling of ferroelastics can be carried out by Giles-Atherton methods if the electric field will be replaced by mechanical stress and a polarization by the strain. The main difference between the Giles-Atherton model and the models considered earlier is that it uses the density function of the domain distribution in the form of analytical integral relations.

## 6. Conclusions

In summary, three-dimensional theories are divided into phenomenological theories, in which the constitutive relationships are formulated without involving the microstructure of the material, and micromechanical, where such a structure and domain switching processes are taken into account. At first glance it seems that the more accurate the model relies on the physics of the phenomenon, the more accurate the results of its work, however and the phenomenological models give results sufficient to describe irreversible processes. As numerical experiments show, models that include many domains give good results in describing quantitative relationships. How to rule, for it need to select only a few parameters, in contrast to the phenomenological, where it is sometimes necessary to introduce empirical laws. It should be noted that at the moment the universal mathematical model of polarization and deformation of polycrystalline ferroelectric materials has not yet been developed. None of the models considered gives completely identical results with experimental data simultaneously for both large and small hysteresis loops. Some authors prefer one model, and others prefer another, it all depends on the purpose of the study. We can say that there are many unsolved problems that have practical significance. Unresolved problems include the following tasks:

(i) small loops of dielectric and strain hysteresis are not fully investigated;

(ii) in the generally accepted models, all possible effects from the action of each of the components of the stress tensor and the electric field vector are not fully reflected when they are simultaneously acted upon the represented volume;

(iii) there are no studies on how the anisotropy of the material changes with the simultaneous action of an electric field and mechanical stresses, when the direction of the electric field vector does not coincide with any of the principal directions of the stress tensor;

(iv) for quasistatic processes there are no models in which it would be possible to look at the picture of the passage of a domain switching wave along the volume of a ferroelectric;

(v) there are practically no studies related to the analysis of similarities and differences in the existing models of Preisach, Rayleigh, Giles-Atherton, plasticity of materials;

(vi) in fact there is no mathematical analysis of the influence of the model parameters on the final result;

(vii) the methods for selecting the model parameters are poorly represented and there is no formulation of the minimum set of parameters;

(viii) very poorly represented models in which the analytical functions of the density of the distribution of domains would be used, with the subsequent description of hysteresis operators.

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# THE TIME-STEP BOUNDARY-ELEMENT SCHEME ON THE NODES OF THE LOBATTO METHOD IN PROBLEMS OF 3-D DYNAMIC POROELASTICITY

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**Abstract.** A boundary-element scheme for analyzing initial boundary-value problems of 3-D porelasticity is considered. The scheme is based on a time-step method of numerically inverting Laplace transform. According to the method, a solution in time is calculated using quadrature formulas, based on complex values of the function in specific points. The choice of the points is determined by Lobatto method being one of Runge-Kutta methods. A possibility of using two- and three-stage Lobatto methods is considered. Using as an example the problem about a force, acting upon end of a prismatic poroelastic body, the effect of time-step on the dynamic responses of the forces is studied. The present results are compared with the results obtained on the nodes of Radau method.

**Keywords:** boundary element method, Runge-Kutta method, poroelasticity, transient dynamic analysis, wave propagation

#### **1. Introduction**

Studying wave propagation in poroelastic bodies subjected to dynamic loading is important in many engineering applications. The results of such studies are used to develop methods of non-destructive check, in soil structure analysis and earthquake seismology. Very often, an analytical solution to wave propagation problems is only possible in some special cases and for particular kinds of boundary conditions, so that numerical approximation methods such as the boundary element method (BEM) have been used. The BEM is especially suitable for wave propagation problems since it requires the formulation of the problem only along the boundary and produces highly accurate solutions.

In BEM-modeling of dynamic processes, three main approaches can be conventionally discerned: solving in time domain [1], solving in Laplace or Fourier transforms with the subsequent inversion of the transforms [2], and the dual reciprocity approach [3]. The numerical accuracy of the time-domain BEM with time-stepping discretization is strongly influenced by the time step size. In particular, the time-marching process becomes numerically unstable when using collocation methods, where the time step size is smaller than the element size. To overcome this difficulty, a number of stabilization techniques were developed [4, 5]. However, the time-domain approach cannot be used to solve wave propagation problems for poroelastic media due to the absence of fundamental solutions in time. Methods working in the frequency domain also have their limitations, as they require

efficient numerical techniques for inverse transforms and are applicable only to problems for which the correspondence principle is valid.

In 1988, Lubich [6,7] introduced the convolution quadrature method (CQM) to discretize the convolution integral. It gained significant interest as a technique (CQ-BEM) for applying the BEM to time-dependent problems where classical time-step schemes suffer from instability and numerical damping [8 – 10]. Later, it was shown in several studies that the CQ-BEM based on implicit Runge–Kutta method provides better accuracy than that based on the linear multistep method [11–15]. Moreover, Banjai and Sauter reformulated CQ-BEM approach to solve decoupled problems in Laplace domain that works as a transformation method [16]. Retaining the numerical stability properties of the original method, this approach has the time step size as the only parameter determined by the physical parameters of the problem. The applicability of the reformulated CQ-BEM to solution of poroelastic problems was demonstrated by Schanz, but only using the linear multistep method [17].

This study presents a modification of such a time-step scheme on the nodes of Runge-Kutta methods, exemplified by 2- and 3-stage Lobatto method. The time-step BEM scheme is based on the stepped method for numerically inverting Laplace transforms. This method is similar in its formulation to the CQM, but in contrast to it is based on the theorem of operational calculus for integrating in time-domain. The application of the scheme to problems of wave propagation in partially saturated media is considered.

#### 2. Governing differential equations

To describe a poroelastic continuum, Biot's mathematical model of a material is used, in which (the material) a solid phase, representing a form-generating skeleton, carrying the main stress load, and two fluid phases – water and air filling the pore system, are discerned. All the three phases are assumed compressible. Temperature variations are neglected. Moreover, porosity  $\varphi$  and saturation degree of the material  $S_f$  are defined as:

$$\varphi = \frac{V_{void}}{V}, S_f = \frac{V_f}{V_{void}}, \qquad (1)$$

where  $V_{void}$  is the volume of interconnected pores in the specimen, V is the total volume of the material,  $V_f$  is the volume of the filler, and it is assumed that f = a for air and f = w for water. Consider a case where the pores are completely filled:

$$S_a + S_w = 1.$$

The bulk density is defined as

$$\rho = (1 - \varphi)\rho_s + \varphi S_w \rho_w + \varphi S_a \rho_a, \tag{3}$$

where the densities of the solid, water and air is denoted by  $\rho_s, \rho_w, \rho_a$ , respectively.

In order to describe mechanical behavior of the partially saturated porous medium, the effective stress principle is used, which was introduced by Terzaghi [18]. The corresponding defining relations in terms of stress are expressed similarly to that adopted for fully saturated conditions [19, 20]:

$$\sigma'_{ij} = \sigma_{ij} + \alpha (S_a p_a - S_w p_w) \delta_{ij}, \tag{4}$$

where  $\sigma'_{ij}$  is the effective stress,  $\sigma_{ij}$  is the total stress,  $p_a$  denotes the pore air pressure,  $p_w$  is the pore water pressure,  $\alpha$  is a Biot constant. The coefficient  $\alpha$  is described by the relationship:

$$\alpha = 1 - \frac{K}{K_s},\tag{5}$$

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where K is the bulk modulus of the solid skeleton and  $K_s$  is the bulk modulus of the solid grains.

The solid skeleton is assumed elastic isotropic. Due to this fact, the effective stress tensor is given by

$$\sigma_{ij}' = \left(K - \frac{2}{3}G\right)\varepsilon_{kk}\delta_{ij} + 2G\varepsilon_{ij}, \qquad (6)$$

where G denotes the shear modulus,  $\varepsilon_{ij}$  denotes the strain tensor. The components of strain tensor  $\varepsilon_{ii}$  of a solid and displacements  $u_i$  are mutually coupled by the geometric relations:

$$\varepsilon_{ij} = \frac{1}{2} \left( u_{i,j} + u_{j,i} \right). \tag{7}$$

To construct equations of motion, defining equations must be combined with the related balance equations of momentum and balance equations of mass for each of the phases (for details see [21]). Using a Laplace transform makes it possible to write down the dynamic equations of a poroelastic medium in the form of a boundary-value problem for unknown displacement functions of the elastic skeleton  $\hat{u}_i$  and the pore pressures of the fillers  $\hat{p}^w$  and  $\hat{p}^a$ :

$$\begin{bmatrix} B_1 \delta_{ij} + B_2 \partial_i \partial_j & B_3 \partial_i & B_4 \partial_i \\ B_5 \partial_j & B_6 & B_7 \\ B_8 \partial_j & B_9 & B_{10} \end{bmatrix} \begin{bmatrix} \hat{u}_i \\ \hat{p}^w \\ \hat{p}^a \end{bmatrix} = \begin{bmatrix} -\hat{F}_i \\ -\hat{I}^w \\ -\hat{I}^a \end{bmatrix},$$
(8)

here

$$B_{1} = G\nabla^{2} - (\rho - \beta S_{w}\rho_{w} - \gamma S_{a}\rho_{a})s^{2}, B_{2} = K + \frac{G}{3}, B_{3} = -(\alpha - \beta)S_{w},$$
(9)

$$B_4 = -(\alpha - \gamma)S_a, \ B_5 = -(\alpha - \beta)S_w s, \ B_6 = -\left(\zeta S_{ww}S_w + \frac{\varphi}{K_w}S_w - S_u\right)s + \frac{\beta S_w}{\rho_w s}\nabla^2,$$
(10)

$$B_{7} = -(\zeta S_{aa}S_{w} + S_{u})s, B_{8} = -(\alpha - \gamma)S_{a}s B_{9} = -(\zeta S_{ww}S_{a} + S_{u})s,$$
(11)

$$B_{10} = -\left(\zeta S_{aa}S_a + \frac{\varphi}{K_a}S_a - S_u\right)s + \frac{\gamma S_a}{\rho_a s}\nabla^2, \qquad (12)$$

where  $K_w$  and  $K_a$  are bulk moduli of the fluid,  $\hat{F}_i$ ,  $\hat{I}^w$ ,  $\hat{I}^a$  are bulk body forces. Symbol "^" denotes Laplace transform with complex variable *s*.

The following abbreviations:

$$\zeta = \frac{\alpha - \varphi}{K_s}, \ S_{ww} = S_w - \mathcal{G}(S_w - S_{rw}), \ S_{aa} = S_a + \mathcal{G}(S_w - S_{rw}),$$

$$g_{+1} \qquad (13)$$

$$S_u = -\frac{\mathcal{G}(S_{ra} - S_{rw})}{p^d} \left(\frac{S_w - S_{rw}}{S_{ra} - S_{rw}}\right)^{\frac{\sigma}{g}},\tag{14}$$

are introduced, where  $S_{rw}$  is the residual wetting fluid saturation and  $S_{ra}$  is the non-wetting fluid entry saturation. The symbol  $p^d$  is the non-wetting fluid entry pressure,  $\mathcal{G}$  is the pore size distribution index. For most rocks,  $\mathcal{G}$  falls between 0.4 and 4. The symbols  $\beta$  and  $\gamma$  are Laplace parameter dependent variables and expressed as

$$\beta = \frac{\kappa_w \varphi \rho_w s}{\varphi S_w + \kappa_w \rho_w s}, \quad \gamma = \frac{\kappa_a \varphi \rho_a s}{\varphi S_a + \kappa_a \rho_a s}, \tag{15}$$

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where  $\kappa_w$  and  $\kappa_a$  the phase permeability of the wetting and the non-wetting fluid are given by  $\kappa_w = K_{rw} k / \eta_w$  and  $\kappa_a = K_{ra} k / \eta_a$ , respectively.  $K_{rw}$  and  $K_{rw}$  denotes the relative fluid phase permeability, k denotes the intrinsic fluid permeability,  $\eta_w$  and  $\eta_a$  are viscosity of the fluid. To evaluate relative phase permeability the following equations are used:

$$K_{rw} = S_e^{(2+3\beta)/\beta}, \ K_{ra} = (1 - S_e)^2 \left( 1 - S_e^{(2+\beta)/\beta} \right), \tag{16}$$

where  $S_e$  denotes the effective wetting fluid saturation degree given by

$$S_{e} = \frac{S_{w} - S_{rw}}{S_{ra} - S_{rw}}.$$
(17)

#### **3.** Laplace transform inversion

The stepped method for numerically inverting Laplace transforms is described in this section in brief. This method is close in its formulation to the CQM, but, in contrast to it, is based on the operational calculus of integrating original f(s) of representation  $\hat{f}(s)$ . In general, the integral

$$y(t) = \int_{0}^{t} f(\tau) d\tau$$
(18)

is approximated as follows [22]:

$$y(0) = 0, y(n\Delta t) = \mathbf{b}^T \mathbf{A}^{-1} \sum_{k=1}^n \mathbf{\omega}_k^{\Delta t}, n = 1, ...N ,$$
(19)

where *N* is the number of equal time steps. In this expression, the quadrature weights  $\omega_k^{\Delta t}$  are determined using Laplace representation  $\hat{f}(s)$  and the Runge-Kutta method. The quadrature weights can be expressed by Cauchy integral form and approximated by using a trapezoidal rule with the number of steps *L* as follows:

$$\boldsymbol{\omega}_{n}^{\Delta t} = \frac{R^{-n}}{L} \sum_{l=0}^{L-1} \hat{f}\left(\frac{\psi(z)}{\Delta t}\right) \frac{\psi(z)}{\Delta t} e^{-nl\frac{2\pi}{L}i}, \quad z = Re^{l\frac{2\pi}{L}i}, \quad (20)$$

$$\psi(z) = \mathbf{A}^{-1} - z\mathbf{A}^{-1}\mathbf{1}\mathbf{b}^{T}\mathbf{A}^{-1},$$
(21)

where  $\psi(z)$  is characteristic function of the Runge-Kutta method and  $\mathbf{1} = (1, 1, ..., 1)^T$ . The parameter *R* can be calculated by

$$R^{L} = \sqrt{\varepsilon} , \qquad (22)$$

where  $\varepsilon$  is the error of the numerical calculation of Equation (20).

The approximation used in deriving formulas (20), (21) is based on using the m-stage Runge-Kutta method written down using Butcher's table:

$$\frac{\mathbf{c} \mid \mathbf{A}}{\mathbf{b}^{T}}, \ \mathbf{A} \in \mathbb{R}^{m \times m}, \ \mathbf{b}, \mathbf{c} \in \mathbb{R}^{m}.$$
(23)

A correct formulation of a time-step scheme requires that the method be A-stable and L-stable. In the assumption of  $\mathbf{b}^T \mathbf{A}^{-1} = (0, ..., 0, 1)$ , the method is automatically L-stable. It is also important to note that the quadrature weights  $\boldsymbol{\omega}_k^{\Delta t}$  and the characteristic function  $\psi(z)$  are *m*-order matrices.

In the present study, Lobatto (Lobatto IIIC) and Radau (Radau IIA) schemes were chosen as a particular example of the Runge-Kutta schemes meeting the formulated conditions.

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#### 4. BEM formulation and numerical procedure

The boundary-element technique is based on the use of a regularized BIE direct approach [23]:

$$\int_{\Gamma} \left( \mathbf{T}(\mathbf{x}, \mathbf{y}, s) \mathbf{u}(\mathbf{x}, s) - \mathbf{T}^{\mathbf{0}}(\mathbf{x}, \mathbf{y}) \mathbf{u}(\mathbf{y}, s) \right) d\Gamma = \int_{\Gamma} \mathbf{U}(\mathbf{x}, \mathbf{y}, s) \mathbf{t}(\mathbf{x}, s) d\Gamma, \mathbf{x}, \mathbf{y} \in \Gamma, \Gamma = \partial \Omega,$$
(24)

where  $\mathbf{U}(\mathbf{x}, \mathbf{y}, s)$  and  $\mathbf{T}(\mathbf{x}, \mathbf{y}, s)$  are matrices of fundamental and singular solutions, respectively [24],  $\mathbf{T}^{0}(\mathbf{x}, \mathbf{y})$  contains isolated singularities,  $\mathbf{x}$  is the integration point,  $\mathbf{y}$  is the observation point,  $\mathbf{u}$  is the generalized displacement vector,  $\mathbf{t}$  is the generalized force vector.

To solve Equation (24), the boundary surface  $\Gamma$  is divided into generalized eight-node quadrangular elements; the coordinates of the points on the *k* element are determined from the relation:

$$\mathbf{x}(\xi) = \sum_{m=1}^{8} N_m(\xi) \mathbf{x}_m^k, \qquad (25)$$

where  $N_m$  are bilinear shape functions,  $\xi = (\xi_1, \xi_2) \in [-1, 1]^2$  are local coordinates,  $\mathbf{x}_m^k$  are global coordinates of nodes [25].

Generalized boundary functions of the first kind are approximated bi-linearly, and generalized boundary functions of the second kind are assumed constant over the element:

$$\mathbf{u}(\xi) = \sum_{l=1}^{4} R_l(\xi) \mathbf{u}_l^k, \, \mathbf{t}(\xi) = \mathbf{t}^k,$$
(26)

where  $R_l(\xi)$  are the bilinear shape functions,  $\mathbf{u}_l^k$  and  $\mathbf{t}^k$  are the values of generalized functions in the nodes of the *k*-th element.

The discrete representation of BIE (24) is constructed at the interpolation nodes of unknown boundary functions (collocation points) and has the following matrix form:  $[\Delta G]{T} = [\Delta F]{U}$ . (27)

Matrices  $\Delta \mathbf{G}$  and  $\Delta \mathbf{F}$  contain integrals of the components of matrices  $\mathbf{U}(\mathbf{x}, \mathbf{y}, s)$  and  $\mathbf{T}(\mathbf{x}, \mathbf{y}, s)$ , multiplied by the form functions. The choice of the numerical integration scheme for computing the integral depends on its type. When a collocation point lies on integration element, the procedure for revealing the feature is performed. To improve the accuracy of integration on an element that does not contain a collocation point, in addition to the Gauss integration formulas, a hierarchical integration algorithm is applied, wherein the element is subdivided until the specified accuracy is achieved.

#### 5. Numerical results

The 3D poroelastic column loaded by a Heaviside function is investigated as example to study the behavior of transformation method. The width of the column is b = 1 m, the height h = 3m. The column has zero displacements on one end and the normal force  $t_3 = -1N/m^2$  on the other end is prescribed. A boundary-element discretization consisting of 896 quadrangular elements is used in the computations. The sketch of problem is shown in Fig. 1. The parameters of the partially saturated porous material correspond to those of sandstone:  $\varphi = 0.23$ ,  $\rho_s = 2650 kg/m^3$ ,  $\rho_w = 997 kg/m^3$ ,  $\rho_a = 1.01 kg/m^3$ ,  $K = 1.02 \times 10^9 Pa$ ,  $G = 1.44 \times 10^9 Pa$ ,  $K_s = 3.5 \times 10^{10} Pa$ ,  $K_w = 2.25 \times 10^9 Pa$ ,  $K_a = 1.1 \times 10^5 Pa$ ,  $k = 2.5 \times 10^{-12} m^2$ ,  $\mu_w = 1.0 \times 10^{-3} N \cdot s/m^2$ ,  $\mu_a = 1.8 \times 10^{-5} N \cdot s/m^2$ .



Fig. 1. Geometry and boundary conditions of a partially saturated poroelastic column

The boundary-element solutions obtained using different methods of the Runge-Kutta family are compared for the values of forces  $t_3$  in the rigidly fixed part of the column. Jumping change of the forces makes it possible to compare the results in the conditions of additional difficulties of approximation. The boundary-element solutions are also compared with a one-dimensional numerical-analytical solution. Time step  $\Delta t$  is taken to be 0.00005 *s* for the 2-stage methods, and 0.0002 *s* for the 3-stage ones. The total number of complex-valued points required for computing a solution is assumed constant for all the methods. The diagrams of forces are present in Figs. 2-5.



Fig. 2. Force solution  $t_3$  at the fixed end versus time for the 2- and 3-stage Radau IIA method



**Fig. 3.** Force solution  $t_3$  at the fixed end versus time for the 2- and 3-stage Lobatto IIIC method

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**Fig. 4.** Force solution  $t_3$  at the fixed end versus time for the 2-stage Lobatto IIIC method compared to the solution for the 2-stage Radau IIA method



Fig. 5. Force solution  $t_3$  at the fixed end versus time for the 3-stage Lobatto IIIC method compared to the solution for the 3-stage Radau IIA method

It is evident in Figs. 2, 3 that the boundary-element solutions obtained at the nodes of the Lobatto and Radau methods are close to the numerical-analytical solution of the onedimensional problem. The 2- and 3-stage Radau methods in problems of boundary-element modeling of the dynamics of fully saturated poroelastic bodies are compared in [12] for the values of flow. The present study corroborates the conclusions made in [12] and makes it possible to extend them to include the case of using 2- and 3-stage Lobatto methods in problems of boundary-element modeling of the dynamics of partially saturated poroelastic bodies. In particular, it can be observed (Figs. 2, 3) that the forces computed using the 3-stage versions of the both Runge-Kutta methods have smaller perturbation amplitude at the jump points. Moreover, the propagation interval of the oscillations is also smaller than the range in the case of using the 2-stage versions. Though in the first case, a long time step is used due to the sensibility of the 3-stage methods to small steps, the force curve is quite smooth. Separate comparison of the 2-stage methods reveals that Radau method yields forces of considerably smaller perturbation amplitude in the jump points and of considerably smaller propagation interval (Fig. 4). In this case, minor oscillations of the forces over the entire time interval are also observed, testifying to the closeness of the time step chosen to its maximal value. At the same time, the forces obtained using the 2-stage Lobatto method do not show any oscillations of this kind. Similar effects, but less pronounced, are observed, when comparing the 3-stage methods (Fig. 5). Based on the conducted investigations, it can be asserted that the use of 3-stage methods of the Runge-Kutta family proves more preferable in the case of step change of the solution.

### 6. Conclusion

A boundary-element scheme on the nodes of 2- and 3-stage Lobatto methods for analyzing dynamic problems of partially saturated poroelastic bodies is present. A mathematical model of a partially saturated poroelastic medium is given. Results of the numerical analyses are present, which corroborate the conclusions of other authors concerning the combined use of BEM and methods of the Runge-Kutta family. The conclusions are extended to include the use 2- and 3-stage Lobatto methods in problems of boundary-element modeling of the dynamics of partially saturated poroelastic bodies.

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# FIRST PRINCIPLE ELECTRONIC, MAGNETIC AND THERMODYNAMIC CHARACTERIZATION OF HEAVY FERMION TERNARY RARE EARTH METAL ALLOYS

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**Abstract.** Ternary rare earth metal alloys (viz. GdInZn, GdTlZn and GdInCd) play a key role in a large range of current research areas, in particular those devoted to heavy fermions, valence fluctuations, magneto-strictive materials, permanent-magnet materials, spin glasses and random anisotropy systems. Thus, to understand the relevant complex behavior of Gd/M/M<sup>1</sup>, M=In, Tl; M<sup>1</sup> = Zn, Cd compounds (viz. GdInZn, GdInCd and GdTlZn), in the present research article, we have been carried out the theoretical investigations on electronic, magnetic and thermodynamic characteristics of Gd/M/M<sup>1</sup> type compounds in the hexagonal P63/mmc phase using density functional theory (DFT).

**Keywords:** structural properties, electronic structure, magnetic properties, thermodynamic properties

#### **1. Introduction**

F-block rare earth (RE) elements show unusual magnetic behaviour when they make alloys with "d" orbital transition metals (M) and other metallic atoms (M<sup>1</sup>). The materials which have high spin polarization at room temperature are highly advantageous because of their broad technological applications in the area of spintronics and permanent magnets. They play a key role in a large range of current research areas, in particular those devoted to heavy fermions, valence fluctuations, magneto-strictive materials, permanent-magnet materials, spin glasses and random anisotropy systems [1-3].

Gd/M/M<sup>1</sup>, M=In, TI; M<sup>1</sup> = Zn, Cd (viz. GdInZn, GdInCd and GdTIZn) are the 1:1:1 stoichiometry systems that may be used in the field of spintronics and magnetic devices. So far, Gd is known as a heavy fermion rare earth atom consisting of 4f unpaired electrons. The study of 4f-states in the ternary rare earth intermetallics is extremely useful tool in reference to electronic and magnetic study. Gd/M/M<sup>1</sup> compounds form CaIn<sub>2</sub> type crystal structure with space group P63/mmc (194) with Wyckoff positions Gd (0, 0, 0); In or Tl (1/3, 2/3, 1/4) and Zn or Cd (1/3, 2/3, 3/4) [4].

A very little literature is available on these alloys. The magnetic and structural properties of Gd/M/M<sup>1</sup>, M=In, Tl; M<sup>1</sup> = Zn, Cd (viz. GdInZn, GdInCd and GdTlZn) intermetallics have been synthesized and analyzed by Morin et al, Mazzone et al and Rossi et al [5-8]. Literature review shows that only a little amount of structural and magnetic studies [5-8] have been made on these compounds and no spin polarized electronic, magnetic and thermodynamic studies have been reported on these intermetallic compounds. Thus, motivation for the present

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work is to examine and give more explanation on (i) spin polarized electronic spectra (ii) magnetic structure and (iii) thermodynamic behavior.

#### 2. Computational approach

In the present computational approach, density functional theory (DFT) [9,10] using Perdew, Burke and Ernzerhof generalized gradient approximation for exchange and correlation (PBE-GGA) [11] have been used to carried out the electronic, magnetic and thermodynamic calculations of Gd/M/M<sup>1</sup> (M=In, Tl; M<sup>1</sup> = Zn, Cd) type compounds. The cutoff energy for the present calculations was chosen as -6.0 Ry and 18 x 18 x 9 k points have been used to calculate the total and partial density of states. For SCF calculations, the charge has been chosen less than 0.0001 ec. The Muffin Tin sphere radius (R<sub>MT</sub>) is the smallest atomic sphere radius in a unit cell. Its value must be small provided no core charge should be leaked out. If charge leaks out then R<sub>MT</sub> is increased such that no charge leaks out. Smaller value of R<sub>MT</sub> needs more plane waves and calculations become more expansive. The RMT values in our case were chosen as 2.50 for each atom in case of GdInZn. In case of GdInCd, RMT values were used as 2.50 for Gd and 2.43 for In and Zn whereas in case of GdTIZn RMT values were used as 2.50 for Gd, 2.48 for Tl and 2.36 for Cd. These values of R<sub>MT</sub> were found to be satisfactory for the calculations. The Fermi energies were found to be 0.4307 eV, 0.4338 eV and 0.4722 eV for GdInZn, GdInCd and GdTIZn (see Table 1) respectively.

Magnetic moment is a crucial quantity which gives the magnetic strength and orientation of magnetization. The magnetic moment here is calculated by spin polarized calculations using DFT under PBE-GGA [11] exchange correlation. Spintronics has been promising area to the researchers since last two decades to fabricate the advanced electronic devices based on spin. Thus, to make more significant our magnetic/spin polarized calculations, we have also calculated the electron spin polarization (P) which plays a key role in making new spin dependent electronic devices. It is a dimensionless quantity given [12] by

$$P = \frac{N \uparrow (E_F) - N \downarrow (E_F)}{N \uparrow (E_F) + N \downarrow (E_F)},\tag{1}$$

where,  $N \uparrow (E_F)$  and  $N \downarrow (E_F)$  are the density of states for majority and minority spin channel at the Fermi level.

The thermodynamic properties of a bulk material are correlated by electronic structure, atomic vibrations and nature of bonding between the atoms. In the present research paper thermodynamic properties are determined by Quasi-harmonic Debye model [13, 14].

In quasi-harmonic Debye model the imbalance condition Gibbs function  $G^*(V; P, T)$  is given by

$$G * (V; P, T) = E(V) + PV + A_{Vib}(\theta \theta(V)T).$$
<sup>(2)</sup>

Here E(V) is the total energy per unit cell of GdInZn, GdInCd and GdTlZn, PV denotes the constant hydrostatic pressure,  $\theta(V)$  is the Debye temperature, and  $Av_{ib}$  is the vibration term which can be expressed using Debye model of the phonon density of states as [13, 14]

$$A_{vib}(\theta \theta T) = nkT \left[ \frac{9\theta}{8T} + 3\ln(1 - e^{-\theta/T}) - D\left(\frac{\theta}{T}\right) \right].$$
(3)

Here, *n* is the number of atoms per formula unit,  $D(\theta/T)$  is the Debye integral. For an isotropic solid,  $\theta$  can be expressed as [13, 14]

$$\theta_{D} = \frac{\hbar}{k} \left[ 6\pi V^{1/2} n \right]^{1/3} f(\sigma(\sqrt{\frac{B_{s}}{M}}.$$
(4)

Here, *M* is the molecular weight per unit cell. The function,  $f(\sigma)$  and adiabatic bulk modulus,  $B_s$  (which is nearly equal to the static compressibility) are given by

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$$f(\sigma) = \left[ 3 \left\{ 2 \left( \frac{2(1+\sigma)}{3(1-2\sigma)} \right)^{3/2} + \left( \frac{1+\sigma}{3(1-\sigma)} \right)^{3/2} \right\}^{-1} \right]^{1/3};$$
(5)

$$B_{s} = B(V) = V \frac{d^{2} E(V)}{dV^{2}}.$$
(6)

The imbalance Gibbs function as a function of (V; P, T) is minimized with respect to volume V:

$$\left[\frac{\partial G * (V; P, T)}{\partial V}\right]_{P,T} = 0.$$
(7)

If we solve the above equation with respect to volume V, one can obtain the thermal equation of state (EOS) V (P, T) and specific heats,  $(C_V, C_p)$  and thermal expansion coefficient,  $\alpha$  can be determined by the following expressions:

$$C_{\nu} = 3nk \left[ 4D \left( \frac{\theta}{T} \right) - \frac{3\theta/T}{e^{\theta/T} - 1} \right];$$
(8)

$$S = nk \left[ 4D\left(\frac{\theta}{T}\right) - 3\ln(e^{\theta/T} - 1) \right];$$
<sup>(9)</sup>

$$\alpha = \frac{\gamma C_v}{B_T V}; \tag{10}$$

$$C_p = C_v (1 + \alpha \gamma T). \tag{11}$$

Here  $\gamma$  represents the Grüneisen parameter, expressed as

$$\gamma = -\frac{d\ln\theta(V)}{d\ln V} \,. \tag{12}$$

#### 3. Results and discussion

**Structural properties.** The known values of energy,  $E_0(V)$  and volume,  $V_0$  (which are determined by optimization method) in equilibrium state are used to determine the structural parameters viz. lattice parameters ( $a_0$ ,  $c_0$ ), bulk modulus,  $B_0$  and its first order pressure derivative,  $B'_0$  by using Birch-Murnaghan's equation of state expressed by equation (13) [15].

$$E_{total} = E_0(V) + \frac{B_0 V_0}{B_0'(B_0'-1)} \left[ B_0 \left( 1 - \frac{V_0}{V} \right) + \left( \frac{V_0}{V} \right)^{B_0'} - 1 \right].$$
(13)

The volume curves determined by optimization energy versus for  $Gd/M/M^1$  (M=In, Tl; M<sup>1</sup> = Zn, Cd) are shown in Figs. 1(a-c). Figs. 1(a-c) reveal that Gd/M/M<sup>1</sup> compounds are well stable with minimum energy values ( $E_0$ )  $\approx$  -75840.011293 eV, -133462.437043 eV and -91039.549934 eV corresponding to equilibrium volume  $(V_0) \approx 942.1371 \text{ a.u}^3, 968.4446 \text{ and } 1036.7237 \text{ a.u}^3 \text{ (see Table 1) for GdInZn, GdTlZn and }$ GdInCd respectively. The calculated lattice parameters  $(a_0, c_0)$ , bulk modulus,  $B_0$  and its first order pressure derivative,  $B_0^{'}$  are shown in Table 2. The calculated values of  $a_0$  and  $c_0$  show close agreement with available experimental values [8]. Bulk modulus  $(B_0)$  has inverse relation with compressibility i.e. larger the value of bulk modulus, smaller will be compressibility. Here, in our case, can be seen from it Table 2 that  $(B_o)_{GdInZn} > (B_o)_{GdTIZn} > (B_o)_{GdInCd}$ . It indicates that compressibility decreases from

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 $GdInCd \rightarrow GdTlZn \rightarrow GdInZn$ , indicating that GdInCd is more compressible than GdTlZn and GdInZn.

	(		0
	GdInZn	GdInCd	GdTlZn
$E_F$	0.4307	0.43385	0.4729
$E_{min}$	-75840.011293	-91039.549935	-133462.437043
$V_0$	942.13	1036.72	968.44

Table 1. Fermi energy,  $E_F$  (eV), Minimum energy,  $E_{min}$ , (Ryd), unit cell volume, V<sub>0</sub> (a. u. ^3) in equilibrium condition (at 0K) for GdInZn, GdInCd and GdTlZn using PBE-GGA

Spin polarized electronic and magnetic properties. The results on spin polarized electronic properties have been expressed in terms of energy band structure and total, partial density of states for spin up (up) and spin down (dn) states. The calculated electron dispersion curves for GdInZn, GdTlZn and GdInCd for spin up and spin dn channel along the high symmetry directions  $\Gamma$ , M, K and A in the Brillouin zone are shown in Figs. 2 (a-f). These Figures indicate that most of the valence bands lie from -7.0 eV to 0.0 eV (where Fermi level, E<sub>F</sub> is considered at origin) in GdInZn, -11.0 eV to 0.0 eV in GdTlZn and -9.0 eV to 0.0 eV in GdInCd. Figs. 2 (a-f) depict that the bands which are existed in GdTlZn at about -11.0 eV are disappear in GdInZn and GdInCd because Tl and In have the electronic configuration [Xe]  $4f^{14}5d^{10}6s^{2}6p$  and [Kr]  $4d^{10}5S^{2}$  (i. e. these bands at about -11.0 eV in GdTlZn are due to dominance of Tl-f bands and In does not contain f valance bands). Furthermore, these electron dispersion curves of GdInZn, GdTlZn and GdInCd for spin up and spin dn channel reveal no bandgap as valance bands and conduction bands are crossing the Fermi level, signifying that GdInZn, GdTlZn and GdInCd have metallic character. This metallic character in all three compounds is caused by bonding of p orbitals of In (or Tl) and Zn. Also, there exist denser bands in spin dn channel at about 0.2 eV above the Fermi level which are available for conduction in all three compounds. These bands are caused by mainly Gd-f orbitals. The total density of states (TDOS) and partial density of states (PDOS) plots for GdInZn, GdTlZn and GdInCd are shown in Figs. 3-5 (a-i). It is clear from Figs. 3 (a) and 5 (a) that in case of GdInZn and GdInCd, there are mainly two peaks for spin up channel at around -7.0 eV and -5.0 eV below the Fermi level whereas spin dn channel have also two peaks at around -7.0 eV below Fermi level and 0.20 eV above the Fermi level.

Table 2. Lattice parameters,  $a_0$ ,  $c_0$  (Å), Bulk modulus,  $B_0$  (GPa), Pressure derivative of bulk modulus,  $B_0'$  (GPa) equilibrium condition (at 0K) for GdInZn, GdInCd and GdTlZn using PBE-GGA

Compounds	$a_0$	$c_0$	$B_0$	$B_0$
GdInZn	4.301	7.408	65.76	5.30
Expt. [8]	4.596	7.602	-	-
GdTlZn	4.691	7.721	60.72	5.13
Expt. [8]	4.778	7.813	-	-
GdInCd	4.583	7.803	45.74	4.13
Expt. [8]	4.810	7.826	-	-



**Fig. 1.** Total energy as a function of unit cell volume for (a) GdInZn (b) GdTlZn and (c) GdInCd with PBE-GGA approximation

Volume [a.u.^3]





**Fig. 2.** Spin polarized electron dispersion curves along high symmetry directions in the Brillouin zone for (a) GdInZn\_up (b) GdInZn\_dn (c) GdTlZn\_up (d) GdTlZn\_dn (e) GdInCd\_up (f) GdInCd\_dn



Fig. 3. Calculated total and partial density of states for (a) GdInZn -Total
(b) Gd-Total and In-Total (c) Zn-Total (d) Gd-s and Gd-p orbital
(e) Gd-d orbital and Gd-f orbital (f) In-s and In-p orbital (g) In-d orbital and In-f orbital
(h) Zn-s orbital and Zn-p orbital (i) Zn-d and Zn-f orbital



(b) Gd-Total and Tl-Total (c) Zn-Total (d) Gd-s and Gd-p orbital
(e) Gd-d orbital and Gd-f orbital (f) Tl-s and Tl-p orbital (g) Tl-d orbital and Tl-f orbital
(h) Zn-s orbital and Zn-p orbital (i) Zn-d and Zn-f orbital



Fig. 5. Calculated total and partial density of states for (a) GdInCd -Total
(b) Gd-Total and In-Total (c) Cd-Total (d) Gd-s and Gd-p orbital
(e) Gd-d orbital and Gd-f orbital (f) In-s and In-p orbital (g) In-d orbital and In-f orbital
(h) Cd-s orbital and Cd-p orbital (i) Cd-d and Cd-f orbital.

Figure 4(a) depicts TDOS for GdTlZn and show that there are three peaks for spin up channel at around -11.0 eV, -7.0 eV and -5.0 eV below the Fermi level whereas spin dn

channel have also three peaks at around -11.0 eV, -7.0 eV below Fermi level and 0.2 eV above the Fermi level. In GdTlZn, the extra peak at around -11.0 eV is mainly caused by hybridization of Gd-p and Tl-d states.

In case of GdInZn, the peak at around -7.0 eV is mainly due to Zn-d states along with strong hybridization of Zn-s and In-s states as well as hybridization of In-p and Zn-p states for both the spin up and spin dn channel. The sharp peak at around -5.0 eV is caused by mainly Gd-f spin up channel with small contribution of Zn-s states. In case of GdTlZn, the peak at around -7.0 eV is mainly due to Zn-d states with small contribution of Tl-s states for both the spin up and spin dn channel. The sharp peak at around -5.0 eV is caused by mainly Gd-f spin up and spin dn channel. The sharp peak at around -5.0 eV is caused by mainly Gd-f spin up channel with small contribution of Zn-s states. In case of GdInCd, the peak at around -7.0 eV is mainly due to Cd-d states along with small contribution of In-s and In-d states for both the spin up and spin dn channel. The sharp peak at around -5.0 eV is caused by mainly Gd-f states for both the spin up and spin dn channel. The sharp peak at around -5.0 eV is caused by mainly Gd-f states for both the spin up and spin dn channel. The sharp peak at around -5.0 eV is caused by mainly Gd-f states for both the spin up and spin dn channel. The sharp peak at around -5.0 eV is caused by mainly Gd-f states with small contribution of Cd-s and In-s states. The sharp peak at about 0.2 eV above the Fermi level for all three compounds is contributed by Gd-f states which are available for conduction.

The calculated total magnetic moments for GdInZn, GdTlZn and GdInCd compounds along with the magnetic moment on individual atom and in the interstitial region have been displayed in Table 3. The values of calculated total magnetic moment of the GdInZn, GdTlZn and GdInCd compounds were found to be 7.66  $\mu_B$  /f. u., 7.72  $\mu_B$  /f. u. and 7.51  $\mu_B$  /f. u. (or  $\mu = 14.67 \ \mu_B$  / cell,  $\mu = 14.75 \ \mu_B$  / cell and  $\mu = 14.47 \ \mu_B$  / cell for GdInZn, GdTlZn and GdInCd). However, experimental values of magnetic moment of GdInZn, GdTlZn and GdInCd are not available in the literature only theoretical value of total magnetic moment for the unit cell for GdTlZn ( $\mu = 14.70 \ \mu_B$  / cell) [16] is available which is in close agreement with our calculated value of magnetic moment ( $\mu = 14.47 \ \mu_B$  / cell). Table 3 depicts that Gd<sup>3+</sup> ions has dominant character in total magnetic moment of GdInZn, GdTlZn and GdInCd in which "f" orbital electrons of Gd atom are mainly accountable for the total magnetic moment.

The value of electron spin polarization (*P*) at the Fermi energy ( $E_F$ ) for a material is calculated by equation (1). The value of "*P*" characterizes the magnetic materials. Zero value of "*P*" defines the paramagnetic materials (because in the paramagnetic materials occupancy of spin up and spin down states is equal) whereas value P < 1, ensures the ferromagnetic material [12]. In our cases, the calculated values of electron spin polarization *P* were found to be nearly equal to -0.47, -0.45 and -0.43 (-47%, -45%, -43%), for GdInZn, GdTlZn and GdInCd respectively as values of  $N \uparrow (E_F)$  are 1.4 eV, 1.1 eV and 1.2 eV and  $N \downarrow (E_F)$  are 3.0 eV, 3.1 eV and 3.2 eV for GdInZn, GdTlZn and GdInCd respectively at the Fermi level. These values of P < 1, employing all the three compounds are ferromagnetic materials. The negative sign of *P* indicates the dominancy of minority spin channel.

**Thermodynamic properties.** The quasi-harmonic Debye model has been used to investigate the temperature and pressure dependent thermodynamic properties of GdInZn, GdTlZn and GdInCd. The effect of temperature has been studied in a wide temperature range 0-600K for GdInZn, GdTlZn and GdInCd, whereas pressure effect has been studied in pressure range 0-15GPa at different temperatures (at 0K, 300K and 600K). Temperature dependent variations in bulk modulus, *B* Debye temperature,  $\theta_D$  Specific heat at constant volume,  $C_V$  thermal expansion coefficient,  $\alpha$  and entropy, *S* for GdInZn, GdTlZn and GdInCd are shown in Figs. 6-8.

	GdInZn	GdInCd	GdTlZn
Interstitial region	0.6637	0.7403	0.5546
Gd	7.0194	7.0023	6.9833
In (or Tl)	-0.0067	-0.0069	-0.0080
Zn (or Cd)	-0.0132	-0.0071	-0.0140
Total	7.6632	7.7286	7.5159
Calculated by VASP [16]	-	-	14.383

Table 3. Calculated spin magnetic moments  $(\mu_B)$  of GdInZn, GdInCd and GdTlZn using PBE-GGA

Figures 6(a-c) show the variation of bulk modulus with temperature. These figures depict that bulk modulus, B decreases with increasing the temperature. Bulk modulus, B is inversely proportional to compressibility. Thus, Figs. 6(a-c) show that all the three compounds (GdInZn, GdTlZn and GdInCd) become more and more compressible with increasing the temperature *i.e.* all the three compounds become flexible with increasing the Debye temperature is a thermodynamic parameter derived from elastic temperature. properties of the materials. It provides some detailed information of a solid material viz. specific heat, melting temperature etc. Figures 6(d-f) display the variation of Debye temperature with temperature and depict that Debye temperature ( $\theta_D$ ) remains nearly constant upto T  $\approx$  50K and then decreases at slow rate with increasing the temperature for all three compounds. The variation in  $\theta_D$  is nearly same as that of bulk modulus [see Figs. 6(a-c) and 6 (d-f)], reflects that Debye temperature is directly proportional to the bulk modulus (i. e. elasticity of a material). Furthermore, it can be seen from Figs. 6 (d-f) that  $\theta_D$  of GdInZn is higher than GdInCd and GdTlZn, indicating GdInZn is stiffer than GdInCd and GdTlZn (as stiff material has high Debye temperature).

Grüneisen parameter  $\gamma$  describes the anharmonicity under vibrational motion of crystal lattices. Figs. 7(a-c) show the variation of the Grüneisen parameter with temperature, depict that the Grüneisen parameter increases with temperature.  $\gamma$  is a function of volume in quasi-harmonic Debye model which depends upon lattice parameters (see equation 12). As temperature increases, the lattice dimensions and hence volume expand with temperature. In expansion process, the atoms of the crystal get large space to vibrate whereas in compression they get small space for vibration. Therefore, the value of  $\gamma$  and hence crystal anharmonicity increases with the temperature. Specific heat,  $C_v$  is an important key which provide essentials insight into the vibrational properties as well as microscopic structure of a crystal. The temperature dependent behavior of the calculated heat capacity at constant volume ( $C_V$ ) is shown in Figs. 7(d-f). It is obvious that  $C_V$  follows the Debye model relationship ( $C_V \propto T^3$  law) up to T  $\approx$  300 K and then (beyond T > 300K)  $C_v$  approaches to Dulong-Petit limit (i. e. a constant value).

Figures 8(a-c) show the variation of thermal expansion coefficient,  $\alpha$  as a function of temperature. The thermal expansion coefficient increases with increasing the temperature sharply as temperature approaches to 300K. Beyond the temperature T > 300K, the effect of temperature on  $\alpha$  becomes less pronounced. Microscopically, entropy (S) is a form of energy produced by the disorder of a system under variational motion of the atoms. The variation of entropy, S with temperature for all three compounds has been shown in Figs. 8 (d-f).

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Figures 8(d-f) show that S is zero at 0 K and as temperature increases, the entropy increases rapidly due to increasing the vibrational contribution.



**Fig. 6.** Temperature induced variation in Bulk modulus, *B* for (a) GdInZn (b) GdTlZn and (c) GdInCd. Temperature induced variation in Debye temperature,  $\theta_D$  for (d) GdInZn (e) GdTlZn and (f) GdInCd



**Fig. 7.** Temperature induced variation in Grüneisen parameter,  $\gamma$  for (a) GdInZn (b) GdTlZn and (c) GdInCd. Temperature induced variation in specific heat,  $C_V$  for (d) GdInZn (e) GdTlZn and (f) GdInCd



**Fig.8.** Temperature induced variation in thermal expansion coefficient,  $\alpha$  for (a) GdInZn (b) GdTlZn and (c) GdInCd. Temperature induced variation in enthalpy, *S* for (d) GdInZn (e) GdTlZn and (f) GdInCd



**Fig. 9.** Pressure induced variation in Bulk modulus, *B* for (a) GdInZn (b) GdTlZn and (c) GdInCd. Pressure induced variation in Debye temperature,  $\theta_D$  for (d) GdInZn (e) GdTlZn and (f) GdInCd





**Fig. 10.** Pressure induced variation in Grüneisen parameter,  $\gamma$  for (a) GdInZn (b) GdTlZn and (c) GdInCd. Pressure induced variation in specific heat,  $C_V$  for (d) GdInZn (e) GdTlZn and (f) GdInCd



**Fig.11.** Pressure induced variation in thermal expansion coefficient,  $\alpha$  for (a) GdInZn (b) GdTlZn and (c) GdInCd. Pressure induced variation in enthalpy, *S* for (d) GdInZn (e) GdTlZn and (f) GdInCd.

Figures 9-11 show the variation in *B*,  $\theta_D$ ,  $\gamma$ ,  $C_V$ ,  $\alpha$  and *S* with pressure for GdInZn, GdTlZn and GdInCd. Figs. 9(a-c) describe the variation in bulk modulus (*B*) with pressure.

Variation in bulk modulus with pressure shows that *B* increases with pressure, indicating that compressibility and hence flexibility of all three compounds decreases with pressure because bulk modulus is inversely proportional to compressibility and hence flexibility. Figures 9(d-f) illustrate the pressure dependent variation in Debye temperature ( $\theta_D$ ), depict that  $\theta_D$  increases with pressure at different temperature. As  $\theta_D$  is the measure of elasticity, thus, elasticity of all the three compounds increases with pressure. It is noticeable from Figs. 9 (a-c) and 9(d-f) that as temperature increases from 0K $\rightarrow$ 300K $\rightarrow$ 600K, the bulk modulus and Debye temperature decreases from 0K $\rightarrow$ 300K $\rightarrow$ 600K, the flexibility and stiffness decreases at each value of pressure.

It is clear from Figs. 10 (a-c), that Grüneisen parameter decreases with pressure, demonstrating that anharmonicity decreases with pressure at each value of temperature. Figures 10 (d-f) display the variation of  $C_V$  with pressure at different temperatures. It is clear from these Figs. that  $C_V$  decreases at faster rate at low temperatures (at T = 300K) while  $C_V$  decreases at smaller rate at higher temperatures (at T = 600K).

Figures 11(a-c) (variation in  $\alpha$  with pressure) depict that for a given temperature,  $\alpha$  decreases significantly with the increasing pressure. From Figs. 11(d-f), it is observed that *S* decreases with pressure. It is caused by decreasing the lattice dimensions and hence contraction of volume with increasing the pressure, results smaller space for vibrational contribution to energy (i. e. atoms are less spread out and hence entropy decreases).

#### 4. Conclusions

In the present research article electronic, magnetic and thermodynamic properties of Gd/M/M<sup>1</sup> (M=In, Tl; M<sup>1</sup> = Zn, Cd) compounds have been investigated using DFT. The obtained structural parameters are in good agreement with the experimental/theoretical data available in literature. The bands structure shows the metallic character of Gd/M/M<sup>1</sup> (M=In, Tl; M<sup>1</sup> = Zn, Cd). Total magnetic moment has been investigated from spin polarized calculations; indicate the dominant contribution of Gd<sup>3+</sup> ions (mainly Gd-f orbital electrons) in the total magnetic moment. Electron spin polarization calculations show that these compounds are ferromagnetic with dominance of minority spin channel.

Temperature and pressure dependent thermodynamic calculations show interesting features on bulk modulus, *B* Debye temperature,  $\theta_D$  specific heat,  $C_V$  thermal expansion coefficient,  $\alpha$  and entropy, *S* for Gd/M/M<sup>1</sup> (M=In, Tl; M<sup>1</sup> = Zn, Cd).

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# A SYNTHESIS OF BA<sub>x</sub>SR<sub>1-x</sub>TIO<sub>3</sub> FILM AND CHARACTERIZATION OF FERROELECTRIC PROPERTIES AND ITS EXTENSION AS RANDOM ACCESS MEMORY

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**Abstract.** Ferroelectric material is generally used in engineering fields for such purposes as sensors, microelectronics, etc. It also provides more advantages compared to ferromagnetic materials, especially those related to a memory storage. This is due to a stored memory produced from magnetic system only consists of 105 bits/cm<sup>2</sup> whereas a memory from ferroelectric can be stored up to 108 bits/cm<sup>2</sup>. The objectives of this study were 1) to develop BST films on Pt (200) / SiO<sub>2</sub> / Si (100) substrates and p-type Si (100) substrates using the chemical solution deposition (CSD) method and 2) to test and study ferroelectric properties, XRD and SEM / EDS structure of the film produced. The research method used was an experiment, starting with the making of BST thin films, then ferroelectric tests, SEM / EDAX tests and XRD tests. The results of ferroelectric test show that all samples have ferroelectric properties. Therefore, annealing temperature affected a remanent polarization value and the coercive area of the sample. Regarding a memory application, BST (BA<sub>x</sub>SR<sub>1-x</sub>TIO<sub>3</sub>)1 M sample with 900°C of annealing temperature is the best material to be used since they have a high remanent polarization and a low coercive field.

Keywords: annealing, BST, ferroelectric, ferromagnetic

#### 1. Introduction

Random Access Memory (RAM) functions as a temporary data storage that can be run randomly when the computer is activated. The material of data storage in RAM is primarily made from ferroelectric thin films. It changes an internal polarization by using a proper electric field and spontaneous polarization of the material which determines a quality of the materials. Some main ferroelectric thin film materials consist of BaSrTiO<sub>3</sub>, PbTiO<sub>3</sub>, Pb (ZrxTi<sub>1-X</sub>) O<sub>3</sub>, SrBaTaO<sub>3</sub>, Pb (Mg<sub>1/3</sub>Nb<sub>2/3</sub>) O<sub>3</sub> and Ba<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>.

Among those ferroelectric thin film materials mentioned above,  $BaxSr_{1-x}TiO_3$  (BST) is widely used as RAM since it has a high dielectric constant and high charge storage capacity [1]. A ferroelectric RAM which has a polarization value of about 10  $\mu$ C.cm<sup>-2</sup> may produce a charge of 1014 electrons per cm<sup>-2</sup> for a memory reading process [2].

This study focused on the thin BST film on Pt (200) /  $SiO_2$  / Si (100) substrates and p-type Si (100) substrates making through *Chemical Solution Deposition* (CSD) method which was then tested for ferroelectric, XRD, and SEM/EDS properties. In addition, BST was chosen because its manufacture can be simply done in a laboratory and in making it environmentally-friendly.

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# 2. Methodology

# 2.1 Materials

The materials used in this study were barium acetate powder [Ba  $(CH_3COO)_2$ , 99%], strontium acetate powder [Sr  $(CH_3COO)_2$ , 99%], titanium isopropoxide [Ti $(C_{12}O_4H_{28})$ , 99.999%], solvent 2- methoxyethanol [H3COCH2CH2OH, 99%], Pt (200) / SiO2 / Si (100) substrate and p-type Si (100) substrate.

# 2.2 BST film making

**Creating BST solvent.** BST Solvent was made by utilizing barium acetate  $[Ba (CH_3COO)_2, 99\%] + titanium isopropoxide <math>[Ti(C_{12}O_4H_{28}), 99,999\%]$  as *precursor* and 2-methoxyethanol  $[H_3COOCH_2CH_2OH, 99,9\%]$  as solvents [3]. After all materials were mixed, the solvent was shaken for one hour. The produced solvent was then combined with acetic acid and then re-shuffled for 30 minutes. After that, it was heated to make all materials to be well-mixed. Finally, the solvent was filtered so that a more homogeneous solvent was obtained.

**Preparing the substrates.** This study used Pt (200) /  $SiO_2$  / Si (100) and p-type Si (100) substrates. In producing the film, cleanliness of the substrate surface was an absolute requirement in order to produce it well and effectively.

Pt (200) / SiO<sub>2</sub> / Si (100) and p-type Si (100) substrates were washed by immersing them in methyl alcohol and then vibrating with ultra-sonic for about 5 minutes (until they were clean). After this process, it was dried by using nitrogen gas for 1 minute [4].

**Growing the film.** A substrate was put on a spin coating reactor which has been affixed with insulation in the middle position, then it was dripped with one drop of precursor solvent and rotated by using a spin coating reactor with a rotating speed of 3000 rpm for 30 seconds. This process was done 5 times to obtain 5 layers on the substrate. After that, the substrate was taken by using tweezers and dried by placing it on the surface of the iron which has been heated for 1 hour at approximate temperature of 120°C.

**Annealing process.** Annealing process was done by applying furnace Neberthem model Type 27. The substrates used were Pt (200)/SiO<sub>2</sub>/Si (100) and Si (100) type-p substrate. Annealing was proceeded at the temperatures of 900°C, 950°C and 1000°C.

The annealing process was carried out gradually. The temperature of the furnace was regulated by increasing the temperature of 100°C per hour to the specified annealing temperature. Temperature detention was executed for 15 hours. Next, the cooling furnace was put into a room temperature. Regarding this, in general, the annealing process is presented in Fig. 1.



Fig. 1. Annealing process

A synthesis of BAXSR1-XTIO3 film and characterization of ferroelectric properties and its extension...

#### 2.3 Characterization

**X-Ray diffraction.** The XRD function is to determine the crystal system (cube, tetragonal, orthorhombic, rhombohedra, hexagonal, monocline, triclinic), resolve the quality of crystals (single crystal, poly crystal, amorphous), crystal symmetry, crystal defects, to reach crystal parameters (lattice parameters, distance between atoms, number of atoms per unit cell), identification of mixtures (e.g. in alloys) and chemical analysis. All observations are made from an angle of  $(2\theta) 40^{\circ}$  to  $60^{\circ}$  with an angle increasing to  $0.02^{\circ}$  every five seconds.

**Ferroelectric test.** This ferroelectric test aims to regulate the ferroelectric properties of the film obtained. The results of this test revealed saturation polarization values (Ps), remanent polarization (Pr) and coercive field (Ec) from the film. A thin film was also transformed into a structure as shown in Fig 2. Besides, this study employed a Radiant Technological A Charge Ver. 2.2. tool.



**Fig. 2.** Structure of Ferroelectric Test. (a) Ferroelectric test on Substrate Pt (200) /SiO<sub>2</sub>/ Si (100), (b) Ferroelectric on Substrate Si (100) type-p

#### 3. Results and discussion

The sample produced in this study can be seen in Table 1.

	2	
Sample Name	Substrate (s)	Annealing Temperature (°C)
BST		900
	Pt(200)/SiO <sub>2</sub> /Si(100)	950
		1000
	Si (100) type-p	900
		950
		1000

### 3.1. XRD test results

In this study, the XRD test was conducted with a diffraction angle of  $(2\theta) 20^{\circ}$  up to  $80^{\circ}$  with an increment angle of  $0.02^{\circ}$ . The XRD test results are displayed in Fig. 3.



**Fig. 3.** XRD BST graphs for: (a) Pt (200)/SiO<sub>2</sub>/Si (100) Substrate and (b) Si (100) Type-p Substrate

In Figure 3, it demonstrates the increment of annealing temperature casuing differences in the nature of the film. All samples grown on the Si (100) substrate have been damaged. In contrast, not all samples grown on substrate Pt (200) / SiO<sub>2</sub> / Si (100) were broken. According to Adem (2003), platinum (Pt) is very well used as a bottom electrode for thin-film ferroelectric-dielectric devices because it has a high thermal conductivity (71.6 Wm<sup>-1</sup>K<sup>-1</sup>) and good stability in an oxygen atmosphere [5].

The higher the temperature of annealing is, to a certain extent, the better the quality of the ctrystal gets. However, too high annealing temperature may impair the crystal. It is indicated in BST samples raised on Pt (200) /  $SiO_2$  / Si (100) substrates, the samples were broken at higher annealing temperatures.

Increasing chemical substances may also affect the sample. BST film layer is crystalizing when the annealing temperature is  $1000^{\circ}$ C mixed with Pt (200) / SiO<sub>2</sub> / Si (100) substrate, while the same treatment to BFST thin film may also be distracted.

Based on the calculation of lattice constants, it is stated that all samples are tetragonal, as presented in Table 2.

Types of Sample	Lattice Parameter (Å)		Crystal Shana	
	А	С	c/a	Crystar Shape
BST-Pt-900	3,8469	4,1174	1,0703	tetragonal
BST-Pt-1000	3,8472	4,1137	1,0693	tetragonal
BST-Si-900	-	-	-	damaged
BST-Si-1000	_	_	_	damaged

Table 2. The calculation result of BST parameter lattice sample

#### **3.2. Ferroelectric test results**

The results demonstrate that all samples made, both BST 1 M and BFST 1 M 10%, were ferroelectric. It can be seen from the hysteresis curve formed from each sample. The treatment of differences in annealing temperature, increasing of chemical substances and subtracting differences also influenced the parameter values obtained from ferroelectric tests. In this study, ferroelectric tests were carried out by providing voltage variations from 5 V to 13 V.

The hysteresis curve of BST 1 M film on Pt (200) /  $SiO_2$  / Si (100) substrates can be seen in Fig. 4.



**Fig. 4.** Hysteresis curve of BST 1 M on Pt (200)/SiO<sub>2</sub>/Si (100) Substrate with annealing temperature 900°C (b) 950°C (c) 1000°C

Figure 4 shows that the greater the voltage applied, the curvier the shape will be. On the curve (a), the width of the curve displays the field strength (kV.cm-2) measured in the sample. This is because the voltage increment causes more orientation of parallel domains so that the strength of the terrain will increase [5].

In BST 1 M film samples with 950 and 1000°C annealing temperatures (see curves b and c in Fig. 4), the curves were no longer perfect. This indicates that the voltage given to the sample has passed the breakdown voltage which causes the sample to no longer be in a ferroelectric state but it has become paraelectric a situation where the sample has no longer spontaneous polarization [5].

Moreover, in Fig. 5, it can be identified that the BST hysteresis curve is varied by an external stress and annealing temperature.



**Fig. 5.** Hysteresis curve BST 1 M on Pt (200)/SiO<sub>2</sub>/Si (100) Substrate to the varied *Annealing* temperature

The variation of external voltage and temperature of annealing slightly affect sample saturation polarization. After saturation is achieved, the voltage does not increase to the saturation polarization value because in this situation, all domains have been oriented in the same direction [5]. After the saturation state, the greater external voltage will cause the sample to lose its ferroelectric properties. Besides polarization, the annealing temperature also affected the remanent polarization (Pr) and the coercive field strength (Ec).

Regarding the remanent polarization (Pr) (see Fig. 5), the higher the annealing temperature, the lower the remanent polarization values can be obtained. The remanent polarization value is lower due to the smaller and standardized grain size [5].

For coercive field values (Ec), this result is in a good agreement with literature. According to Koutsaroff et al., the temperature of annealing leads to the grain size formed in the sample. As a result, the higher the temperature, the more grain size formed [6]. Under the size of the critical grain size, there is a transition from a multi-domain structure to a more stable mono-domain. Hence, re-orienting the domain in an external electric field becomes more difficult as it is increasing the coercive field [7]. In BST samples grown on Pt (200) / SiO<sub>2</sub> / Si (100) substrates, the increment of annealing temperature influenced the grain size to be smaller (this can be seen from the XRD peak shape) and the sample coercive field decreased (see Fig. 5).

The BST 1 M film hysteresis curve on p-type substrate Si (100) can be seen in the Figs. 6a, 6b, and 6c.



**Fig. 6.** Hysteresis curve of BST 1 M on Si (100) type-p substrate to the annealing temperature (a) 900, (b) 950, and (c) 1000°C

Figure 6 (a) displays the results of ferroelectric test showing that the greater the voltage applied, the more curved the shape of the figure- or commonly known as *Ferroelectric*. For curves (b) and (c) at external voltages of 12V, the curves formed were no longer perfect. Consequently, the sample did not act as ferroelectric but it became a *paraelectric*.

Figure 7 presents hysteresis curve of BST which is varied by annealing temperature.



Fig. 7. Hysteresis curve BST 1 M on Si (100) Type-p Substrate to the varied annealing temperature

In addition, variation of external voltage and temperature of annealing slightly affected a sample of saturation polarization. Once it was done, the addition of external voltage did not change the saturation polarization value since all domains had been oriented in the same direction [5].

In BST 1 M samples increased to p-type Si (100) substrate, annealing temperature increment caused the remanent polarization values and decreased a coercive field. This is due to the condition of the sample that had been damaged.

#### 3.3. An Analysis of SEM/EDS

SEM / EDS analysis is required to determine the phases and chemical compositions. Observations from the results of SEM / EDS are presented in Fig. 8.



Fig. 8. The results of EDS to BST (Anil 1000°C) on Pt Substrate

From the SEM / EDAX BST data shown previously, Si (100) at annealing temperature of 1000°C, Ba, Sr and Ti elements were detected. The results of SEM / EDAX BST on Pt (200) at annealing temperature of 900°C, are displayed in Fig. 9.


Fig. 9. The results of SEM/EDAX BST on Pt (200) of annealing temperature 900°C

Results of SEM / EDAX, BST data on Pt substrate (200) at annealing temperature of 900°C, Ba, Sr and Ti elements were detected. Whereas if the annealing temperature of 1000°C, Sr element is no longer detected as presented in Fig. 10.



**Fig. 10.** The Results of SEM/EDAX BST on Pt (200) Substrate of annealing temperature 1000°C

# 4. Conclusion

BST film has ferroelectric properties as shown from the hysteresis curve produced based on ferroelectric tests. The temperature of annealing has a dominant influence on the value of the coercive field and a remanent polarization. This is due to the fact that the higher the annealing temperature, the greater the grain size produced. However, too high annealing temperature may also affect the sample to suffer a damage as resulted in a decrease in the coercive field value and the remanent polarization of the sample. After saturation has been achieved, the greater external voltage will lose ferroelectric properties of the sample. Film samples grown on Pt (200) / SiO<sub>2</sub> / Si (100) substrates, and increment of chemical material cause the coercive field value and breakdown voltage to increase. As for the p-type Si (100) substrate, the increment of chemical material is not clearly visible since the sample has been damaged. For

memory applications, BST 1 M samples with annealing temperature of 900°C are the best option because they have a high remanent polarization and a low coercive field.

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# PREPARATION AND PHYSICO-CHEMICAL PROPERTIES OF GRACILARIA/PVA/GA/CNT-BASED HYDROGEL FOR SLOW/CONTROLLED RELEASE MATERIAL

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**Abstract.** In this study, we synthesized a hydrogel from the extract of *gracillaria* (GR), poly-(vinyl alcohol) (PVA), glutaraldehyde (GA), and carbon nanotube (CNT). To confirm the synthesis of hydrogel, several characterizations were done, including fourier transform infra red (FTIR) and scanning electron microscope (SEM). Analysis on the material performance under various parameters (such as swelling ratio and release behavior of potassium from hydrogel into aqueous media) was also carefully evaluated based on weight measurement and flame-photometry instrumentation. FTIR spectra showed that the interaction of hydrogel components (GR, PVA, GA, CNT and Kalium-related material) involved some functional groups such as C-O, C-N, C=O, C-H sp<sup>3</sup> as well as O-H which predominantly occurred through hydrogen bonding. The swelling ratio of technical-grade PVA-based hydrogel was higher than that of pro-analytical-grade. The hydrogel showed a typical slow release behavior for potassium ion with the release rate is 8.89 ppm for first ten minutes and the release rate average is 0.0134 ppm/minutes for the normal phase.

Keywords: hydrogel, gracilaria, poly-(vynil alcohol), CNT

#### **1. Introduction**

Due to its potentiality in wide range of application, especially for slow/controlled release components that are available in fertilizer, drug delivery, ion exchanger, and absorbent materials, hydrogel has been becoming an attractive material and being a great interest of many scientists [1,2]. The use of hydrogel as a medium for a slow/controlled release fertilizer is now getting popular, indicating that there is a positive trend on lifting up the possible applications in practical agriculture. Moreover, exploration of new possible resources for preparing hydrogel matrixes has evidently become a hot topic within two past decades.

Among the main sources in developing a hydrogel for slow/control-release fertilizer holder, poly-(vinyl alcohol) (PVA) and gluteraldehyde (GA) are two main materials frequently used [3]. PVA is a synthetic polymer that is water soluble because of its hydroxyl groups. PVA has a relatively simple chemical structure with a pendant hydroxyl group. PVA is also a non-toxic synthetic polymer and has been available in large scale commercial production. This material is also utilized in various industrial applications, such as fibers, films, hydrogels, and glues [4,5].

For searching environmental compatibility, many scientists have been concerned on incorporating natural polymers into hydrogel matrix. Among many possible sources for natural polymer, red alga has become a major concern because of its alginate content. Alginate is an anionic linear polysaccharide composed of two saccharides. Alginate can be regarded as a binary copolymer composed of  $\alpha$ -I-guluronic acid (G) and  $\beta$ -D-mannuronic (M)

that are covalently bonded through 1,4-glycosidic linkage and arranged into either homopolymeric block (MM and GG) or alternating block (MGMG) along the polymeric backbone [4-12].

Accordingly, the polymer blend (PVA with alginate) can generate the polymeric materials, improving physical properties, lowering cost of basic polymer materials, simplifying the process ability in the film formation, and making the material biologically acceptable [3,10]. Both polymers are hydrophilic, making combination of PVA and alginate to bring positive impacts on improving chemical, physical, and mechanical properties [11,12].

Other potential material that could be used to modified the properties of hydrogel- based controlled-release fertilizer is carbon nanotube (CNT). Carbon nanotubes are nano-scale carbon materials having unique mechanical and thermal properties, offering many advantages for application in various fields. In addition to the distinctive characteristics of CNT (i.e., superior surface area, high electrical conductivity, and low percolation properties when it is dispersed into polymer matrix), CNT has been selected as one of the excellent candidates of polymer filler [13]. The insertion of CNT into polymer matrix can improve physico-chemical properties of polymer [14].

Potassium, in its various forms, plays somewhat important roles in plant growth system. Comprehension of its release behavior into its vicinity may give many valuable insights in developing potassium-based fertilizer system. Release and sorption behavior of a chemical substance from a hydrogel into its vicinity and permeation of a chemical from one phase to another separated by a membrane are affected by several physical and chemical conditions of its environment. It was found that desorption of kalium from PVA-Borate hydrogel was favorable in the aqueous system. The polarity of solvent influences the kinetics of desorption [15]. In other works, it was concluded that the release behavior of a composite lignin-based hydrogel, called LBPAA, is sensitive to pH, temperature, and ionic strength [16].

In this study, *glacilaria sp* and CNT were incorporated into PVA/gluteraldehyde polymer matrix, and its performance such as swelling power and its release behavior were examined. The study used potassium chloride as the working material release.

# 2. Material and method

# 2.1. Material

Several materials were used: *Gracillaria sp* (taken from regional farmer), poly-(vinyl alcohol) pro analytical-grade (*Mr* 6000) (Merck, Germany), poly-(vinyl alcohol) technical-grade (Brataco, Indonesia), glutaraldehyde (25% pro analytical-grade; Merck, Germany), methanol (96% pro analytical-grade; Merck, Germany), sulphuric acid (97%; pro analytical-grade; Merck, Germany), acetic acid (pro analytical-grade; Merck, Germany), graphene oxide (Japan), multiwall carbon nanotubes functionalized (Japan), and potassium chloride (KCl; pro analytical-grade; Merck, Germany).

#### 2.2. Method

**Preparation of Reactants.** PVA solution was prepared by dissolving 20 mg of PVA in 100 mL of deionized water, and stirred while heated at 90°C for about 3 hours. Crosslinker solution was prepared by mixing methanol (50%), acetic acid (10%), sulfuric acid (10%), and glutaraldehyde (1,25%) with a volume ratio 3:2:1:1, respectively. CNT dispersion was prepared by dissolving 1 mg of CNT into 100 mL of graphen oxide solution (1% w/v in deionized water). Then, the solution was sonicated for about 30 minutes. *Gracillaria sp* extract was prepared by macerating 40 g of dry-powdered *gracillaria* (100 mesh) in 200 mL of methanol solution (70%) for about 96 hours, and after while the macerated solution was separated from the residue.

Preparation and physico-chemical properties of gracilaria/PVA/GA/CNT-based hydrogel for slow/controlled...

**Preparation of hydrogel.** The GR/PVA/GA/CNT hydrogel was prepared by mixing the extract of *gracillaria*, PVA solution, crosslinker solution, and CNT solution with a volume ratio of 2:2:2:1, respectively. The technique was as follow: a quantity of PVA solution, crosslinker solution, and CNT solution were successively poured into a quantity of extract of *gracillaria sp*, then stirred gently using magnetic stirrer at 50°C until it is homogenous. The homogenized solution was poured into a hydrogel mold (bar coating plate) and dried in an open air for about five days. The GR/PVA/GA hydrogel was prepared in the same method but it was prepared using a volume ratio of 1:1:1 for GR, PVA, and GA, respectively.

**Swelling Ratio.** Swelling ratio parameter of the hydrogel was determined by soaking a quantity of dried hydrogel (the mass is exactly known as  $W_0$ ) into 25 mL of deionized water and allowed to swell at room temperature. After 10 minutes, the swollen hydrogel was separated from the rest of deionized water and drained by filtering using a 100-mesh of aluminum sieve, weighed, and noted as  $W_t$ . The swelling ratio of water (*SR*) was calculated using equation (1).

$$SR = \frac{(W_t - W_0)}{W_0} \times 100,$$
 (1)

where  $W_0$  is the weight of dried hydrogel, and  $W_t$  is the weight of the swollen hydrogel [17].

**Release behavior examination.** As much as 4 pieces of the GR/PVA/GA/CNT hydrogel with a specific dimension  $(1 \text{ cm} \times 1 \text{ cm} \times 0.04 \text{ cm})$  was soaked into 200 mL of KCl 1.00 M solution for about 48 hours. Then, after they were dried for about 30 minutes, the 4 pieces of mounted hydrogel is named as GR/PVA/GA/CNT-K. The rest of potassium ion in the solution was determined using the flame-photometer. To examine the desorption profile, the GR/PVA/GA/CNT-K was immersed into 200 mL of deionized water in a beaker glass and continuously stirred. In the certain time, 10 mL of the solution was taken. Then, 10 mL of deionized water was added to the rest of solution to maintain the total volume to be constant. The potassium content in the sampled solution was then determined using a flame-photometer.

# 2.3. Characterizations

During this study we used a Fourier Transform Infra Red (FTIR; Shimadzu, Japan), Scanning Electron Spectroscope (SEM; JEOL JSM-6510LA, JEOL, Japan), Flame-photometer Corning 410 (CIBA-Corning, Madrid, Spain).

# 3. Results and Discussion

# 3.1. Material structure and morphology

The typical FTIR spectrum for GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K were represented in Fig. 1. It could be noticed in Fig. 1 that the three spectra of hydrogel demonstrated the peaks at the same wavenumber, but they have different intensities, which means that the GR/PVA/GA hydrogel becomes the main part in all modified hydrogel. The addition of CNT and/or CNT-K into the GR/PVA/GA hydrogel did not generate any structural changes. It is most likely that CNT and/or CNT-K stick physically onto hydrogel framework.



**Fig. 1.** FTIR spectra of GR/PVA/GA (blue line), GR/PVA/GA/CNT (green line), and GR/PVA/GA/CNT-K (purple line)

The FTIR spectra of GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K have the absorption peaks at wavenumbers of 3400 cm<sup>-1</sup> for O-H, 2800-2900 cm<sup>-1</sup> for C-H stretching from C-H sp<sup>3</sup>, 1600 cm<sup>-1</sup> for C=O specific from aldehyde [18], 1200 cm<sup>-1</sup> for C-N, and 1100 cm<sup>-1</sup> for C-O/C-O-C. There was a shifting of peak for OH at GR/PVA/GA/CNT, where the peaks for O-H at GR/PVA/GA/CNT is wider than that of GR/PVA/GA, supposedly caused by existence of intramolecular and intermolecular interaction (hydrogen bond) between O-H and CNT. Addition of CNT and/or CNT-K into GR/PVA/GA/CNT framework strengthen the intensity at the adsorption peaks of 3400 cm<sup>-1</sup>, 2900 cm<sup>-1</sup>, 1600 cm<sup>-1</sup>, and 1100 cm<sup>-1</sup>, for O-H, C-H aldehyde, C=O, and C-O functional groups, respectively. This peaks are different from the types of carbon material [19].

Surface morphologes of GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K were determined using the SEM as shown in Fig. 2. The images were taken at the cross sectional position with the angle 80 degrees. The SEM images in Fig. 2 show that the surfaces of GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K are not smooth, but rather rough, for which the tension on the surfaces could provide active sites for adsorbing any charged particles. It is look likely that the level of surface roughness increased in the series of GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K hydrogel.



**Fig. 2.** SEM images of hydrogel: (a) GR/PVA/GA (5000 times), (b) GR/PVA/GA/CNT (5000 times), and (c) GR/PVA/GA/CNT-K (1000 times)

#### **3.2.** Material performances

In this work, the performance study of hydrogel was focused on swelling ratio and release behavior parameters.

**Swelling Ratio.** The typical feature of swelling ratio of GR/PVA/GA/CNT hydrogel based on the variation of PVA purity-grade were represented in Fig. 3. In this case, the GR/PVA/GA/CNT hydrogel where the PVA is in technical-grade is marked as GR/PVA/GA/CNT (TG), while the GR/PVA/GA/CNT hydrogel where the PVA is in pro analytical-grade is encoded as GR/PVA/GA/CNT (PAG).

Fig. 3 represents the plot of swelling ratio versus immersion time of GR/PVA/GA/CNT hydrogel prepared using PVA with technical and pro analytical grades. The hydrogel prepared using PVA technical-grade has a higher swelling ratio compared to that of hydrogel prepared using PVA pro analytical-grade. Utilization PVA technical-grade produced hydrogel with a high capacity in swelling ratio parameter, which may be caused by its high flexibility in absorbing water. The viscosity of PVA in technical-grade is lower than that in pro analytical-grade, in which this is because the intermolecular interaction is easier to form [20].



Fig. 3. Swelling Ratio of various GR/PVA/GA/CNT hydrogel as function of time of immersion

Furthermore, effect of addition of potassium ion on swelling ratio of GR/PVA/GA/CNT hydrogel is presented in Fig. 4. The addition of potassium ion into the GR/PVA/GA/CNT hydrogel matrix increases the swelling ratio of the hydrogel both for hydrogel prepared using PVA technical and pro analytical-grades. The graphical profile on the Fig. 4 shows that the presence of potassium ions increases the hydrogel accommodation capacity of water. Although the exact mechanism could not be determined yet, the ability of potassium ions to capture water seemingly plays an important role in achieving the conditions of increasing the hydrogel absorption capacity. The increases in the hydrogels flexibility are due to the presence of potassium ions. They can be inferred from the graph of swelling profiles of GR/PVA/GA/CNT-K (TG) and GR/PVA/GA/CNT-K (PAG) versus time, indicating that the hydrogels are still be able to make flexing at the time of immersion in long period (about 8 days).



**Fig. 4.** Profile of Swelling Ratio (SR) of GR/PVA/GA/CNT hydrogel with and without potassium ion [Note: (TG = use technical-grade PVA, PAG = use pro analytical-grade PVA)]

Potassium Release Behavior. The potassium release profile from the loaded hydrogel as a function of time is given in Fig. 5. The release behavior pattern potassium from hydrogel matrix into aqueous phase, as demonstrated in Fig. 5, shows that the overall time release could be divided into three time periods, i.e., the initial period (first five minutes), followed by transient period (between 5 and 10 minutes), and normal period. These periods were attained after 10 minutes of the desorption processes. The pattern of the releasing profile is quite similar to result found by other researcher for potassium chloride release [21,22]. The graph in the Fig. 5 shows that at the initial period, there was a sudden dissolution of potassium chloride into bulk. This fact could be inferred that at the initial period the potassium release was mainly occurred from the surfaces of hydrogel into bulk, which was most probably followed by the occurrence of solvent intrusion into the hydrogel. At the transient period, the release seemed to be the combination between surface release and the release of potassium from the inner part of gel into solvent, where the rate of inner desorption gradually increased as the surface release decreased. At the normal period, the releasing phenomenon may be expected only or mainly from the inner part of gel into solvent. The excessive potassium releases in the early period. Typically, the time period was from zero to five minutes, indicating that most of potassium chloride did not exhibit the inner part of the gel but adsorbed at the surfaces. This condition provoked the occurrence of catastrophic dissolution when the loaded hydrogel was immersed into solvent. Furthermore, if we take the 10<sup>th</sup> minute of the initial time in the normal releasing phenomenon and the 80<sup>th</sup> minutes (as the longest limit of observation time), the average of release rate in the time period is 0.0134 ppm per minute.



Fig. 5. The total desorbed potassium chloride into aqueous phase during the dissolution processes

It is interesting to look deeper on the release phenomenon after 10 minutes of the processes. The graph on the Fig. 5 demonstrates that there was an increase in the quantity of potassium released over the same time period. The increase in the release rate seems to be fairly regular. The increment of the releasing rate may be visualized in term of the value differences between the concentrations of KCl in the series of releasing time. The typical feature of the graph is presented as Fig. 6. With increasing time, there should be a decrease in

the concentration inside the gel. If the process was done within a period of 10 to 80 minutes, the amount of potassium released is very small compared to the initial concentration. Thus, the concentration inside the gel can be practically unchanged. At the period between 10 and 40 minutes, the increase in release rate can be expected as a result of broadening the pores within the hydrogel, allowing material run less retarded from the hydrogel into the environment. The stagnant release rate, between 40 and 70 minutes, can be explained as the maximum expansion of gel volume, which was attained at the 40<sup>th</sup> minute of the gel immersion. Meanwhile, the sudden change in release rate after 70<sup>th</sup> minute of immersion could be due to physical deformation such as gel abrasion or torn. This assumption is also supported by the fact that the swelling ratio of hydrogel increases with the length of immersion time.



Fig. 6. The increment of potassium chloride release in series of time at the normal period

#### 4. Conclusion

We have successfully prepared a hydrogel based on *glaciallias sp* (GR), poly-(vinyl alcohol) (PVA), glutaraldehyde (GA), and carbon nanotube (CNT), which was called GR/PVA/GA/CNT hydrogel. The FTIR spectra showed that the interaction of hydrogel components involved some functional groups such as C-O, C-N, C=O, C-H sp<sup>3</sup> and O-H which predominantly occurred through hydrogen bonding. Meanwhile, the SEM images indicated that the level of surface roughness increased in the series of GR/PVA/GA, GR/PVA/GA/CNT, and GR/PVA/GA/CNT-K hydrogel. The hydrogel prepared using PVA in technical-grade has a higher swelling ratio compared to that prepared using PVA in pro analytical-grade. The hydrogel showed a typical slow release behavior for potassium ion with the release rate is 8.89 ppm for first ten minutes and the release rate average is 0.0134 ppm/minutes for the normal period. The release mechanism of potassium ions from hydrogel was supposed to begin from the hydrogel surface into bulk, followed by the intrusion of water into hydrogel matrix, which eventually exerted potassium ions from the inner part of hydrogel.

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# INFLUENCES OF SOLVENT TYPES ON THE FORMATION OF GRAPHENE IN THE ELECTROCHEMICAL EXFOLIATION METHOD T. Kurniawan<sup>1\*</sup>, M.A. Anwar<sup>1</sup>, R. Oktiani<sup>2</sup>, R. Ragadhita<sup>2</sup>, A.B.D. Nandiyanto<sup>2</sup>, M. Aziz<sup>3</sup>

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**Abstract.** The aim of this study was to evaluate the effect of different solvents in sonication process on the formation of graphene from the electrochemical exfoliation of graphite. In short, graphite rod was exfoliated by electrochemical process with ammonium sulfate as salt-electrolyte. The exfoliated powder then sonicated under two different solvents, which are Dimethylformamide (DMF) and aqueous solution to form graphene. It was found that similar structure of graphene was obtained from both types of solvent. However, the amount of graphene produced was different due to the differences in graphene stability. Graphene is more stable in DMF solvents compared to the aqueous solution. The aqueous solution can allow the reversible reaction that can reform graphite oxide from graphene due to the existence of hydroxyl component in the aqueous solution.

Keywords: graphene, graphite, electrochemical exfoliation, solvent, sonication

#### **1. Introduction**

Graphene is a two-dimensional block of carbon allotropes originating from every other dimension [1]. Further, this material has several distinctive properties, including extremely strength, high thermal, electrical conductivity, transparency, and flexibility [2]. Based on those excellence properties, this material has a high potential be applied in various applications, such as electronic devices, supercapacitors, batteries, composites, flexible transparent displays, sensors [2] and corrosion inhibitor [3].

There are two methods for synthesizing graphene, namely top-down and bottom-up methods [2]. Several methods in the top-down method are micromechanical cleavage, exfoliation of graphite oxide, electrochemical exfoliation, exfoliation of graphite intercalation compounds (GICs), solvent-based exfoliation, arc discharge, and unzipping carbon nanotubes. Bottom-up methods include epitaxial growth on silicon carbide, chemical vapor deposition, and miscellaneous methods. The processes using the top down method have more advantages compared with that using bottom up method. Specifically, the processes using the top down process allow for the obtainment of large size and unmodified graphene, inexpensive and scalable synthesis procedure, a single step functionalization and exfoliation, and the production of graphene with high electrical conductivity [4]. Among the top down process, the electrochemical exfoliation method is one of the most popular methods for the production of graphene because of its simplicity, short-time process, and potentiality in producing high

quality of grapheme [5]. An example of this technique was reported by Liu et al. [6] which produced graphene flakes using this method added with an ultrasound sonication process. The results showed that the final product synthesized by the sonication had largely bi-layer graphene flakes, in which the result is thinner in layers compared with the process without sonication. Although the reports in the synthesis of graphene using the electrochemical exfoliation are well-documented, there is no report on the investigation of solvent types on the successful formation of graphene.

Here, this study evaluated the synthesis of graphene using an electrochemical exfoliation process under various types of solvents during sonication process. The selection of solvents during this sonication process is important in the graphene synthesis because it will affect the product of graphene, including the long-term dispersing stability of graphene. Two different solvents were used, namely Dimethylformamide (DMF) and aqueous solution. These solvents were selected based on Paredes et al. [7], stating that these are the best solvent for providing and diluting graphene oxide (GO). However, their study concerned only on GO (not in graphene).

The finding of DMF and aqueous solution effects on the graphene synthesis would be good for providing information that can contribute in the industrial world or engineering application. Specifically, DMF and aqueous solution are able to disperse graphene without additional surfactant. Thus, when we understand this solvent parameter, we can estimate and predict the way for minimizing the amount of surfactant and stabilizing agent. The surfactant and stabilizing agent are sometimes undesirable for most applications.

In short of the experimental procedure, graphene was synthesized from graphite rods using the electrochemical exfoliation method. To support the synthesis process, a sonication process was added to decipher the graphene layer, whereas the centrifugation process was to remove large agglomerates.

In addition, this study focused on understanding the effect of solvent types on the formation of graphene. Thus, this study did not concern on the number of layers in the graphene. Indeed, the present method allowed the formation of multilayer of graphene (MG) and graphene oxide (MGO) from both solvents. This is probably because of the limitation in the processing time used in the electrochemical exfoliation as well as sonication process.

#### 2. Experimental method

**Synthesis of graphene via electrochemical exfoliation.** Graphite rods with a purity of 95% and a dimension of diameter and length of 0.40 and 10 cm were used as an anode and a cathode electrode. Prior to being used, both graphite materials were immersed into 300 mL ammonium sulfate solution (0.1 M; R&M chemicals, UK). The electrochemical exfoliation process was carried out for 5 hours with a 10 V. This process consumed three graphite rods in the anode site. During the process, a black product is gradually formed, which indicated that exfoliation of graphite is in progress. Then, electrolyte was filtrated using a vacuum filtration. The residue was dried, and the dried residue was a black powder. The dried black powder was dissolved in a 300 mL of specific solvent (i.e., N,N-Dymethylformamide (DMF; R&M Chemicals, UK) or aqueous solution). The amount of dried black powder was fixed at 2 wt%, in which this is due to the fact that graphite fine powder is well-suspended in the concentration range of 1-2% during the sonication process [8]. Indeed, concentration of 2% was selected to get maximum yield of graphene. The dissolved black powder was sonicated for 3 hours, and the result was filtered using a vacuum filtration. The final product was a black filtrate. Detailed information for the synthesis process was shown in Fig. 1.



Fig. 1. Steps of graphene synthesis by electrochemical exfoliation method followed by sonication process

**Characterizations.** Chemical properties of the product were investigated using a Fourier Transform Infrared (FTIR, Nicolet iS50 FT-IR) in the range of 400-4000 cm<sup>-1</sup>. A Raman Spectroscope (Raman, Horiba LabRam HR Evolution) was used to analyze the chemical composition and characteristics of the products at 514 nm. A Transmission Electron Microscope (TEM, FP 5022/12 Tecnai G2 20 Twin) was used for the analysis of the morphology of graphene. Analysis of the effect of solvents on the products produced was also done by a UV-Vis spectroscope (UV/VIS Spectrometer, Lambda 1050 PerkinElmer), where the solution before and after centrifugation were investigated.

#### 3. Results and discussion

The FTIR analysis (presented in Fig. 2) shows that the process using various solvents can allow the formation of graphene from graphite. Detailed analyses are in the following.

In the case of process with aqueous solution, there are two peaks at the wavelengths of 3331 and 1636 cm<sup>-1</sup>, which indicated the vibration of the -OH group and the aromatic C = C group. The -OH group is from the water molecule.

In the sonication process with DMF, there are peaks at wavelengths of 1254, 1096, 1062, and 660 cm<sup>-1</sup>, which were due to the vibrations of C-N groups. The peak at wavelength of 1651 cm<sup>-1</sup> was also found, corresponding to the vibration of C = O group. This result was in a good agreement with the results reported by Tatariants et al. [9]; this is due to the existence of DMF. In addition, peaks at wavelengths of 1496, 1438, and 1411 cm<sup>-1</sup> were due to a vibration of the C = C aromatic group [10]. The C = C aromatic group was also found in sample produced using the aqueous solution, in which this is due to the possible formation of graphene or graphene oxide.

The results of the Raman Spectroscopy analysis (see Fig. 3) showed that the use of different solvents did not have impacts on the chemical components of the product. Three types of chemical compositions were obtained, namely multilayer graphene (MLG 1 and 2) and graphene oxide (GO). In the three Raman spectras, there are two main peaks, namely G and 2D peaks. The G peak is located at 1580 cm<sup>-1</sup> and peak 2D at 2700 cm<sup>-1</sup>, which arises due to the optical vibrations in the center of the  $E_{2g}$  degeneration zone and second-order zone on the phonon boundary. In addition, there is a secondary peak, namely the D peak located at

1350 cm<sup>-1</sup>. This peak arises in defected graphene, indicating the existence of carbon impurities (as the main impurities component) that are released from imperfect exfoliation process [11].



Fig. 2. The FTIR analysis results of graphene after the sonication process using DMF and aqueous solution

The Raman Spectra can be used as a reference in determining the quality and number of graphene layers based on 2D shape, width, and peak position [1]. MLG 1 and 2 indicated from G peak is higher than 2D peak. The both spectras from MLG 1 and MLG 2 are in accordance with the results of the study by Niilisk et al. [12] that the higher the 2D peak intensity, the more the number of layers in MLG. Therefore, MLG 2 has more layers than MLG 1. Actually, the specific analysis of single layer graphene can be done, by justification through Raman Spectroscopy analysis to show sharp single 2D peaks with higher intensity than G [1]. However, this study is for comparing the aqueous solution and DMF only; thus, we did not concern this specific peaks in our results.

The results of TEM analysis of the both sample produced with different solvents are shown in Fig. 4. Different morphologies were obtained, but they are almost the same. Their morphologies are rolls and wavy sheets forms. The rolls and wavy sheets are an intrinsic characteristics of grapheme [13-15]. The analysis showed dark and transparent areas. The dark areas can occur due to the existence of a number of graphene sheets, oxygen groups from graphene oxide, graphite, and impurities attached to the surface of the products. The transparent areas are the parts of thin layers from graphene. The more transparent has correlations to the thinner sheets or fewer groups of oxygen [16].



Fig. 3. The results of the Raman Spectroscopy analysis of compounds contained in the product



**Fig. 4.** The results of TEM analysis of graphene with sonication process using DMF (a) and aqueous solution (b)

Figure 5 shows the results of UV-Vis spectrophotometry before and after the centrifugation process. In the use of DMF, a peak did not change at 275 nm, which is an absorption area of graphene [17]. In the use of aqueous solution, the absorption changed from 265 to 256 nm, in which these represented the graphene absorption area [18-19]. There is no peak change in DMF solvents, confirming that graphene in DMF is more stable than that in aqueous solution.

Aqueous solution can allow the reversible reaction that can reform graphite oxide from graphene. This is due to the existence of hydroxyl components in the aqueous Solutions. In the case of DMF, this type of solvent has better effects on producing more graphene in the final product. No reversible reaction is formed in DMF process. As a consequence, this solvent is also able to produce high quality single layer graphenes compared to aqueous solution. However, since this study focused on understanding the effect of solvent types on the formation of graphene, we did not concern on the number of layers in the graphene. Indeed, the present method allowed the formation of multilayer of graphene and graphene oxide from both solvents. We believe that the main reason is due to the limitation in the processing time used in the electrochemical exfoliation as well as sonication process.



**Fig. 5**. The results of UV-Visible spectrophotometry analysis of graphene with sonication process using aqueous solution (a) and DMF (b) solvents before and after centrifugation

#### 4. Conclusion

The electrochemical exfoliation process of graphite has successfully led the production of multilayer graphene (MLG) product with layers of 1-6 and graphene oxide (GO). The results indicated that both types of solvents can promote the formation of graphene from graphite. Similar structure of graphene was obtained. However, the amount of graphene produced was different, in which this is due to the differences in graphene stability.

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