ФИЗИКА КОНДЕНСИРОВАННОГО СОСТОЯНИЯ

EPR, OPTICAL AND OTHER PHYSICAL STUDIES OF Cr³⁺-DOPED MgO-BaO-B₂O₃-TeO₂ GLASSES

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Physical, optical and electron paramagnetic resonance (EPR) studies of $15MgO\text{-}15BaO\text{-}(59.8-x)B_2O_3\text{-}(10.0+x)TeO_2\text{-}0.2Cr_2O_3$ ($x = 0, 10, 20, 30$ mole %) glass samples have been reported. EPR spectra exhibited some resonance signals. The first one ($g = 4.80$) had a large zero field splitting parameter (D) and $E/D \leq 1/3$, it was attributed to isolated Cr^{3+} centers in strongly distorted octahedral sites; the second one ($g = 1.98$) was assigned to Cr^{3+} centers at axially distorted octahedral sites. The resonance signal at $g = 4.26$ was assigned to Fe^{3+} ions, which were in the glass matrix as unwanted impurities. The resonance signal at $g = 1.91$ indicated the $Cr^{3+}\text{-}Cr^{3+}$ exchange coupled pairs. In the optical absorption spectra, the two observed broad optical bands with 16025 cm⁻¹ and 23474 cm⁻¹ were assigned to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transitions, respectively. The site symmetry of Cr^{3+} is C_{4v} or C_{3v}. Racah parameters, crystal field (Dq) parameters and energy gap were evaluated from the optical spectra. Various other physical parameters like density, etc., are also reported.

Key words: borotellurite glass; electron paramagnetic resonance (EPR); optical absorption; physical properties

ИССЛЕДОВАНИЯ ЭПР, ОПТИЧЕСКИХ И ДРУГИХ ФИЗИЧЕСКИХ СВОЙСТВ СТЕКОЛ СОСТАВА MgO-BaO-B₂O₃-TeO₂, АКТИВИРОВАННЫХ ИОНАМИ Cr³⁺

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Представлены исследования электронного парамагнитного резонанса (ЭПР), оптических и других физических свойств стекол системы $15MgO\text{-}15BaO\text{-}(59,8-x)B_2O_3\text{-}(10,0+x)TeO_2\text{-}0,2Cr_2O_3$ ($x = 0, 10, 20, 30$ мол. %). В спектрах ЭПР обнаружено несколько резонансных сигналов. Сигнал с

$g = 4,80$, высоким значением параметра тонкого расщепления в нулевом магнитном поле (D) и значением отношения $E/D \le 1/3$ приписан изолированным центрам Cr^{3+} в сильно искаженных октаэдрических позициях. Сигнал с $g = 1,98$ отнесен к центрам Cr^{3+}, локализованным в аксиально искаженных октаэдрических позициях. Резонансный сигнал с g-фактором, равным 4,26, идентифицирован как парамагнитное поглощение СВЧ ионами Fe^{3+}, которые присутствуют в матрице стекла как нежелательная примесь. Резонансный сигнал с $g = 1,91$ указывает на присутствие обменно-связанных пар ионов хрома Cr^{3+}-Cr^{3+}. Спектры оптического поглощения характеризуются двумя широкими полосами на частотах 16025 и 23474 см$^{-1}$; они соотнесены с переходами $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ и $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ соответственно. Симметрия позиций ионов $Cr^{3+} - C_{4v}$ или C_{3v}. По оптическим спектрам оценены параметры Рака, параметр кристаллического поля Dq и величина энергетического зазора. Дополнительно приводятся другие физические параметры стекла, такие как плотность и пр.

Ключевые слова: боротеллуритное стекло; электронный парамагнитный резонанс (ЭПР); оптическое поглощение; физические свойства

1. Introduction

Currently, a great scientific revolution has been carried out by means of telecommunication, through mobile phones or via the Internet. People are connected to the entire world through the Internet and the world has become a global village. The entire high-speed telecommunication signal transmission basically depends on the optical fiber network. The optical fiber network requires switches and routers. These electronic boxes particularly cannot meet the demands of the communication industry [1] because their linear and nonlinear properties play an important role in determining the features [2, 3]. For example, linear properties like the refractive index of transparent medium change with the intensity of light travelling through it [4]. Thus, the glass industry plays a crucial role in glass fibers, whereas organic materials show very poor mechanical and thermal properties. Finally, an amorphous material like glass is a very good option for high intrinsic transparency, fast response time [5], excellent resistance to atmospheric conditions, mechanical and chemical durability. Hence glass is an important material in the field of optics [6] and optical communication systems.

Boric acid (H_3BO_3) is one of the important oxides for the glass formation. It exhibits a variety of structural changes when combined with different alkali and alkaline earth oxides. Linear and nonlinear properties of borate glasses change with the composition of oxides [7]. It is also used as dielectric and insulating medium as a shield against infrared radiation [8]. TeO_2-based glasses are used in nonlinear devices due to their property of forming glasses with a higher refractive index ($n > 2$), good thermal stability and low melting temperature [9]. The desired linear and nonlinear optical susceptibility changes can be obtained by the combination of B_2O_3 and TeO_2 in the glass matrix. Addition of different oxides and transition-metal ions in borotellurite glasses will tend to increase the photoluminescence response.

Transition-metal ion chromium (Cr^{3+}) is used in the fabrication of stainless steel and alloys. This ion has an incomplete $3d^n$ ($n < 10$) shell, so it can be used as a paramagnetic spin probe. Several researchers [10 − 13] have carried out studies of EPR spectral response and optical studies of Cr^{3+}-doped alkali and alkaline earth oxide borate glasses. To the best of our knowledge, until now no studies in the properties of MgO-BaO-B_2O_3-TeO_2 glasses have been conducted. In this context, we would like to focus on the effect of variation of B_2O_3 and TeO_2 concentrations on various physical, optical and EPR properties of these glasses.

Table 1

Composition of glass samples and their physical parameters

Glass code	MgO	BaO	B_2O_3	TeO_2	Cr_2O_3	M	ρ_{th}	V_M	n	A_{th}
	mole %					g/mole	g/cm³	cm³/mol		
MBBTCr-1	15	15	59.8	10	0.2	125.8	3.34	37.67	2.74	0.173
MBBTCr-2	15	15	49.8	20	0.2	129.4	3.70	34.98	2.77	0.152
MBBTCr-3	15	15	39.8	30	0.2	133.0	4.06	32.76	2.78	0.131
MBBTCr-4	15	15	29.8	40	0.2	136.6	4.43	30.84	2.79	0.110

Notations: M ($\pm$ 0.001) is the average molecular weight; ρ_{th} ($\pm$ 0.001) is the theoretical density; V_M ($\pm$ 0.01) is the molar volume; n is the refractive index; A_{th} is the interaction parameter.

2. Experimental procedure

The melt-quenching technique was used to prepare the glass samples in the composition 15MgO-15BaO-(59.8 − x)B_2O_3-(10.0 + x)TeO_2-0.2Cr_2O_3 (x = 0, 10, 20, 30 mole %). Analar grade boric acid (H_3BO_3), tellurium oxide (TeO_2), magnesium oxide (MgO), barium oxide (BaO) were used for the preparation of present glasses. These oxides were weighed proportionally in mole % and then transferred to porcelain crucibles and kept in an electrically heated furnace at a temperature of around 1000°C. It took approximately an hour to melt the mixtures congruently. The molten liquid was poured onto a steel plate (maintained at 200 °C) and then pressed with another steel plate. The glasses obtained by this way were transparent and bubble-free. To relieve mechanical stress, the samples were annealed at around 200 °C for 2 hrs. The variations of chemical composition in these glasses are given in Table 1. The amorphous nature of the samples was confirmed by X-ray diffraction. EPR spectra were recorded for dry and perfectly powdered glass samples at room temperature using an EPR spectrometer JEOL FE 1X operating at X-band frequency (9.205 GHz) with a modulation frequency of 100 kHz. The optical absorption spectra were recorded with a UV-VIS-NIR spectrophotometer in the wavelength range of 300 − 800 nm at room temperature.

3. Results and discussion

3.1. Density and molar volume. The following empirical equation [14] was used to calculate the theoretical densities of the prepared glass samples

$$\rho_{th} = 0.53\Sigma\,(M_i \cdot x_i)/[\Sigma\,(V_i \cdot x_i)], \qquad (1)$$

where x_i is the mole fraction of different oxides; M_i is the molecular weight of each oxide; V_i is the packing density parameter of each oxide, calculated using the relation

$$V_i = (4/3)\pi\,N_A(X \cdot r_m^3 + Y \cdot r_o^3), \qquad (2)$$

where N_A is the Avogadro number; r_m, r_o are (respectively) the ionic radii of metal and oxygen atoms for M_XO_Y oxide .

The calculated density and molar volume values are presented in Table 1. The density values are reproducible to ±0.02 g/cm³, the molar volume (V_M) is calculated using the relation

$$V_M = M_t / \rho_{th},$$

where M_t is the total molecular weight of the multicomponent glass, ρ_{th} is the density.

Fig. 1 shows changes in the density ρ_{th} and the molar volume V_M with the TeO_2 content. By substituting TeO_2 for B_2O_3 we observed an increase in density values from 3.34 to 4.43 g/cm³, whereas the molar volume decreased from 37.67 to 30.84 cm³/mol. The changes are attributed to the structural rearrangement of TeO_2 atoms in the borate glass network. TeO_2 acts as a network modifier causing the creation of more nonbridging oxygen atoms. Hence packing of molecules becomes denser as the concentration increases, and thereby there is an increase in density [15]. A reduction in the molar volume is due to a decrease in the bond length or interatomic spacing between the atoms.
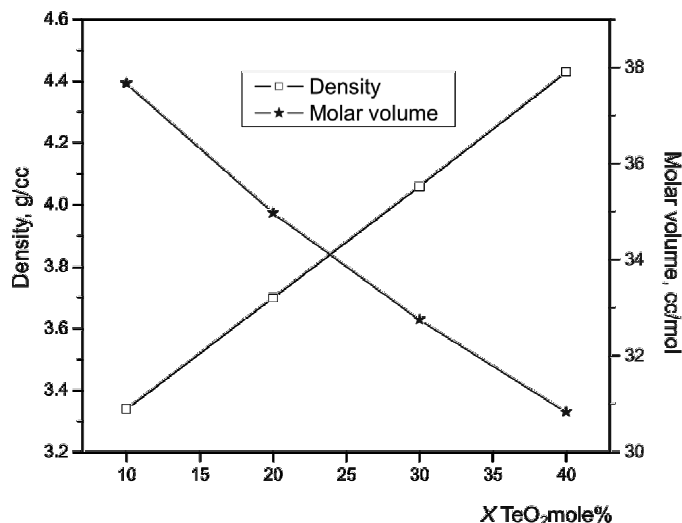
Fig. 1. Changes in the density and the molar volume
of the multicomponent glasses with TeO$_2$ content

3.2. Optical absorption. The spectra of Cr^{3+} (3d^3) free ion are characterized by two states, the ^4P, ^4F quartet state (Fig. 2, *a*) and the ^2G, ^2H doublet state (Fig. 2, *b*). The quartet state purely depends on the crystal field, where as the double state does not depend on the crystal field. An octahedral crystal field symmetry (quartet state) exhibits broad spin-allowed absorption bands due to

$$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F),$$
$$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F),$$
$$^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$$
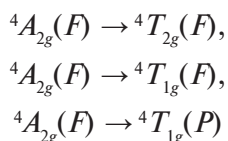
transitions.

In a weak field, the ground state represents the t_{2g}^3 orbital (Fig. 3, *a*). On the other hand, the two spin-forbidden bands are due to

$$^4A_{2g}(F) \rightarrow {}^2E_g(G),$$
$$^4A_{2g}(F) \rightarrow {}^2T_{1g}(G)$$
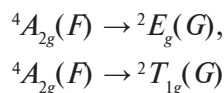
transitions (Fig. 3, *b*).

Fig. 4 shows the optical absorption spectra of glass samples. These spectra exhibited various broad bands. The band at a wave number of 16025 cm^{-1} was assigned to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ spin-allowed transition. Such an assignment argues for the site symmetry of Cr^{3+} as either C_{4v} or C_{3v} in the glass structure. The other band with the wave number of 23474 cm^{-1} was assigned to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ spin-allowed

transition. A low-resolved optical absorption band with a wave number of 28011 cm^{-1} may be masked by the fundamental absorption edge; it was assigned to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition [16]. The dip in the absorption spectra around 700 nm indicates the presence of the Fano
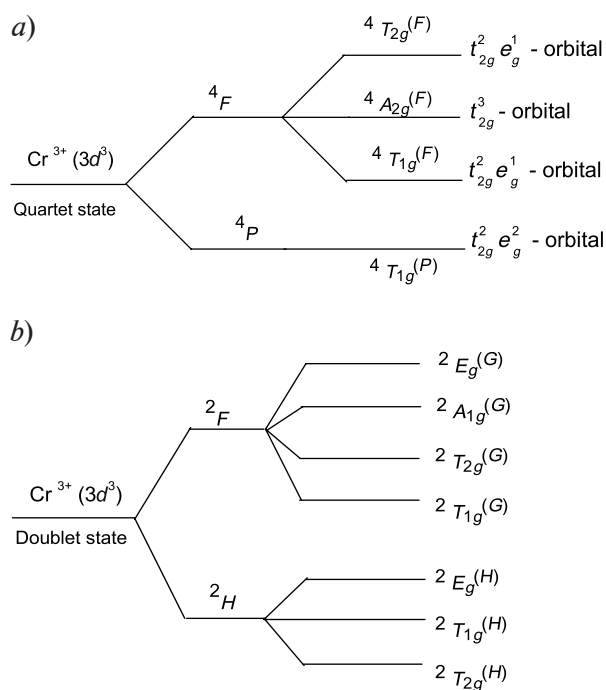
a)

b)

Fig. 2. Splitting scheme of energy levels for the ^4P, ^4F quartet (*a*) and the ^2G, ^2H doublet (*b*) states in the crystal field of the octahedral symmetry

a)

^4F Ground state of Cr^{3+}

$4\,T_{1g}(F)$

$4\,A_{2g}(F)$

$4\,T_{1g}(P)$

b)

^4F Ground state of Cr^{3+}
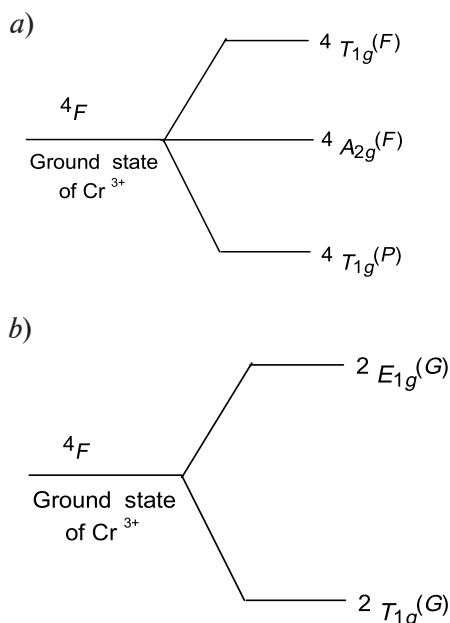
$2\,E_{1g}(G)$

$2\,T_{1g}(G)$

Fig. 3. Spin-allowed (*a*) and spin-forbidden (*b*) transitions in the weak crystal field; the former depend on the field, the latter do not

antiresonance [17 − 19].

Optical absorption spectra can be used to obtain additional information such as the structural and bonding nature of Cr^{3+} ions in the boric oxide from the Racah parameters (*B*, *C* and *Dq*). These parameters can be calculated from the following relations [16]:

$$Dq = E(^4A_{2g} - {^4}T_{2g})\,/10; \qquad (3)$$

$$Dq/B = 15(X - 8)\,/\,(X^2 - 10X), \qquad (4)$$

where $X = (E_1 - E_2)\,/\,Dq$;

$$(^4A_{2g} - {^4}T_{2g}) = 10Dq + 4B + 3C; \qquad (5)$$

$$h = [(B_{free} - B)\,/\,B_{free}]/K_{Cr3+}, \qquad (6)$$

where Dq is the (1/10)-th of the energy of the $^4A_{2g}(F) \rightarrow {^4}T_{2g}(F)$ transition, $B_{free} = 918$ cm^{-1}, B is the interelectron repulsion in the d-shell, C is the bonding between Cr^{3+} ion and its ligand, $K_{Cr3+} = 0.21$ [20].

The calculated Racah parameter values are in good agreement with Cr^{3+}-containing glasses [21]. The value $Dq\,/\,B < 2.3$ corresponds to the $^4A_{2g}(F) \rightarrow {^4}T_{2g}(F)$ spin-allowed transition. This transition has had an impact on laser applications and it indicates that Cr^{3+} centers are mostly localized in the low field sites [22]. The parameter h indicates the nephelauxetic function of ligands. The h parameter indicated an increase with increasing TeO$_2$ content in the glass samples under study. This result points to an increase of ionic-bond nature between Cr^{3+} and its ligands in the glass matrix.

It is known that the Dq/B value is less than 2.3 in the weak crystal-field sites, greater than 2.3 in the strong ones, and this value is equal to 2.3 in the intermediate fields. In the present work, the $Dq\,/B$ value was found to be
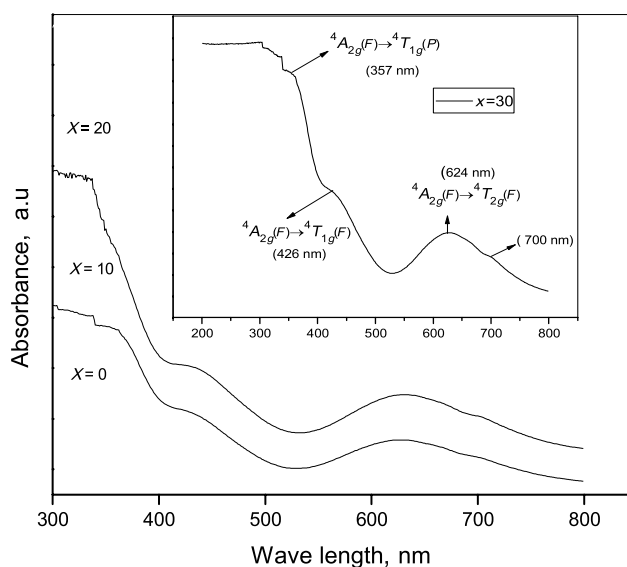
Fig. 4. Optical absorption spectra of 15MgO-15BaO--(59.8 − x)B$_2$O$_3$-(10.0 + x)TeO$_2$ glasses doped with Cr^{3+}

Table 2

Optical absorption spectra identification and some parameters of chromium ions in the glass systems MBBTCr

Transition, parameter		Parameter value			
		MBBTCr-1	MBBTCr-2	MBBTCr-3	MBBTCr-4
$^4A_{2g}(F) \to {}^2T_{1g}(P)$	λ, nm	357	360	357	351
	λ^{-1}, cm^{-1}	28011	27777	28011	28490
$^4A_{2g}(F) \to {}^4T_{1g}(F)$	λ, nm	426	430	431	440
	λ^{-1}, cm^{-1}	23474	23255	23201	22757
$^4A_{2g}(F) \to {}^4T_{2g}(F)$	λ, nm	624	630	633	640
	λ^{-1}, cm^{-1}	16025	15873	15797	15625
h		0.659	0.665	0.665	0.883
Dq/B, cm^{-1}/cm^{-1}		2.03	2.01	2.00	2.09
B, cm^{-1}		790	787	789	747
C, cm^{-1}		2940	2915	3018	3291
Ip		0.63	0.60	0.58	0.55

N o t a t i o n s : λ, λ^{-1} are the wavelength and the wave number for the optical absorption peak positions; Dq/B, B, C are the Racah parameters; h is the nephelauxetic parameter; Ip is the Cr^{3+} ionic porocity.

N o t e s : According to Ref. [24], the Racah parameters are the following: $Dq/B = 2.65$, $B = 619$ cm^{-1}, $C = 2233$ cm^{-1}

around 2.0. This indicated that Cr^{3+} ions are in the weak ligand field sites. Different calculated Racah parameters are given in Table 2.

By correlating EPR and optical data, the chemical bonding parameter α is evaluated using the following relation [23]:

$$g_0 = g_e - 8\alpha\lambda/\Delta, \qquad (7)$$

where g_e is the g-factor of a free electron ($g_e = 2.0023$), λ is the spin-orbit coupling constant ($\lambda = 91$ cm^{-1}), $\Delta(^4A_{2g}(F) \to {}^4T_{2g}(F))$ is the energy gap between the excited and the ground levels. The value $g_0 = 1.98$ was taken.

3.3. Energy gap, refractive index and interaction parameters. In the ultraviolet region, the studies of optical absorption edge from the absorption spectra have revealed various optical transitions such as a direct and an indirect band transitions. It is well-known that Cr^{3+} ions have three unpaired electrons in the $3d$-shell, hence, in the presence of electromagnetic waves, these unpaired electrons exchange their energies in the valence band and shift to the conduction band. Various anions, involved in the glass composition system as glass-forming oxides, influence the conduction band, even though the significant role of cations should not be

ignored [24].

Fig. 4 shows the optical absorption spectra of 15MgO-15BaO-(59.8 − x)B$_2$O$_3$-(10.0 + x)TeO$_2$-0.2 Cr$_2$O$_3$ glasses. The absorption edges of these glasses are not sharp as seen from the figure. Diffuse absorption edges are characteristic of amorphous nature. The shifting of absorption edges towards the higher wavelength may be due to a decrease in the rigidity of glasses as the TeO$_2$ concentration increases over that of B$_2$O$_3$.

The relationship between the photon energy $\hbar\omega$ and the optical energy gap E_{opt} is given by the following relation [25]:

$$\alpha(\omega) = [\text{const}/(\hbar\omega)]/(\hbar\omega - E_{opt})^r. \qquad (8)$$

The direct and indirect allowed transitions are given by $r = 1/2$ and $r = 2$, respectively.

Plotting the graphs for $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ yields direct band gap (E_{opt}) energies, while plotting the graphs for $(\alpha\hbar\omega)^2$ versus $\hbar\omega$ yields indirect band gap (E_{opt}) energies, known as Tauc's plots. Optical band gaps calculated from Tauc's plots are shown in Fig. 5,a. By extrapolating the linear portion of $(\alpha\hbar\omega)^{1/2}$ and $(\alpha\hbar\omega)^2$ curves at $\hbar\omega = 0$ we obtain the direct and indirect band gap values (in eV). The optical
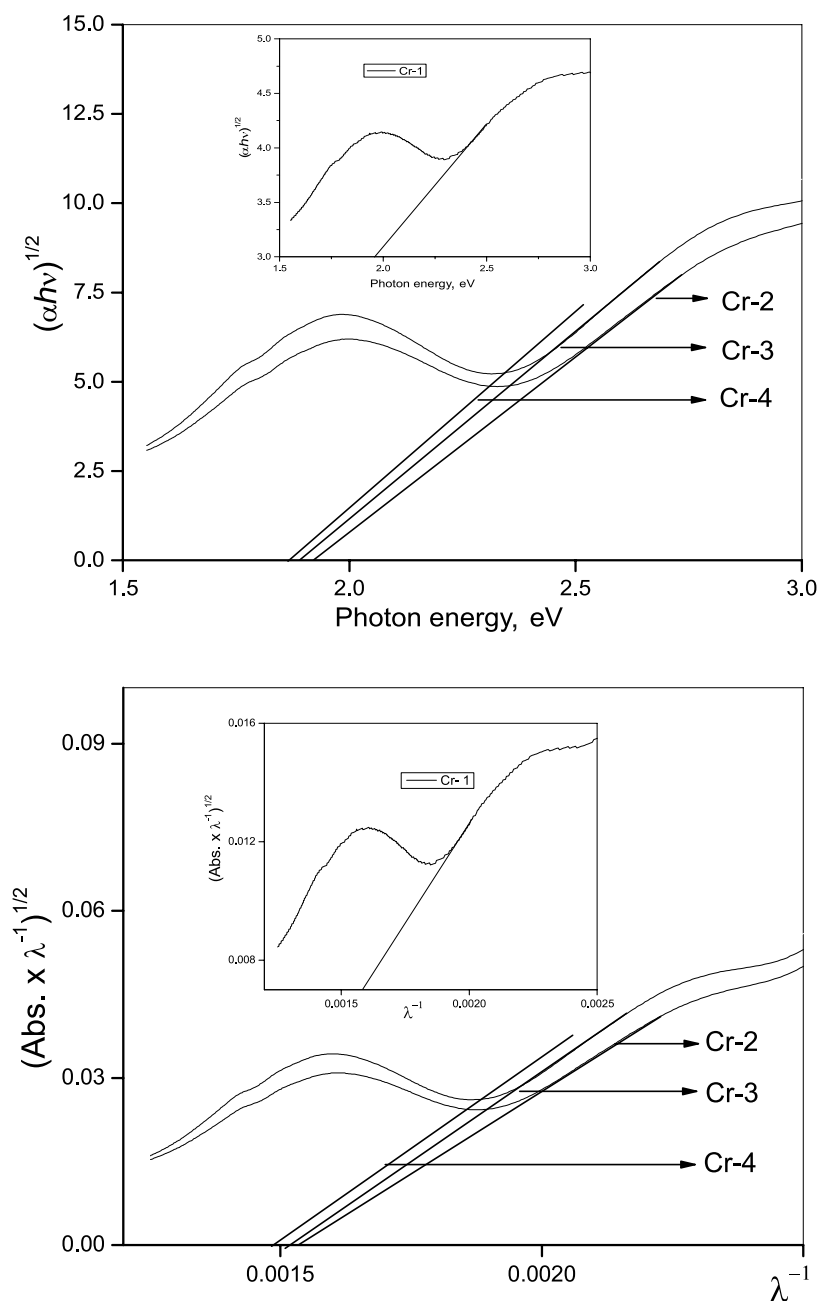
Fig. 5. The Tauc's (*a*) and the absorption spectrum fitting (ASF) (*b*) plots of all glass samples

band gap values can also be obtained from the absorption spectrum fitting (ASF) method proposed by Escobar − Alarcon, et al. [26]. Energy band gap values calculated by the ASF method are denoted as E_{opt}^{ASF} and obtained by extrapolating the linear portion of the $(a/\lambda)^{1/r}$ versus $(1/\lambda)$ curve (Fig. 5, *b*) at $(a/\lambda)^{1/r} = 0$.

The value of the band gap E_{opt}^{ASF} in eV can be obtained from the parameter λ_g using the expression

$$E_{opt}^{ASF} = 1239.83 / \lambda_g. \qquad (9)$$

The direct and indirect band gap values are given in Table 3. The optical band gap values obtained from Tauc's plots are in agreement with those obtained by the ASF method (Fig. 6). The decrease in energy gaps from 1.96 to 1.86 eV for indirect band transitions and from 3.15 to 3.05 eV for direct ones indicates that the structure of the resulting glasses has become less

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Table 3

Optical energy gaps and some other parameters obtained from optical and EPR spectra of Cr³⁺-doped glasses

Glass code	E_g, eV		E_{opt}^{ASF}, eV		R_i ,Å	α	$N \times 10^{22}$, (kg)⁻¹	$\chi \times 10^{-3}$, m³(kg)⁻¹
	$r = 1/2$	$r = 2$	$r = 1/2$	$r = 2$				
MBBTCr-1	1.96	3.15	1.95	3.13	21.84	0.490	1.35	1.35
MBBTCr-2	1.91	3.10	1.90	3.09	21.31	0.486	5.43	5.45
MBBTCr-3	1.89	3.08	1.87	3.07	20.85	0.480	8.90	8.95
MBBTCr-4	1.86	3.05	1.84	3.03	20.44	0.470	13.22	13.28

N o t a t i o n s: E_g, E_{opt}^{ASF} are the optical energy gaps, obtained using the Tauc's and the absorption spectrum fitting (ASF) plots, relatively; $r = 1/2$ and $r = 2$ correspond to the direct and indirect allowed transitions, relatively; R_i is the interionic distance; α is the chemical bonding parameter; N is the spin concentration; χ is the magnetic susceptibility.

ordered. The increase in TeO_2 concentration results in the breaking of regular structure of borotellurite glasses, which leads to a decrease in the energy gap [2]. The decrease may also be due to an increase in disorder in the glass and a further extension of localized states within the gap according to Ref. [27]. It was also observed that the indirect band gap values were larger than the direct ones.

The relation proposed by Dimitrov and Sakka [28] is in the form

$$(n^2 - 1)/(n^2 + 2) = 1 - (E_{opt} / 20)^{1/2} \quad (10)$$

and used to calculate the refractive index n.

The molar refraction R_m (expressed in cm³)

is related to the structure of the glass given by the Lorentz − Lorentz equation

$$R_m = (n^2 - 1) V_m / (n^2 + 2), \quad (11)$$

where V_m is the molar volume; the quantity

$$(n^2 - 1)/(n^2 + 2)$$

represents the reflection loss.

From relation (10), it is clear that as E_{opt} decreases, the refractive index n shall obviously increase. As V_m decreases, n shall increase. However, as the TeO_2 content increases in the glass matrix, Te − O − Te bonds break up and nonbridging oxygen is created. Thus, the ionic character of bonding in the glasses increases [7].
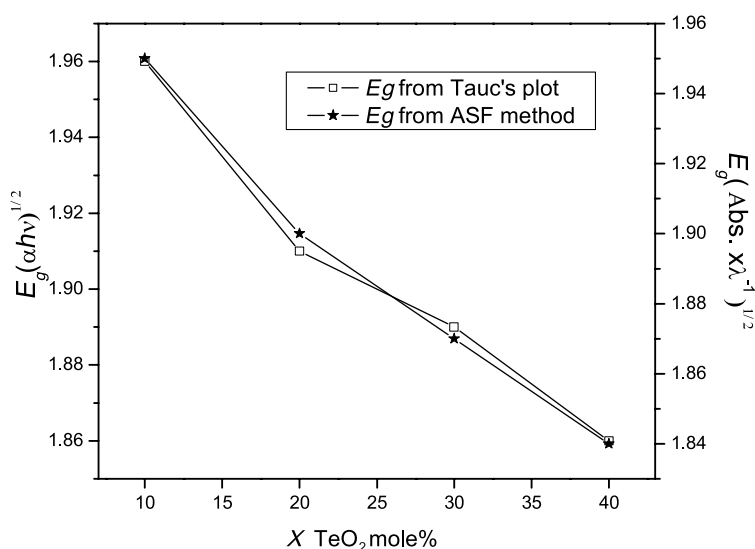

Fig. 6. E_g as functions of TeO_2 concentration obtained from Tauc's and ASF plots for glasses with 0.2 mol% of Cr³⁺ ions

The theoretical interaction parameter A_{th} was calculated using the following relation:

$$A_{th} = X_{MgO}A_{MgO} + X_{BaO}A_{BaO} + $$
$$+ X_{B2O3} A_{B2O3} + X_{TeO2} A_{TeO2} + \qquad (12)$$
$$+ X_{Cr2O3} A_{Cr2O3};$$

their values along with R_i are presented in Table 3.

Average oxide ion polarizability of the ion is described by A_{th}, and indicates the interatomic interaction.

3.4. Electron paramagnetic resonance (EPR). In the glass matrix, Cr^{3+} ions may exist as isolated Cr^{3+} ions and exchange-coupled Cr^{3+}-Cr^{3+} ion pairs [24]. The ground state of a Cr^{3+} free ion is ^4F. It belongs to the $3d^3$ electronic configuration. In the absence of a magnetic field, spin-orbit coupling splits one state level into the Kramer's doublet ($|\pm 1/2>$ and $|\pm 3/2>$) separated by $2D$ energy distance, where D is the zero field splitting parameter. In the presence of the external magnetic field, the spin-orbit coupling splits into various transitions like

$$|-3/2> \leftrightarrow |-1/2>, |-1/2> \leftrightarrow |1/2>,$$
$$|1/2> \leftrightarrow |3/2>$$

at $g\beta B - 2D$, $g\beta B$, $g\beta B + 2D$, respectively. In all the transitions the maximum separation is $4D$ [29].

$^4A_{2g}$ is the ground state level of Cr^{3+} ion in an octahedral crystal field. In this field ^4F state splits into the $^4A_{2g}$ singlet, $^4T_{1g}$ and $^4T_{2g}$ orbital triplets [24]. A large separation in spin-orbit transition leads to two resonance signals at $g \approx 2 - 5$ [30 − 33]. So far EPR spectra of Cr^{3+} ion-doped borate glasses [34] and borotellurite glasses [35, 36] were reported. Spin-Hamiltonian parameters of the 15MgO-15BaO--(59.8 − x)B$_2$O$_3$-(10.0 + x)TeO$_2$-0.2Cr$_2$O$_3$ glass systems under consideration were calculated by the following relation [22]:

$$H = \mu_B(BgS) + $$
$$D\{S_z^2 - [S(S+1)/3]\} + E(S_x^2 - S_y^2), \qquad (13)$$

where μ_B is the Bohr magneton; B is the magnetic field; D, E are the fine structure constants for axial and rhombic fields, respectively.

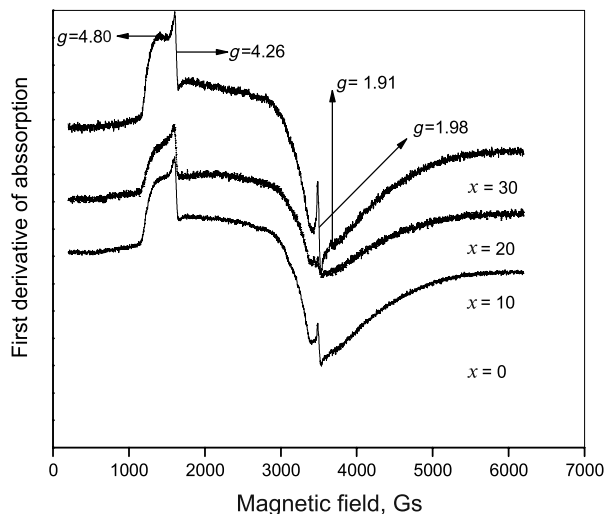EPR spectra of the glass samples doped with chromium are shown in Fig. 7.

Fig. 7. EPR spectra of 15MgO-15BaO--(59.8 − x)B$_2$O$_3$-(10.0 + x)TeO$_2$-0.2 Cr$_2$O$_3$ glasses for various x at room temperature

The resonance signal at $g = 4.80$ assigned to Cr^{3+}(I) indicated isolated Cr^{3+} centers in strongly distorted octahedral sites. This resonance signal exhibited a large zero field splitting paramer D; $E > g \cdot \mu_B B$, and $E/D \leq 1/3$ [30, 31]. The resonance signal at $g = 1.98$ assigned to Cr^{3+}(II) indicated isolated Cr^{3+} centers in axially-distorted octahedral sites. This resonance signal also has a large value of D and $E/D \ll 1/3$. The resonance signal at $g = 1.91$ indicates Cr^{3+}-Cr^{3+} exchange-coupled pairs [13]. Apart from these resonance signals, one more resonance signal at $g = 4.26$ was observed and assigned to Fe^{3+} ions, which were unwanted impurities and can be also present in the undoped glasses [20, 37]. The values of g obtained for the glass compositions in the present study are in tune with other glass systems reported in the literature [24, 38].

3.5. Number of spins and susceptibility. The variations in the number of spins N and the susceptibility χ with TeO$_2$ content are shown in Fig. 8 and the values are given in Table 3. The number N of spins participating in the resonance at $g = 1.98$ was obtained from the formula given by Weil, et al. [39]:

$$N = (A_x/A_{std}) \cdot [(Scan_x)^2/(Scan_{std})^2] \times$$
$$\times (G_{std}/G_x) [(H_m)_{std}/(H_m)_x] [(g_{std})^2/(g_x)^2] \times$$
$$\times \{[S(S+1)]_{std}/[S(S+1)]_x\} \times \qquad (14)$$
$$\times [(P_{std})^{1/2}/(P_x)^{1/2}] \cdot std,$$

where A is the area under the absorption curve, which can be obtained by double integrating the first derivative of the EPR absorption curve; Scan is the magnetic field corresponding to a unit length of the chart; G is the gain; H_m is the width of the modulation field; g is the g-factor; S is the spin of the system in its ground state; P is the power of the microwave source. The subscripts x and std represent the corresponding quantities for the glass and the standart samples $(CuSO_4 \cdot 5H_2O)$, respectively.

The susceptibility χ of the sample can be calculated using the formula [40]:

$$\chi = Ng^2\beta^2 J(J + 1)/(3k_B T), \qquad (15)$$

where N is the number of spins per m³; the other symbols have their usual meaning.

N can be calculated from Eq. (14) while calculating the χ values; $g = 1.98$ was taken. In borate glasses the addition of TeO_2 content results in the increase of open network, thus the number of nonbridging oxygens increases in the glass network, and this effect weakens the O^{2-} bonds for every Cr^{3+} ions. Hence, the interatomic distance between Cr^{3+} ions decreases and so the number of spins participating in the resonance increases.

4. Conclusions

On the basis of EPR and optical absorption studies on $15MgO$-$15BaO$-$(59.8 - x)B_2O_3$-$(10.0 + x)TeO_2$-$0.2\ Cr_2O_3$ the following conclusions can be made.

i. Optical absorption spectra showed two broad bands (16025 and 23474 cm⁻¹) due to spin-allowed transitions that were assigned to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and to $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transitions. The $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition revealed that the site symmetry of Cr^{3+} was either C_{4v} or C_{3v}. The unresolved broad band corresponding to 28011 cm⁻¹ was assigned to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition.

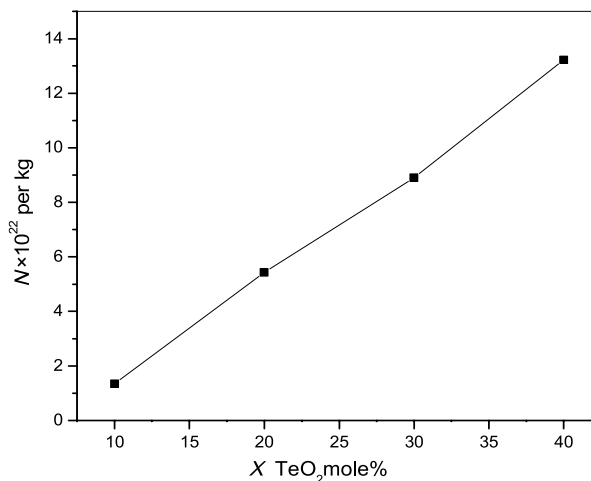*ii.* The value of Dq/B around 2.0 (which is less than 2.3) indicated that Cr^{3+} ions were

Fig. 8. The concentration of spins N for the resonance signal at $g \approx 1.98$ as a function of TeO_2 concentration

in the weak-field ligand sites. The increase in nephelauxetic (h) values indicated the increasing ionic nature between Cr^{3+} and its ligands in the glass.

iii. The decrease of the energy gap from 1.96 to 1.86 eV for indirect band transitions and from 3.15 to 3.05 eV for direct band transitions was attributed to the structure of the resulting glasses becoming less ordered. The increase in TeO_2 concentration results in the breaking of the regular structure of borotellurite glasses and, hence, is responsible for the decrease in the energy gap.

iv. The resonance signal at $g = 4.80$ was attributed to isolated Cr^{3+} centers in strongly distorted octahedral sites. The resonance signal at $g = 1.98$ was assigned to Cr^{3+} centers at axially distorted octahedral sites.

v. In addition to this, two more resonance signals at $g = 4.26$ and $g = 1.91$ were also observed. The resonance signal at $g = 4.26$ was assigned to the presence of unwanted impurity Fe^{3+} ions, and the resonance signal at $g = 1.91$ indicated the Cr^{3+}-Cr^{3+} exchange-coupled pairs.

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