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Thermal and Physical properties of Yb^{3+} ions doped Zinc Lithium Sodium Alumino Tungsten Tellurite Glasses

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Abstract

Glass of the system: (35-x) TeO_2:10ZnO:10Li_2O:10Na_2O:15Al_2O_3:25 WO_3: xYb_2O_3, (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the glasses was confirmed by X-ray diffraction studies. DTA Thermogram is used to study the thermal stability of the glass systems. The physical parameters like density, dielectric constant and electrical susceptibility have been evaluated. refractive index, electronic polarizability and optical basicity varies with increasing mole% of Yb_2O_3 respectively. The metallization criterion has been calculated on the basis of refractive index and energy gap. The large value of metallization criterion indicates that the glass materials are insulators.

Keywords: ZLSATT glass; Thermal stability, Optical basicity; Metallization criterion.

Introduction:

Rare earth ions doped in different glass hosts to achieve favourable potential applications in a variety of optical devices such as lasers and fiber amplifiers [1–4]. Ceramic materials is the combination of easy fabrication and outstanding mechanical properties. Tellurite glasses have many advantages in comparison with other glasses due to their high transparency, low-melting temperature**,** good mechanical stability and flowest cut-off phonon energy so these glasses are good hosts for rare earth ions [5-8]**.** Tungsten–tellurite glass has the advantages of higher phonon energy and higher softening. addition of ZnO improve chemical durability and thermal stability of the glasses[9] .The optical properties of rare-earth ions doped glass systems like silicates, phosphates, borates, germinate and tellurites have earlier been reported in the literature [10-14]. Due to low melting point (T_m) and glass transition temperature (T_g) [15, 16], preparation of tellurite glasses are comparatively easier than other glass families.

Recently, tellurite glasses have attained great attention in synthesis, structure and physical properties due to their high refractive index, high density and high dielectric constant. The aim of the present study is to prepare the Yb^{3+}doped zinc lithium sodium alumino tungsten tellurite glass with different Yb_2O_3concentrations and to study the effect of Yb_2O_3 content on the various physical parameters such as density, refractive index, molar refractivity and thermal properties.

Experimental:

Preparation of glasses:

The following Yb^{3+} doped Zinc Lithium Sodium Alumino Tungsten Tellurite Glasses glass samples (35-x) TeO_2:10ZnO:10Li_2O:10Na_2O:15Al_2O_3:25 WO_3: xYb_2O_3. (where x=1, 1.5.2) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of TeO_2, ZnO, Li_2O, Na_2O, Al_2O, $WO_3$and Yb_2O_3. All weighed chemicals were powdered by using an Agate pestle mortar and mixed thoroughly before each batch (10g) was melted in alumina crucibles in silicon carbide based an electrical furnace.

Silicon Carbide Muffle furnace was heated to working temperature of 1020^0C, for preparation of Zinc Lithium Sodium Alumino Tungsten Tellurite glasses, for two hours to ensure the melt to be free from gases. The melt was stirred several times to ensure homogeneity. For quenching, the melt was quickly poured on the steel plate & was immediately inserted in the muffle furnace for annealing. The steel plate was preheated to100^0C.While pouring; the temperature of crucible was also maintained to prevent crystallization. And annealed at temperature of 350^0C for 2h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. The glass samples so prepared were of good optical quality and were transparent. The chemical compositions of the glasses with the name of samples are summarized in **Table 1.**

Table 1: Chemical composition of the glasses

Sample	Glass composition (mol %)
ZLSATT (UD)	35 TeO_2:10ZnO:10Li_2O:10Na_2O:15Al_2O_3:25 WO_3.
ZLSATT (YB 1)	34 TeO_2:10ZnO:10Li_2O:10Na_2O:15Al_2O_3:25 WO_3: 1Yb_2O_3.
ZLSATT (YB 1.5)	33.5 TeO_2:10ZnO:10Li_2O:10Na_2O:15Al_2O_3:25 WO_3: 1.5Yb_2O_3.
ZLSATT (YB 2)	33 TeO_2:10ZnO:10Li_2O:10Na_2O:15Al_2O_3:25 WO_3: 2Yb_2O_3.

ZLSATT (UD) -Represents undoped Zinc Lithium Sodium Alumino Tungsten Tellurite glass specimens.
ZLSATT (YB) -Represents Yb^{3+} doped Zinc Lithium Sodium Alumino Tungsten Tellurite glass specimens.

Results and Discussion:

XRD Measurement:

Figure 1 presents the XRD pattern of the samples shows no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

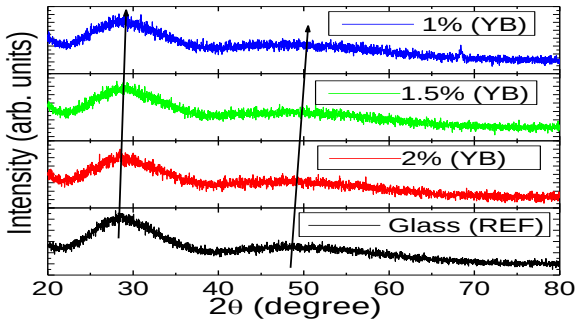

Fig.1: X-ray diffraction pattern of TeO_2: ZnO: Li_2O: Na_2O:Al_2O_3: WO_3: Yb_2O_3 glasses.

Thermal Studies:

Fig. 2 depicts the DTA thermogram of powdered ZLSATT sample show an endothermic peak corresponding to glass transition event followed by an exothermic peak related to crystallization event. The glass transition temperature (T_g), onset crystallization temperature (T_x), crystallization temperature (T_c) were estimated to be 518 ^{0}C, 586^{0}C and 612^{0}C respectively. From the measured value of T_g, T_x and T_c , the glass stability factor ($\Delta T = T_x - T_g$) has been determined to be 68^{0}C indicating the good stability of the glass . Therefore, the present glass composition could also be used to draw fiber and used to determine the required heat temperatures applied to induce crystallization.

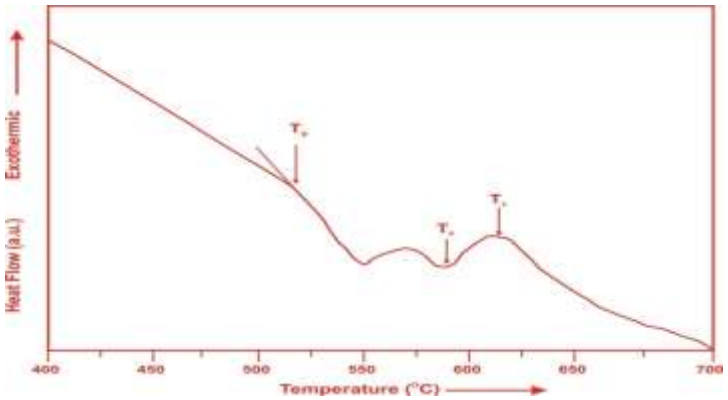

Fig.2: DTA thermogram of powdered ZLSATT sample.

Obtained results indicate that by increasing the amount of mol% Yb_2O_3, the T_g of the samples also increases, the small increase of T_g in these glasses shows that the structure is strongly and progressively modified. The thermal stabilities ΔT of the ZLSATT reference glass and Yb^{+3} doped ZLSATT glass has been evaluated from their T_g, T_c and T_c values, the results are listed out in Table 2. Hruby's parameter also calculated by using eq. (1), the greater values of the Hruby's parameter indicate higher glass forming tendency, the values of H in our glasses increased with the addition of the Yb_2O_3. Eqs. (2) and (3) present the GS parameter of Weinberg[17] and Lu and Liu [18], respectively.

$$H=\frac{T_X-T_g}{T_c-T_X} \quad (1)$$

$$K_W=\frac{T_X-T_g}{T_c} \quad (2)$$

$$K_{LL}=\frac{T_X}{T_g+T_c} \quad (3)$$

Table 2: Thermal parameters determined from the DTA traces of ZLSATT (YB) glasses.

Sample Name	% Yb_2O_3	T_g ^{0}C	T_X ^{0}C	T_C ^{0}C	ΔT	H	K_W	K_{LL}
ZLSATT (YB1.0)	1	518	586	612	68	2.62	0.1111	0.5186
ZLSATT (YB 1.5)	1.5	520	589	614	69	2.76	0.1124	0.5194

ZLSATT (YB 02)	2	524	594	619	70	2.80	0.1131	0.5197

Physical properties:

Density measurement:

The density of all glasses was measured by using Archimedes principle with xylene as immersing liquid. The relation used is

$$\rho(gm/cm^3) = \frac{W_a}{W_a - W_b} \times \rho_b \quad (4)$$

Where W_a is the weight of glass sample in air, W_b is the weight of glass sample when immersed in xylene and ρ_b is the density of xylene(0.86gm/cm^3).

The molar volume of the glass samples can be calculated from following expression:

$$V_m = \frac{M_T}{\rho} \quad (5)$$

Where ρ is the density of the sample and M_T is the total molecular weight of the multi-component glass system given by

$$M_T = X_{TeO2} Z_{TeO2} + X_{ZnO} Z_{ZnO} + X_{Li2O} Z_{Li2O} + X_{Na2O} Z_{Na2O} + X_{Al2O3} Z_{Al2O3} + X_{WO3} Z_{WO3} + X_{Yb2O3} Z_{Yb2O3} \quad (6)$$

Where X_{TeO2}, X_{ZnO}, X_{Li2O}, X_{Na2O}, X_{Al2O3}, , X_{WO3}, X_{Yb2O3} are the molar fraction of the constituent oxides and Z_{TeO2}, Z_{ZnO}, Z_{Li2O}, Z_{Na2O}, Z_{Al2O3}, Z_{WO3}, X_{Yb2O3}, are the molar weights of the constituent oxides.

Refractive index measurement:

The refractive index were measured by using an Abbe refractometer with sodium vapor lamp as the light source emitting the light at a wavelength λ of 589.3nm and having mono-bromonaphthalene as the contact layer between the sample and prism of the refractometer.

Reflection loss:

The reflection loss from the glass surface was computed from the refractive index using Fresnel's formula [19]

$$R_L = \left[\frac{(n-1)}{(n+1)}\right]^2 \quad (7)$$

Where n is the refractive index.

Molar refractivity:

The molar refractivity of the glass samples were calculated using the formula which is well known as Volf and Lorentz-Lorentz formula [20]

$$R_m = \left[\frac{(n^2-1)}{(n^2+2)}\right] \times V_m \quad (8)$$

Where n is the refractive index of the glass sample, V_m is the molar volume.

Energy gap:

According to Duffy the energy gap is given by [21]

$$E_g = 20\left(1 - \frac{R_m}{V_m}\right)^2 \quad (9)$$

Molar electronic polarizability:

The molar electronic polarizability of the material can be calculated from following expression [22]

$$\alpha_m = \frac{R_m}{2.52} \quad (10)$$

Dielectric constant:

The dielectric constant was calculated using refractive index of the glass [23]

$$\varepsilon = n^2 \quad (11)$$

Where n is the refractive index.

Optical dielectric constant:

The optical Dielectric Constant refractive index of the glass [24]

$$p\frac{dt}{dp} = (\varepsilon - 1) = n^2 - 1 \quad (12)$$

Where ϵ is the dielectric constant.

Electronic polarizability:

The electronic polarizability was cal calculated using the formula [25]

$$\alpha_e = \frac{3\left(n^2 - 1\right)}{4\Pi A_V\left(n^2 + 2\right)} \quad (13)$$

Where A_V is the Avogadro number.

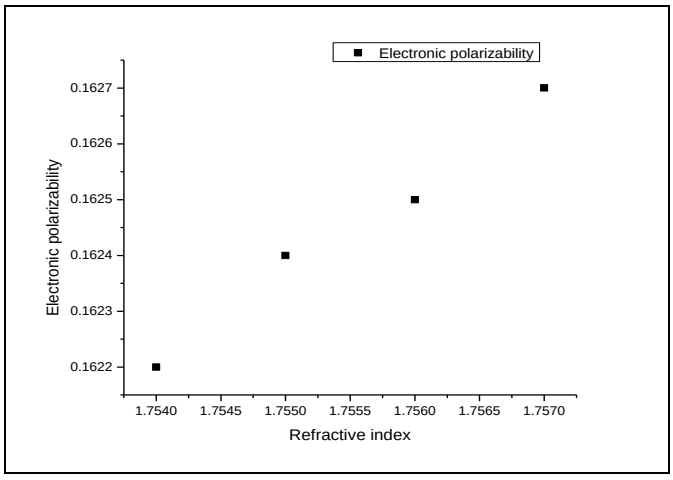

Fig.3: Varation of Electronic polarizability with Refractive Index.

Ionic concentrations:

The ionic concentrations of the glass samples are determined using the following relation [26]

$$N\ (ions/cm^3) = \frac{(Avogadro's\ number)(glass\ density)}{(Average\ molecular\ weight)} \times (mol\%\ of\ rare\ earth) \qquad (14)$$

Polaron radius:

The polaron radius was calculated using the formula [27]

$$R_p = \frac{1}{2} \times \left(\frac{\Pi}{6N}\right)^{\frac{1}{3}} \qquad (15)$$

Where N is the ionic concentrations.

Inter-ionic distance:

Inter-ionic distance of the glass samples is given as [27]

$$R_i = \left(\frac{1}{N}\right)^{\frac{1}{3}} \qquad (16)$$

Where R_i is the ionic concentrations.

Field strength:

The field strength was calculated using the formula [28]

$$F\ (cm^3) = \left(\frac{Z}{R_p^{\ 2}}\right) \qquad (17)$$

Where Z is the thickness of the samples.

Oxygen packing density:

The oxygen packing density of the glass samples were calculated using the following relation [29]

$$O.P.D. = n\left(\frac{\rho}{M}\right) \times 1000 \qquad (18)$$

Where ρ the density of desired glass samples, M is the molecular weight of the sample and n is the number of oxygen atoms in the composition.

Insulating nature:

According to the Herzfeld theory of metallization, If $R_m/V_m > 1$ and $R_m/V_m < 1$ predicting metallic or insulating [30]. Subtracting by 1 gives the metallization (M)

$$M = \left(1 - \frac{R_m}{V_m}\right) \qquad (19)$$

Table 3: The physical and optical properties of TeO_2: ZnO: Li_2O: Na_2O:Al_2O_3:WO_3:Yb_2O_3: glasses.

Physical properties	**ZLSATT (UD)**	**ZLSATT (YB01)**	**ZLSATT (YB1.5)**	**ZLSATT (YB02)**
Refractive Index (n)	1.754	1.755	1.756	1.757
Density (ρ) (gm/cm^3)	4.152	4.265	4.354	4.462
Thickness(Z)	0.246	0.246	0.246	0.246
Average molecular weight M(gm)	141.34	143.68	144.86	146.03
Rare earth ions concentratio(N)	--	1.788	2.716	2.355
Dielectric Constant (ϵ)	3.077	3.080	3.084	3.087
Optical Dielectric Constant (pdt/dp)	2.077	2.080	2.084	2.087
Molar Volume V_m (gm/cm^3)	34.017	33.69	33.270	32.727
Reflection losses(R_L)	7.495	7.510	7.525	7.539
Molar refractivity (R_m)	13.914	13.794	13.636	13.427
Energy gap(E_g)	6.985	6.975	6.965	6.956
Polaron radius R_p(A^0)	--	3.320	2.889	2.610
Interionic distance R_i (A^0)	--	0.8239	0.7168	0.6477
Electronic polarizability (α_e)	0.1622	0.1624	0.1625	0.1627
Field strength(F)	--	0.2231	0.2948	0.3611
Molar polarizability(α_m)	5.521	5.474	5.4111	5.328
Oxygen packing density(OPD)	60.264	61.147	62.068	63.250
Metallization criterion (M)	0.5910	0.5905	0.5901	0.5897
Optical basicity	0.9017	0.9021	0.9024	0.9026
Oxideion polarizability	2.365	2.329	2.293	2.247
Electrical susceptibility (χ)	0.1653	0.1655	0.1658	0.1661

Optical basicity:

The optical basicity addresses the ability of oxide glass in contributing the negative charges in the glass matrix. In other words it defines the electron donating power of the oxygen in the oxides glass. The theoretical optical basicity can be calculated by the equation proposed by Duffy and Ingram [31]

$$\Lambda_{th} = X_1 \Lambda_1 + X_2 \Lambda_2 + X_3 \Lambda_3 + X_4 \Lambda_4 + X_5 \Lambda_5 + X_6 \Lambda_6 + X_7 \Lambda_7 \quad (20)$$

Where X_1, X_2, X_3 ,X_4, X_5, X_6, X_7 are equivalent fraction based on the amount of oxygen each oxide contributes to the overall glass stoichometry and Λ_1, Λ_2,Λ_3,Λ_4, Λ_5,Λ_6,Λ_7. are basicities assigned to the

individual oxides. The values of optical basicity of each oxide are: Λ (TeO_2) =0.93, Λ (ZnO) = 0.95, Λ (Li_2O) =1.00, Λ (Na_2O) =1.11, Λ (Al_2O_3) = 0.40, Λ (WO_3) = 1.05, Λ (Yb_2O_3) =0.95.

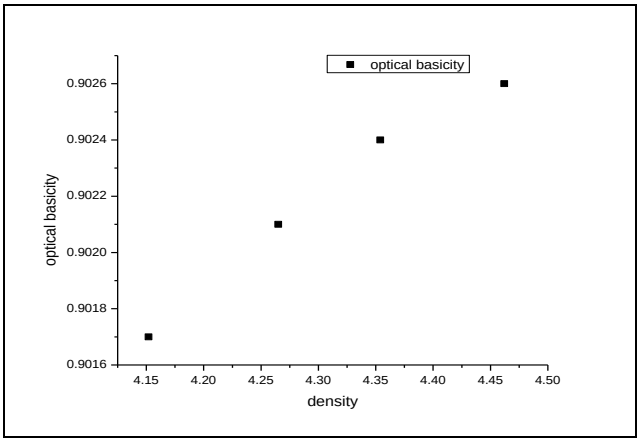

Fig.2: Variation of optical basicity with density.

Electronic polarizability of oxide ions:

The Electronic polarizability of oxide ions has been calculated using the equation proposed by Dimitrov and Sakka [32]

$$\alpha_O^{2-(n)} = \left[\frac{R_m}{2.52} - \sum \alpha_i\right]\left(N_o^{2-}\right)^{-1} \qquad (21)$$

Where $\sum \alpha_i$ In the above equation is molar cation polarizability and N_O^{2-} is the number of oxide ions in the chemical formula. The molar cation Polarizability (α) values are $\alpha_{Te=}$1.595Å^3, $\alpha_{Zn=}$0.283Å^3, $\alpha_{Li=}$0.024 Å^3, $\alpha_{Na=}$0.179 Å^3, α_{Al} =0.052 Å^3 , $\alpha_{Wo=}$ 0.147 Å^{3}and α_{Yb} =0.86 Å^3.

Electrical susceptibility (χ):

The Electrical susceptibility was calculated using the formula [33]

$$\chi = \left(\frac{n^2-1}{4\pi}\right) \qquad (22)$$

Conclusion:

The Yb^{3+} doped Zinc Lithium Sodium Alumino Tungsten Tellurite gasses were prepared at various doping concentration of Yb_2O_3 and characterized for their physical properties. The electronic polarizability and optical basicity increases with an increase in concentration of Yb_2O_3 Glass stability was calculated by taking the difference of T_c and T_g. Higher the value, higher is the glass stability and is a suitable candidate for fibre drawing. The greater values of the Hruby's parameter indicate higher glass forming tendency .The optical basicity found to increase in glasses with Yb_2O_3 content. The decrease value of metallization criterion indicates that the glass material is metalizing.

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