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Electrical characterization of sodium cadmium borate glasses doped with TiO_2

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Abstract – A glass series sodium cadmium borate glasses doped with titanium has been formed using melt quench technique within the composition $20Na_2O$-(20-x)CdO- $60B_2O_3$-$xTiO_2$ ($0 \leq x \leq 5$ mol%). The composition was prepared to study the effect of dopant (TiO_2) on physical, optical and electrical properties of the glass series under study. The results of physical parameter i.e. density and molar volume show some structural changes at higher concentration of TiO_2 doping. Some theoretical optical parameter parameters (*n*, R_m, α_m and $\pi_{J\,P}$) were calculated and displayed in Table 2 & 3. The dc conductivity of the glasses is found temperature dependent. The conductivity value ranges in between $2.45x10^{-6}$ – $3.47x10^{-6}$ Scm^{-1} at 523 K temperature indicates the insulating behavior of these glasses.

Keywords – oxide glasses; borate glasses; electrical properties

Introduction

The research on oxide glasses containing transition metals have become a very active research field in the area of optoelectronics, optoelectronic communication devices because they are considered as good material for synthesizing low loss optical fibres, refractive index dispersion and their properties can be tuned for laser devices and optical amplifier media [1]. However, oxide glasses have some drawbacks such as low/high absorption, limited wavelength range and slower response times [2]. From literature survey it is seen that it can be overcome by the addition of suitable dopant in the oxide glasses. In oxide glasses borate glasses are the most popular and widely studied glasses for optoelectronic applications due to its good glass forming ability with different dopant materials (i.e. alkali metals, transitional metal, heavy metal oxides etc.). It has high optical transparency, low cost of production, excellent mechanical and thermal stability too. It has been reported that TiO_2 is an interesting transition metal oxide among all transition metals and is used to modify the glass's optical properties, as it has low coordination numbers. It is found that it exists in two forms trivalent (Ti^{3+}) as well as tetravalent (Ti^{4+}) in the glass matrix. Which contributes as glass modifier in the form of TiO_6 structural units and as a glass former as TiO_4 [3-5]. Normally, TiO_2 exist in Ti^{4+} state and sometimes with TiO_5 (comprising of trigonal bipyramids) structural units in the glass network. There is possibility for the reduction of Ti^{4+} ions into Ti^{3+} ions during synthesis and annealing process [3]. The valency of TiO_2 in the glass matrix depends on

many factors like chemical composition and melting temperature. Morinaga et al. reported that Ti^{3+} is absent in borate glasses having high concentration of alkali metal oxides, even the melting temperatures of glass is 1500 C [6]. Oxide glass needs some additives to improve physicochemical properties for obtaining the desired property. In the present glasses, Na_2O introduced into the borate network to lower the melting point [3]. Na_2O react with B_2O_3 to modify borate structure from tri-angular boron to tetrahedral coordination to have unique properties due to two coordination states in their network structure [7]. Upon addition of Na_2O to the B_2O_3 covalent network causes considerable change, resulting in the creation of anionic sites occupied by modifying Na_2O. Cadmium oxide CdO was introduced to reduce the solidification time of glasses when the melt is quenched. Addition of CdO in the glass matrix also enhances the chemical stability and has less thermal expansion too [8]. The aim of present study is to investigate the electrical properties of sodium cadmium borate glasses with TiO_2 concentration. So that industrialist can get a better insight to use such glasses in wave guide cable and other optoelectronic devices.

EXPERIMENTAL

The TiO_2 doped sodium cadmium borate glass series was synthesized via a conventional melt quenching technique with a series formula $20Na_2O$-(20-x)CdO-$60B_2O_3$-xTiO_2 where x was varied from 0 to 5 mol%. Analytical grade chemicals H_3BO_3, Li_2CO_3, CdO and TiO_2 from Merck with high purity (99%) were used to perform this study. The raw materials with specified ratios are given in Table 1. Weighed amount of raw materials were taken and thoroughly mixed with the help of quartz mortar pestle to form a batch of 20 g. The mixed material was shifted into porcelain crucible and then melted at 1373 K temperature for 1 hour in an electric muffle furnace. To ensure the homogeneity of the sample, the melt was stirred regularly after each 15 min. Then melt was quenched using stainless steel plates. Thus we obtained coin shaped glass sample of thickness around 1.0 – 1.5 mm. The obtained samples were annealed for 1 hour at 673K for further removal of impurities in the glass sample. The following characterizations were done of synthesized samples:

Density and molar volume was calculated using Archimedes principal, theoretical optical parameters optical basicity, molar refraction, electronic polarizability, ion concentration and refractive index were calculated using theoretical equations. The temperature dependence dc conductivity of all the glass samples was measured in the temperature range 300 K – 623 K using 2480 Keithley source meter at constant voltage 20V.

RESULTS AND DISCUSSION

To find out the physical parameters of glasses under study the following equations were used:

Table 1

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Sample code and composition ratio of the glass samples.

	20	20	60	0
	20	20	60	1
	20	20	60	2
	20	20	60	3
	20	20	60	4
	20	20	60	5

The measurement of density of each glass sample was done using the conventional Archimedes' method in which xylene (ρ_x = 0.850-0.865 g/ml at 20°C) was used as buoyant liquid. The density (ρ) of the glasses was calculated using equation (1).

$$\rho = \frac{W_a}{W_a - W_b}\rho_x \quad (1)$$

Here W_a is the sample weight measured in air; W_b is the sample weight measured in buoyant liquid.

The calculated amount of chemicals for synthesizing the 20 g sample were measured in digital balance aczet model CY224 at room temperature.

To find out the molar volume (V_M) of each glass sample the following equation was used

$$V_M = \frac{\sum_i M_i}{\rho} \quad (2)$$

The optical basicity represents the covalent or ionic nature of glass based on the electron donor power of oxygen [9]. Higher is the Λ_{th} values lesser the ionic character of the glass network and vice versa. Duffy [10] proposed the relationship (3) between the oxide ion polarizability ($\alpha_{O^{2-}}$) and optical basicity (Λ_{th}) for various oxide ions.

$$(\Lambda)_{th} = 2.782\left(\frac{2}{\alpha_{O^{2-}}}\right) \quad (3)$$

The theoretical optical basicity (Λ_{th}) values of the present glass samples were calculated using the following equation (4)

$$\Lambda_{th} = \chi_{B_2O_3}\Lambda_{B_2O_3} + \chi_{CdO}\Lambda_{CdO} + \chi_{Na_2O}\Lambda_{Na_2O} + \chi_{TiO_2}\Lambda_{TiO_2} \quad (4)$$

Where $\Lambda(Na_2O)$, $\Lambda(CdO)$, $\Lambda(B_2O_3)$ and $\Lambda(TiO_2)$ are optical basicity values of constituent oxides and $\chi_{B_2O_3}$, χ_{CdO}, χ_{Na_2O} and χ_{TiO_2} are equivalent molar fractions of different oxides [11]. The values of $\Lambda(Na_2O)$, $\Lambda(CdO)$, $\Lambda(B_2O_3)$ and $\Lambda(TiO_2)$ are available in the literature [12].

Refractive index (n) of synthesized glass samples is calculated using Equation (5)

$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{E_g/20} \quad (5)$$

E_g is the optical band gap calculated from the UV-VIS spectroscopy (has not been discussed here).

Other optical parameters i.e. molar refraction (R_m), electronic polarizability (α_m) and ion

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concentration (N) are obtained from the following equations.

$$\text{[illegible]} = \frac{\text{[illegible]}}{\text{[illegible]}}$$

(6)

Where (n) is the refractive index and (V_m) is the molar volume of the prepared sample.

$$\text{[illegible]} = \frac{\text{[illegible]}}{\text{[illegible]}}$$

(7)

Where (R_m) is the Molar refractivity and (N_A) is the Avogadro's No.

$$\text{[illegible]} = \frac{\text{[illegible]}}{\text{[illegible]}}$$

(8)

Where (ρ) is the density, mol% is the dopant concentration, (N_A) is the Avogadro's No. and (M_i) is the average molecular weight of the sample.

The calculated values of D and V_m are displayed in Table 1 and compositional dependence plot has been shown in Fig. 1. The study of these physical parameters gives the degree of compactness and variation of geometric structure of the glasses. In general, the density is influenced by two factors that are size and the weight of the dopant. In the present

Table 2

Density (D), molar volume (V_m), optical basicity (Λth) of NCBT Series.

	gcm^{-3}	cm^{-3}mol^{-1}	-
	3.200	38.007	0.719
	2.838	42.686	0.716
	2.745	43.959	0.714
	3.024	39.739	0.713
	2.860	41.849	0.711
	2.745	42.429	0.709

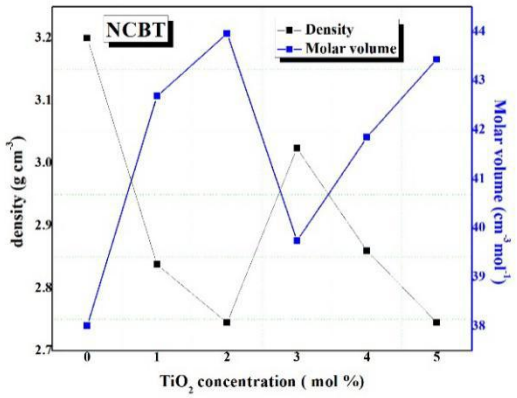

Fig.1. Variation of density(ρ) and molar volume (V_M) with TiO_2/CdO ratio for NCBT glasses.

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glass system density and molar volume show opposite behaviour. The density of glass samples decreases with addition of TiO_2 concentration upto 2 mol%. This is due to the reduction in the molecular weight of the glass (molecular weight of CdO is 128.4g/mol and that for TiO_2 is 78.86g/mol). However, there is some nonlinear change is observed in density at x ≥ 3 mol% and similar behaviour is seen in molar volume results. This may be due to the change in coordination number of Ti ions causes to modify the glass network. The data shows that in the present glass system structure is more opened at lower concentration of TiO_2.

The calculated values of Λ_{th} of NCBT glass series is given in Table 1. The compositional dependent optical basicity plot is shown in Fig. 2. Optical basicity is calculated from the electron donor power of the oxide species present in the glass system. In the present glasses, the decreasing trend of optical basicity values indicates the increasing covalent nature of these glasses. This behaviour can be explained from equation (3), the oxide ion polarizability (α_0^{2-}) of CdO and TiO_2 is 2.993 and 2.278 A^0 respectively and decreasing with increase in TiO_2/CdO ratio.

Calculated vales of molar refraction (R_m), electronic polarizability (α_m), ion concentration (N) and refractive index (n) are given in Table 3. The addition of TiO_2 into these glasses increases the electronic polarizability leads to decrease the refractive index in comparison to un-doped glasses.

Fig. 3 shows the temperature dependence of dc conductivity for NCBT glasses. The calculated values of dc conductivity at two different temperatures (523 K and 563 K) are displayed in Table 4. The calculated value of activation energy of each glass sample is also given in Table 4. It can be seen from Fig. 3 and Table 4 that the conductivity is increasing with increase in temperature for all the glass samples. This is due to the thermal stimulation process, which increases the energy of charge carrier with rise in temperature [13]. The compositional dependence of σ_{dc} (Table 4) show some structural changes

	cm^3mol^{-1}	($\times10^{-23}cm^3$)	($\times10^{23}$)	
	22.9829	0.9124	0	2.3653
	24.4462	0.9705	0.2139	2.2407
	25.2280	1.0015	0.4139	2.2451
	22.8777	0.9082	0.6840	2.2520
	24.2348	0.9621	0.8625	2.2647
	24.6767	0.9797	1.0348	2.2738

Table 3

Molar refraction (R_m), electronic polarizability (α_m), ion concentration (N) and refractive index (n) of NCBT

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series.

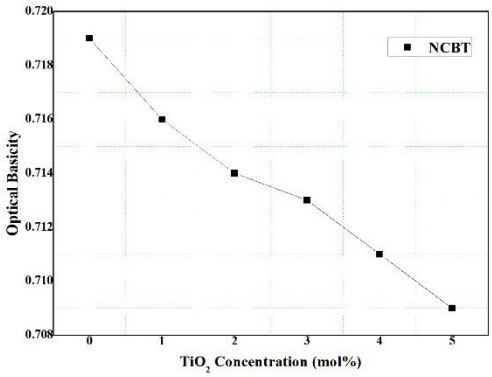

Fig.2. Variation of Optical Basicity (Λ_{th}) with TiO_2/CdO ratio for NCBT glasses.

Table 4

DC Conductivity values at 523 K and 563 K and activation Energy (E_{act}) of NCBT glasses.

Glass	σ(523K) (Scm^{-1})	σ(563K) (Scm^{-1})	E_{act}(eV)
NCBT0	2.49307E-06	1.15982E-05	0.380
NCBT1	2.8779E-06	1.44008E-05	0.400
NCBT2	7.3193E-06	3.16301E-05	0.372
NCBT3	3.48519E-06	1.73209E-05	0.396
NCBT4	3.12784E-06	1.27376E-05	0.379
NCBT5	3.75615E-06	1.83616E-05	0.391

beyond 2 mol% of TiO_2. Where the conductivity starts decreasing at both temperatures. These results again indicate the structural modification taking place at this concentration of TiO_2 in these glasses as discussed in density and molar volume results. It has been reported that in Ti doped glasses TiO_2 enters as Ti^{4+} (glass former) and Ti^{3+} (glass modifier) [14-15]. It is assumed that in the present glasses at lower concentration Ti^{3+} ions dominate over Ti^{4+} ions cause to increase the conductivity. Which indicates that Ti^{3+} ions contribute the non-bridging oxygen in the glass matrix and act as glass modifier and later beyond 2 mol % coordination number changes from $Ti^{3+} \rightarrow Ti^{4+}$ as stated by Morinaga et al. [6] and Reddy et al [3] it takes part as glass former causes to decrease in conductivity of the glasses under study. These results also favour the molar volume and density results as the creation of NBOs opens the structure and molar volume increases [16].

CONCLUSION

The decrease in density and increase in molar volume at lower concentration of Ti_2O suggests that the volume of NBOs sites produces the interstitial space within the network. At higher concentration due to the structural changes network shrinks and there is less space for ion movement. This behaviour also supports the fact depicted for optical basicity, molar refraction, electronic polarizability and refractive index values. The variation dc conductivity values reveal that at lower concentration the conductivity increases due

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to the presence of interstitial sites and higher concentration the presence of TiO_4 structural units are responsible for decrease in conductivity.

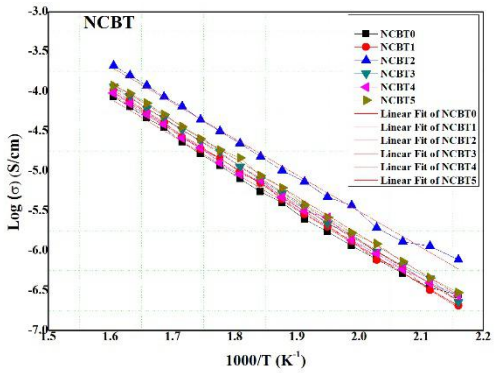

Fig 3. DC conductivity plots for NCBT glasses.

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