Investigation of optical parameters of titanium substituted strontium borate glasses by Mott Davis's and hydrogenic excitonic model

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Strontium borate glasses are synthesized by melt-quench technique and amorphous nature is confirmed by X-Ray diffraction pattern. The calculated values of density are found to decrease with TiO_2 while molar volume shows the reverse trend. The optical band gap values have been estimated from the fitting of Mott- Davis's and Hydrogenic Excitonic Model (HEM). The absorption edge has been determined from the extrapolation of optical absorption data which shift towards higher wavelength. Other optical parameters such as refractive index, molar refractivity, oxide ion polarizability, Urbach energy, optical basicity and metallization criterion has been also discussed.

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1. Introduction

Borate glasses containing transition metal ions (TMI) have attracted attention among researchers due to their potential applications in optical glasses, solid state laser, electrochemical, electro-optic devices, electronic, compact lenses and switching devices [1-5]. Borate glasses is usually used to make dielectric and insulating materials because of their low melting point, high transparency, and high thermal stability [6-10]. Multi-component borate glasses which consist primarily of BO_3 triangles and BO_4 tetrahedra are formed by combination with alkali and alkaline earth oxides etc. [10-16].

Addition of alkaline earth oxides (SrO, CaO, and BaO) as glass modifiers into borate glasses have important applications for optical communications, laser hosts, optical filters, photonic devices [17-20]. Titanium dioxides have unique properties like high refractive index, excellent chemical stability, large band gap and transparent to visible light. Titanium oxide is a conditional glass former which has two valances (i.e. Ti^{3+} and Ti^{4+}) and form the glass with other glass formers or modifiers [21]. Glasses with high concentration of TiO_2 have attracted great interest in basic research and technological applications [22]. The present work emphasized on the modification of physical and optical properties of titanium borate glasses.

2. Experimental details

Borate glasses having compositions $xTiO_2$-$60B_2O_3$-(40-x) SrO [where x=0, 5, 10 and 15 mol%] were synthesized by the melt quenching method. The raw materials were taken in the appropriate amount and mixed thoroughly for half an hour. Porcelain crucible containing fused material kept in an electrical furnace at temperature 1200˚C for one hour. After that the melts was quickly pour on the stainless steel plate to quench.

X-ray diffraction pattern were carried out using Rigaku Table Top X-ray diffractometer at room temperature with a scanning rate of 4˚/min. Density measurement has been done by Archimedes' methods with Xylene as an immersion liquid using SI-234 Denver Instrument. The glass transition temperature (T_g) of glass samples is measured by differential scanning calorimetry (DSC) technique at a heating rate of 20˚C/min in nitrogen atmosphere.UV-VIS absorption spectra of polished glass samples having different thickness was recorded spectrophotometer in the wavelength range 200-800 nm using 3100 MC Shimadzu.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of prepared glass compositions $xTiO_2$-$60B_2O_3$-(40-x) SrO. The absence of any identifiable crystalline species in X- ray diffractogram or presence of a broad hump confirms the amorphous nature of prepared glass samples [9]. Archimedes's principle has been used to measure the values of density (ρ) and the measured density of prepared glass samples are decreases with increase in concentration of TiO_2 corresponding x = 0 to x = 15 which is an expected result as the relative molecular weight of TiO_2 is lower than SrO [23]. The following relation is used to calculate the molar volume (V_m) of glass samples:

$$V_m = \frac{\sum_i y_i W_i}{\rho} \quad (1)$$

where y_i is molar fraction, W_i molecular weight of i^{th} component and ρ is density of sample. The calculated values of density and molar volume are given in Table 1.

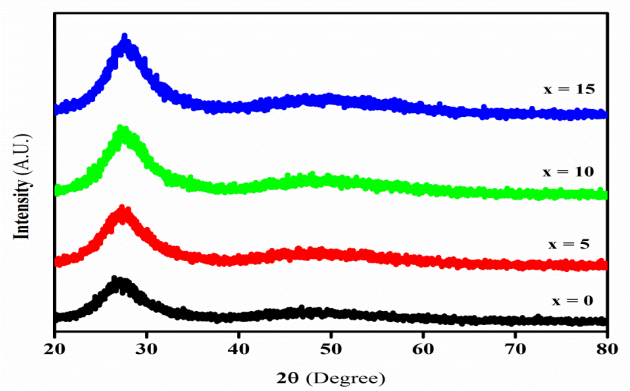

Fig. 1. X-ray diffraction patterns of different $xTiO_2$-$60B_2O_3$-(40-x) SrO glass composition

This increase in molar volume may be due to rearrangement of lattice and decreasing porosity [14].

The glass transition temperature (T_g) provides information related to glass network rigidity and strength of interatomic bonds. The glass transition temperature decreases as the concentration of titanium increases which is shown in Fig. 2.

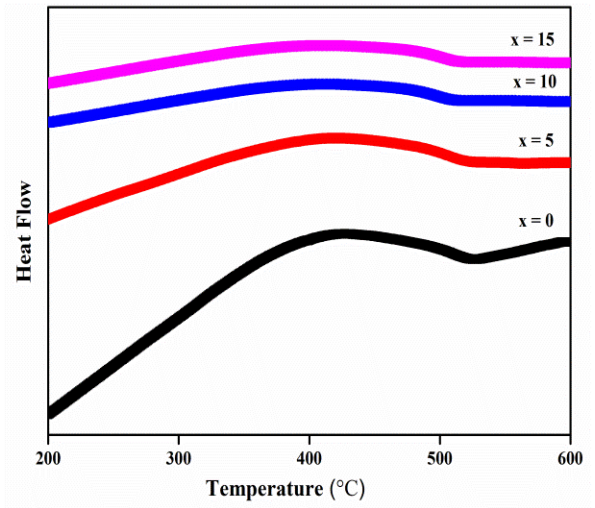

Fig. 2. DSC curves for different compositions

3.1. Optical properties

Optical absorption spectra have been done in the spectral range 200–800 nm at room temperature of all the prepared glass samples which is shown in Fig. 3. The absorption edge is signified by the cut-off Wavelength ($\lambda_{cut\text{-}off}$).

The values of $\lambda_{cut\text{-}off}$ and optical band gap (E_g) are determined from the extrapolation of optical absorption data which is given in Table 1. It can be seen that $\lambda_{cut\text{-}off}$ shifts toward the higher wavelength which shows a red-shift. This increase may be due to the increase in the number of non bridging oxygen (NBO) with TiO_2 [25].

The following relation is used to calculate the absorption coefficient:

$$\alpha(\nu) = \frac{A}{d} \quad (2)$$

where A and d are the absorbance and sample thickness.

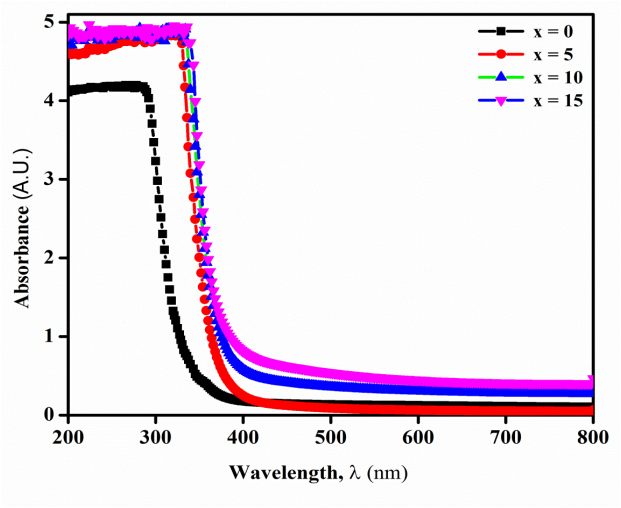

Fig. 3. Optical absorption spectra of $xTiO_2$-$60B_2O_3$-(40-x) SrO glass composition

The optical absorption coefficient α (ν) and photon energy hν are related as [26, 27]:

$$\alpha h\nu = C\left(h\nu - E_{g1}\right)^n \quad (3)$$

where α (absorption coefficient), hν (incident photon energy), C (energy independent constant), E_g (the optical band gap energy) and the index n is a constant which have different values such as 1/2, 2, 1/3 and 3 respectively corresponding to direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions.

Table 1. Density(ρ), molar volume (V_m), Cut-off wavelength ($\lambda_{cut-off}$), optical band gap (E_g), refractive Index (n),molar refractivity (R_m), Oxide ion polarizability(α_o^{2-}), Optical basicity(Λ), Urbach energy (ΔE) and metallization criterion (M) of $xTiO_2$-$60B_2O_3$-(40-x)SrO glasses for different value of x

Parameters	x=0	x=5	x=10	x=15
ρ (gm/cm^3)	6.878	6.657	6.411	6.200
V_m (cm^3/mole)	19.373	19.504	19.725	19.851
T_g	520	517	508	503
$\lambda_{cut-off}$ (nm)	331	365	372	375
E_{g1} (eV)	3.284	3.160	3.054	3.040
μ	2.252	2.291	2.310	2.320
R_m (cm^3)	11.158	11.429	11.665	11.788
α_o^{2-} (E_{opt})	1.855	1.876	1.891	1.886
Λ (E_{opt})	0.769	0.779	0.785	0.786
ΔE (eV)	0.319	0.195	0.227	0.212
M	0.424	0.414	0.408	0.406

Here we adopted two models to calculate the band gap i.e. Mott and Davis's model and Hydrogenic Excitonic Model. The indirect optical band gap values have been estimated from the fitting of Mott and Davis Model denoted by E_{g1} which is shown in Fig.4. The optical band gap energy for presently studied samples has been found to decrease with the concentration of transition metal oxides i.e. TiO_2. Mott and Davis's model have been failed to account the contribution of electron hole pair (exciton) which plays a major role for increment in optical transition rate. Therefore, we adopted Hydrogenic Excitonic Model (HEM) to extract the contribution of excitionic transitions.

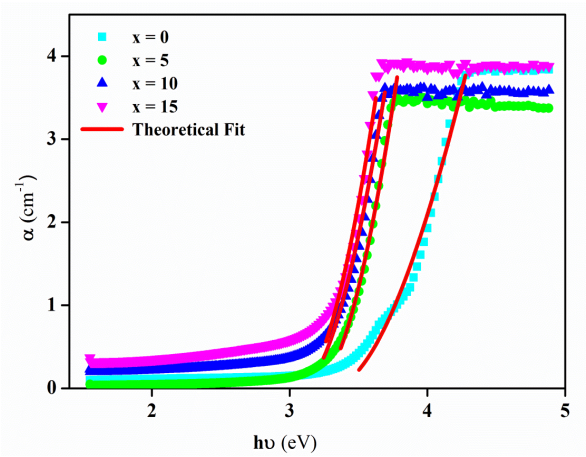

Fig. 4. Fitting of absorption coefficient (α) using Mott and Davis's model with r = 2 for different compositions of $xTiO_2$-$60B_2O_3$-(40-x) SrO glass system

Hydrogenic Excitonic Model (HEM) have already been discussed elsewhere which is used to obtain the direct band gap values [9-12] and the related parameters are listed in Table 2. The absorption coefficient (α) is also calculated using the empirical relation:

$$\alpha(E)=\frac{C_0R^{1/2}}{E}\left\{\sum_{m=1}^{\infty}\frac{2R}{m^3}\frac{\Gamma_m}{\left(E-E_m\right)^2+\Gamma_m^2}+\frac{1}{2}\left[\frac{\pi}{2}+\arctan\left[\frac{\hbar\omega-E_{g2}}{\Gamma_c}\right]\right]\right.$$

$$\left.-\sum_{m=1}^{\infty}\frac{R}{m^3}\frac{\Gamma_C}{\left(E-E_m\right)^2+\Gamma_C^2}+\frac{\pi}{2}\frac{\sinh\left(2u^+\right)}{\cosh\left(2u^+\right)-\cos\left(2u^-\right)}\right\} \quad (4)$$

with

$$u^{\pm}=\pi\left(\frac{R}{2}\right)^{1/2}\left[\frac{\left[\left(E-E_{g2}\right)^2+\Gamma_c^2\right]^{1/2}\pm\left(E-E_{g2}\right)}{\left(E-E_{g2}\right)^2+\Gamma_c^2}\right]^{1/2}$$

$$E_M=E_{g2}-\frac{R}{m^2}$$

and

$$\Gamma_m=\Gamma_c-\left(\Gamma_c-\Gamma_1\right)/m^2\,, \qquad \text{m = 1, 2, 3.}$$

where the parameters C_0, E, E_{g2} and R denotes the absorption strength parameter, photon energy, optical band gap energy, excitonic binding energy. Γ_1 and Γ_c are the line widths for m = 1 state and of the continuum, respectively. The estimated band gap values from both the models were found to decrease with TiO_2 and fitted data of absorption coefficient using HEM is shown in Fig. 5.

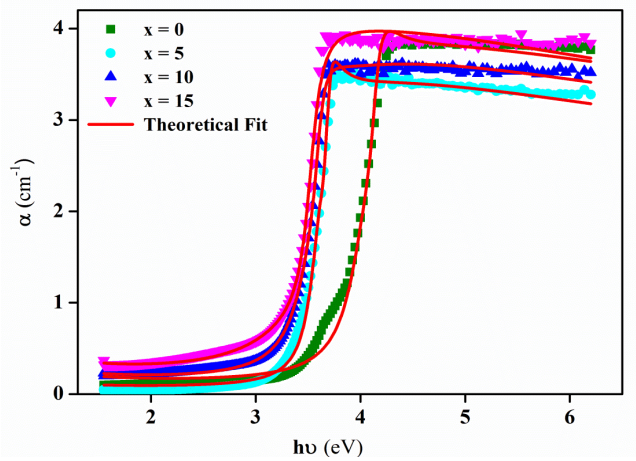

Fig. 5. Fitting of absorption coefficient (α) using Hydrogenic excitonic model for different compositions of $xTiO_2$-$60B_2O_3$-(40-x) SrO glass system

Table 2. Values of optical energy band gap (E_{g2}), excitonic binding energy (R), line widths for m = 1 state (Γ_1), line width of continuum (Γ_c) and absorption strength (C_0), Best fit parameter (R^2) and reduced chi square (χ^2) obtained from the fitting of experimental data of absorption coefficient spectrum with Hydrogenic excitonic model (Eq. (6)) for $xTiO_2$-$60B_2O_3$-(40-x)SrO glass system

x	E_{g2} (eV)	R (eV)	Γ_1 (eV)	Γ_c (eV)	C_0 ($eV^{1/2}$/cm)	R^2	χ^2
0	4.152	0.092	0.191	0.066	17.482	0.995	0.008
5	3.696	0.074	0.117	0.035	15.209	0.998	0.004
10	3.603	0.063	0.203	0.076	16.769	0.999	0.003
15	3.539	0.066	0.594	0.094	17.742	0.998	0.003

In crystalline and amorphous materials, Urbach energy is characterized by the degree of disorderness which can be obtained by the Urbach equation:

$$\alpha(\nu) = B\exp(h\nu / \Delta E) \tag{5}$$

where B is constant and ΔE is Urbach energy. The equation (5) can be rewritten as:

$$\ln\alpha(\nu) = h\nu / \Delta E + cons\tan t \tag{6}$$

The Urbach energy (ΔE) can be determined by taken the reciprocal of the slope of linear region of the curve plotted between ln(α) verses hν (Fig.6). The obtained values of ΔE lies in range 0.319-0.195 eV which indicates that the prepatred materials have fewer tendencies to convert weak bonds in to defects [26, 28].

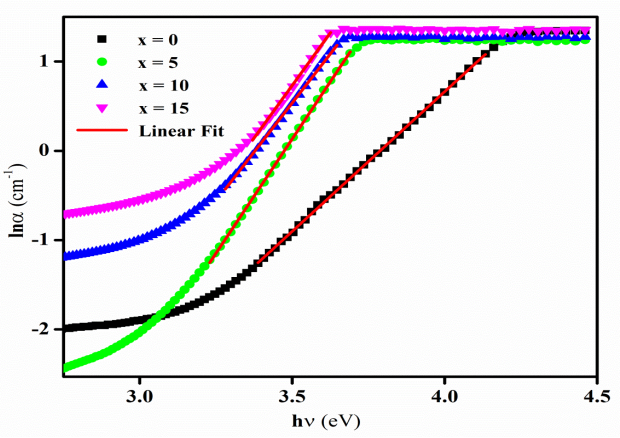

Fig. 6. Urbach's plots for different compositions of $xTiO_2$-$60B_2O_3$-(40-x) SrO glass system

Dimitrov and Sakka proposed a relation between refractive index (μ) and optical band gap energy [29]:

$$\frac{\mu^2 - 1}{\mu^2 + 2} = 1 - \sqrt{\frac{E_{g1}}{20}} \tag{7}$$

The observed value of refractive index and optical band gap energy (E_g) shows the opposite trend (listed in table 1). The increase in refractive index may be due to the lower cation polarizability of Ti^{4+} than sr^{2+} [30].

The molar refractivity (R_m) and E_g is related by the relation:

$$R_m = V_m\left[1 - \sqrt{E_g / 20}\right] \tag{8}$$

The oxide ions polarizability is given by relation proposed by Dimitrov and Sakka:

$$\alpha_o^{2-}(E_{opt}) = \left[\left(\frac{V_m}{2.52}\right)\left(1 - \sqrt{\frac{E_g}{20}}\right) - \sum\alpha_i\right] / N_{o^{2-}} \tag{9}$$

where $\Sigma\alpha_i$ is the molar cation polarizability and the values of α_i for B^{3+}, Ti^{4+}, and Sr^{2+} ions are respectively 0.002 $Å^3$, 0.184 $Å^3$ and 0.861 $Å^3$ [30, 31] and $N_{o^{2-}}$ is the number of oxide ions in chemical formula.

Optical basicity (Λ) has been calculated by using the formula given by [32]:

$$\Lambda = 1.67\left(1 - \frac{1}{\alpha_{o^{2-}}}\right) \tag{10}$$

The calculated values of optical basicity and oxide ion polarizability (shown in table 1) increases in concentration of titanium which may be due to increase in number of non bridging oxygen (NBO) in a glass matrix [33].

The metallization criterion (M) of an oxide is given by the relation:

$$M = 1 - R_m / V_m \quad (11)$$

The calculated value of metallization criteria lies in the range 0.424-0.406 which is less than 1 (shown in Table 1). Metallization criterion helps us to predicting metallic or insulating behavior in the condensed state. If M is close to 1 then the material are typical insulators. In opposite, if M is close to zero means that the width of both valence and conduction bands become large, resulting in a narrow band gap and increased the metallicity of the solid [29].

4. Conclusions

Transition metals have a profound effect in the properties of borate glasses in borate strontium glass matrix. The XRD pattern confirms the amorphous nature of prepared glass system. The calculated values of density by using Archimedes' principle have been found to decrease with the transition metal ions. The absorption edge shifted towards higher wavelength resulting in a red shift. The optical band gap energy of experimental absorption coefficient data calculated from fitting of Mott and Davis Model and HEM which found to decrease with TiO_2. The calculated values of the other optical parameters like refractive index, molar refractivity, oxide ion polarizability and optical basicity were increases with titanium. The Urbach energy for studied glass samples lies in the range 0.319 – 0.195 eV which suggests low defect concentration.

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