Optical studies of tellurium based quaternary glasses

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Abstract- *The glasses with composition $64TeO_2$-15CdO-(20-x)ZnO-xBaO-$1V_2O_5$ (x= 0, 5, 10, 15 and 20 mol%) were prepared by conventional melt quenching technique. X-ray diffraction method was used to confirms the non crystalline behavior of the glass samples. The optical absorption studies shows that the cut-off wavelength decreases while optical band gap energy (E_{opt}) and Urbach energy (ΔE) values increase with an increase of BaO composition. The Refractive index (n) calculated from E_{opt} was found to decrease with an increase of BaO mol percentage. The physical parameters such as density (ρ), molar volume (V_m), oxygen packing density (OPD), molar refraction (R_m) and metallization criterion (M) estimated and discussed.*

Keywords**:** XRD, Optical absorption, Refractive index and Physical parameters.

Introduction

The tellurium based glasses shows linear and nonlinear high refractive indices. These materialsare used in photonic applications such as lasers, optical fiber amplifiers, non-linear optical devices, etc., [1-6]. A pure tellurium dioxide does not form a glasseasily and needs glass network oxides, modifiers and intermediates like BaO, ZnO, CdO, Bi_2O_3 etc. [1-6]. The metal oxides such as ZnO, PbO and Bi_2O_3,etc are conditional glass modifiers. Glasses containing these types of metal oxides give rise to higher order non-linear optical properties [6]. Hence BaO, ZnO and CdO were chosen as modifiers and intermediates respectively in the present glass system. In recent years, the attention of researchers has attracted CdO due to their wide range of applications in the field of optoelectronic devices such as solar cells, photo transistors, diodes, and transparent electrodes [7]. The addition of alkaline earth oxides like BaO to TeO_2 glasses has been shown to increase the transition temperatures and improve the thermal stability of tellurite glasses [8]. The structure of telurite glass network consists of TeO_4 trigonal bipyramids linked by Te-O-Te linkages [8]. Addition of ZnO, CdO and BaO to TeO_2 results in breakage of Te-O-Te linkages thereby resulting in a systematic conversion of TeO_4 to TeO_3 structural units. In the present study ZnO and BaO have been taken to modify the glass structure and to study the effect of BaO and ZnO on the physical and optical properties of CdO-TeO_2 glasses.

Preparation Techniques

The present chemical composition $64TeO_2$-15CdO-(20-x)ZnO-xBaO-$1V_2O_5$ glass with x = 0, 5, 10, 15, 20 mol% were made by melt quenching method. Required amount of high purity TeO_2

(99+ purity), CdO (99.9% purity), ZnO (99.9% purity) and BaO (99.9% purity) and V_2O_5 (99.9% purity) for each chemical composition were added in mortar and pestle. Each of this prepared glass sample was collected in a porcelain crucible and placing it in a high temperature furnace at 850 to 900 ^oC for milting the sample. During the melting process, the melt was thoroughly mixed to ensure the homogeneity of the composition. The melt was then poured onto a smooth polished steel plate and immediately pressed by another polished steel plate, where the steel plates were maintained at 200 ^oC. All the obtained samples were annealed at 200 ^oC for 6hrs to remove the thermal stresses resulted during the quenching. The prepared samples were clear, bubble free and transparent.

XRD analysis was confirm the amorphous nature of the glass samples using Philips PW (1140) diffractometer using Cu K_α (1.54 Å) source.

The optical absorption spectra of the present glass sample were observed by using a double beam schimadzu UV-Vis-NIR-3100 spectrophotometer in the wavelength range 250 to 800 nm at room temperature. The error value is observed in wavelength is about ±1nm.

Results and discussion

3.1 Physical Properties

The detailed mol percentage of the glass samples and their corresponding codes were presented in Table 1.

The X-ray diffraction patterns of the present glass samples are shown in Fig. 1. This shows no peaks, which are characteristic for the amorphous nature of the samples.

The densities of the tellurium based glass sample were calculated by using Archimedes principle at normal temperature with the following equation.

$$\rho = \frac{a}{a-b} \times \rho_x \qquad (1)$$

where a = weight of the glass sample in air

b = weight of the glass sample when immersed in xylene

ρ_x= density (0.865 g/cm^3) of xylene liquid

The densities (ρ) of the glass samples evaluated and listed in Table 2. It is found that the density decreases from 5.631 to 5.535 g/cm^3 with the addition of BaO content at the expense of ZnO content. From the density (ρ) values, the molar volume (V_m) of the glass samples was calculated using the following relation.

$$V_m = \frac{\sum M}{\rho} \qquad (2)$$

where M = molecular weight of the glass sample

The molar volume (V_m) of the present glasses increased from 24.772 to 29.398 cc/mol with the increase of BaO content. The oxygen packing density of glass samples were calculated using the equation and the result values are mentioned in Table2

$$\text{Oxygen Packing Density (OPD)} = \frac{\rho}{M} \times O_n \qquad (3)$$

where O_n is number of oxygen atoms per formula

From Table 2, it is clear that the OPD values are decreases from 67.814to 57.145 mol/l. This decrease in OPD values could be due to the increase in molecular weight of the glass samples and decrease in the density of glass samples.

3.2 Optical Absorption Studies

Fig.2 shows the optical absorption spectra of present glass system. It is observed from Table 3 that the fundamental absorption edge shifts to lower wavelength side with an increase of BaO content of glass samples. Absorption coefficient near the edge of each curve was determined at a wavelength by using the relation.

$$\alpha(\nu) = \frac{2.303A}{t} \qquad (4)$$

where t is the thickness of the glass sample.

A is the absorbance.

The main feature of the absorption edge of amorphous materials, particularly at the lower values of absorption coefficient is an exponential increase of the absorption coefficient $\alpha(\nu)$ with photon energy $h\nu$ in accordance with an empirical relation [9].

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{\Delta E}\right) \qquad (5)$$

Where α_o a constant is ΔE is the Urbach energy and ν is the frequency of radiation.

David and Mott [10] gave the following forms of absorption coefficient $\alpha(\nu)$ as a function of photon energy $(h\nu)$ for direct and indirect transition.

$$\alpha(\omega) = \frac{B(h\nu - E_{opt})^n}{h\nu} \qquad (6)$$

Where n=1/2 for direct allowed transition and n=2 for indirect allowed transition and B is constant. Using the above two equations, $(\alpha h\nu)^{1/2}$ was plotted as a function of photon energy $h\nu$ Fig. 3 shows the corresponding $(\alpha h\nu)^{1/2}$ Vs $h\nu$ graph for all samples. The respective values of optical band gap (E_{opt}) are obtained by extrapolating to $(\alpha h\nu)^{1/2}$ = 0 for indirect transitions and are tabulated in Table 3. It is observed that E_{opt} increase from 2.208 to 2.394 with an increase

of BaO content. The increase in the value of E_{opt} with increasing the BaO content could be due to the formation of Te-O^{-}…Ba^{2+} bonds in the place of Te-O-Te, Te-O-Zn and Te-O-Cd as observed from structural analysis. Moreover, the band gap of BaO (4.8 eV) is higher than that of ZnO (3.4) and CdO (2.3 eV) [11]. This suggests that the band gap values are increases when higher band gap content replacing the lower band gap content in the glass system. It is clear from Fig. 2 that strong visible absorption bands were observed from the glass samples.

Theoretical optical basicity for the glass system has been calculated by assigning basicity to the individual oxides on the basis of the following equation proposed by Duffy and Ingram [12,13].

$$\Lambda_{th}=x(TeO_2)\Lambda(TeO_2)+x(CdO)\Lambda(CdO)+x(ZnO)\Lambda(ZnO)+x(BaO)\Lambda(BaO)+x(V_2O_5)\Lambda(V_2O_5) \quad (7)$$

Where $x(TeO_2)$, x(CdO), x(ZnO), x(BaO), and $x(V_2O_5)$ are the equivalentfractions of different oxides and $\Lambda(TeO_2 = 0.93)$, Λ(CdO = 1.115), Λ(ZnO = 1.08), Λ(BaO = 1.22) and $\Lambda(V_2O_5 =$ 1.04) are optical basicity values [14]. The calculated values of 0.988 to 1.016 optical basicity are shown in Table 2. It can be observed that from the table basicity has increased with an increase in BaO content. This could be due to the larger basicity of BaO than that of lower basicity of ZnO. Thus, replacement of lower basicity by higher basicity has resulted as an increase in the optical basicity. This also suggests an increase in the oxide ion polarizability with increasing optical basicity. Band tailing parameters were determined from the Fig.3 and the value lies between 4.071 to 2.698.

Refractive index (n) is determined from optical energy gap using the relation proposed by Dimitrov and Sakka [15].

$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_{opt}}{20}} \quad (8)$$

The values of refractive index decreased (n) from 2.650 to 2.582. This is in agreement with earlier literature values [16,17]. Because the refractive indices of CdO (2.49), ZnO (2.008) and TeO_2 (2.27) are greater than that of BaO (1.98). For all the glass samples, plots were drawn between $\ln(\alpha)$ Vs $h\nu$ as shown in Fig. 4. The values of ΔE were calculated by taking the reciprocals of the slopes of the linear regions of the curve in the lower photon energy region of $\ln(\alpha)$ Vs $h\nu$.Urbach energy which corresponds to the width of localized states is used to characterize the degree of disorder in amorphous and crystalline systems. The values of ΔE of the present glass system lie in the range 0.590 to 0.868 eV for all the glass samples. The increase in Urbach energy with BaO content could be due to increased number of defects.

The molar Refractivity (R_m) is directly proportional to the polarizabilities of the constituent ions of the glass, and is given by the expression

Sample code	**TeO_2**	**CdO**	**ZnO**	**BaO**	**V_2O_5**

$$R_m = V_m \left[\frac{n^2-1}{n^2+2}\right] \quad (9)$$

Where V_m is the molar volume of the glass and n is the refractive index. In the present case, the molar refractivity is found to increase from 16.540 to 19.225 with the increase of BaO in mol%. The refractive index values are decreases from 2.650 to 2.585 with the increase of BaO content. In general, the refractive index (n) of the glasses increases with an increase in molar volume (V_m), molar refraction (R_m) and optical basicity (Λ) etc. of the glasses. But in the present case we have observed that the refractive index (n) of the glasses decreases with increase in V_m, R_m and Λ. Therefore, the decrease in refractive index (n) suggests that this could be due to the decrease in density and oxygen packing density [18].

The condition for predicting metallic or insulating behavior in the condensed state matter in metallization criterion [19] was given by the expression

$$M = 1 - R_m/V_m \quad (10)$$

If $R_m/V_m > 1$ then the material show metallic behavior and if $R_m/V_m < 1$ it exhibits insulating behavior. These 'M' values are presented in Table 3. The metallization criterion (M) increases from 0.332 to 0.346 as BaO content substituting ZnO content. This result may indicate that the width of both valence and conduction bands become smaller, resulting in a higher optical band gap [20].

Conclusion:

The absence of the sharp peaks in X-ray diffraction pattern confirms the amorphous nature of the present glass system. From optical absorption spectra of tellurium based glass system it is observed that with increase of BaO fundamental absorption edge shifts lower wavelengths increasing the optical energy gap. The shift in fundamental absorption edge indicates structural rearrangement of relative concentrations of various fundamental units. Decrease in Urbach energy indicates that fragility nature of glasses decreased with increase of BaO content. The refractive index obtained from optical energy gap decreased with BaO content.

Density decreased and molar volume increased for the present glasses with increase of BaO. It is observed that density and molar volume are inversely proportional. Oxygen packing density decreases with increase of BaO content.

ZB1	64	15	20	0	1
ZB2	64	15	15	5	1
ZB3	64	15	10	10	1
ZB4	64	15	5	15	1
ZB5	64	15	0	20	1

Table1. Compositions of tellurium based glass system (mol %).

Fig. 1. XRD patterns of tellurium based glass system

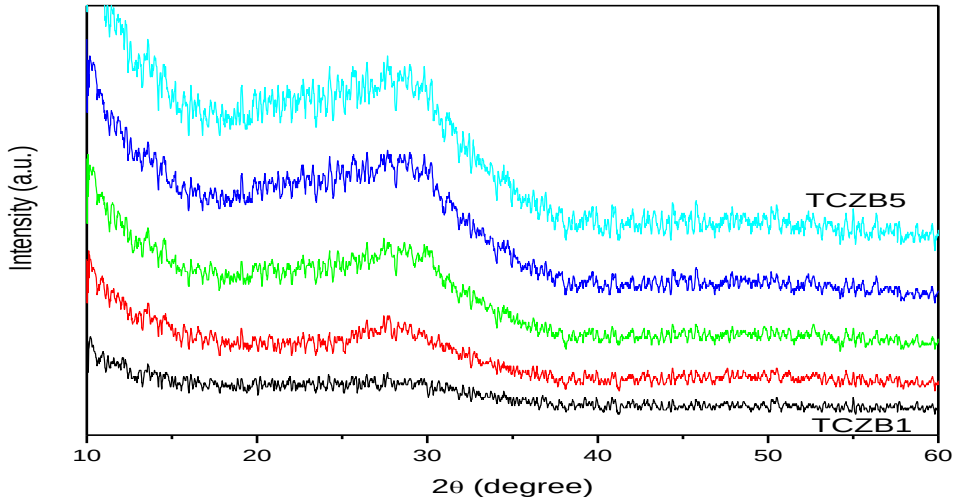

Table 2. Physical parameters of tellurium based glass system.

Sample Code	Density ρ (g/cc) (±0.001)	Molar Volume V_m(cc/mol)	Oxygen Packing Density(O.P.D)(mol/l)	Optical basicity (Λ)
ZB1	5.631	24.772	67.814	0.988
ZB2	5.611	25.896	64.873	0.995
ZB3	5.585	27.056	62.092	1.002
ZB4	5.550	28.273	59.420	1.009
ZB5	5.535	29.398	57.145	1.016

Fig.2. Optical absorption spectra of tellurium based glass system

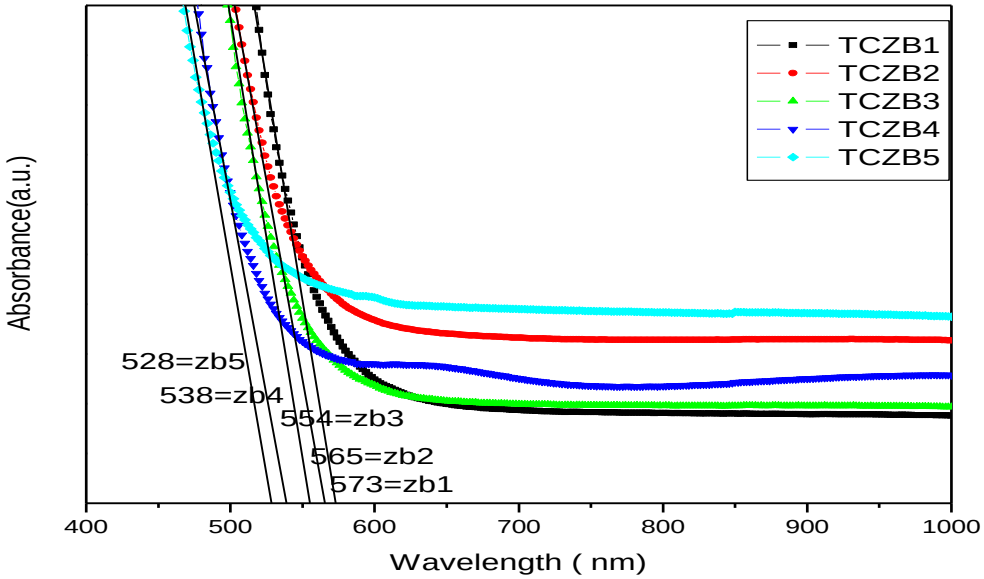

Fig. 3. Tauc's plots of tellurium basedglass system.

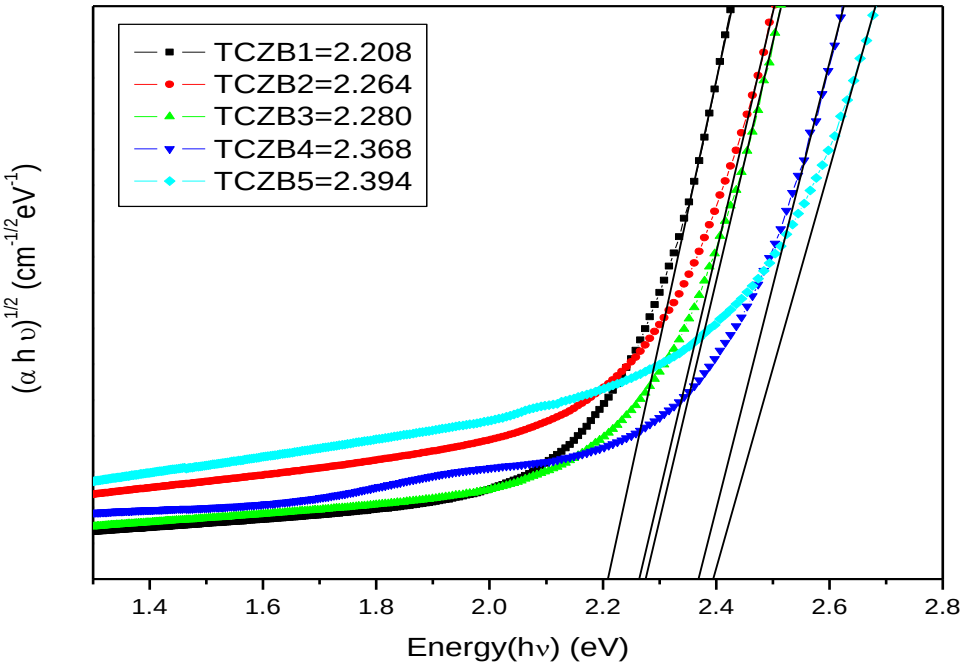

Fig.4. Urbach plot of tellurium based glass system.

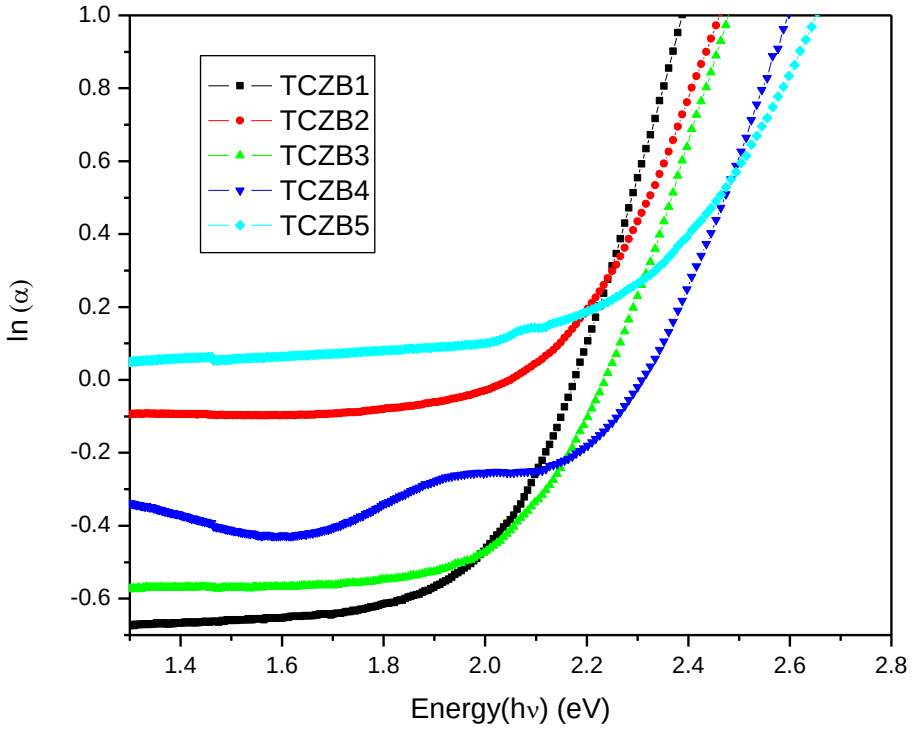

Table 3. Optical parameters of tellurium based glass system.

Sample code	CutOffWave Length (nm)	Optical EnergygapE$_{opt}$(eV)	Urbach Energy ΔE (eV)	BandTailing Parameter (B) (cm eV)	Refractive Index (n)	Molar Refractivity (R_m)	Metallization Parameter (M)
ZB1	573	2.208	0.590	4.071	2.650	16.540	0.332
ZB2	567	2.264	0.979	3.434	2.630	17.182	0.336
ZB3	555	2.279	0.684	4.093	2.624	17.921	0.337
ZB4	537	2.368	0.992	2.430	2.591	18.543	0.344
ZB5	527	2.394	0.868	2.698	2.582	19.225	0.346

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