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Thermal and Physical properties of Tm^{3+} ions doped Lead Lithium Borophosphate Glasses

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Abstract: *Glass of the system: (50-x) P_2O_5:10Li_2O: 15PbO:25 B_2O_3: xTm_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. The physical parameters like density, dielectric constant and electrical susceptibility have been evaluated. Dielectric constant, refractive index, electronic polarizability varies with increasing mole% of Tm_2O_3 respectively. The metallization criterion has been calculated on the basis of refractive index and energy gap. It was found to be decreased with increasing refractive index and decreasing energy gap. The large value of metallization criterion indicates that the glass materials are insulators.*

Keywords*: Thulium based glass; Electrical Susceptibility; Metallization criterion.*

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I. Introduction

Among different glass hosts, phosphate glasses have unique properties. They have high thermal stability, high transparency, a low melting point, a high gain density and low dispersion rates. Phosphate glasses are one of the most important materials for the optical applications among the all other oxide glasses. Phosphate glasses are considered as prominent materials because of their verity of applications in several areas of interest. Wide range of special properties of phosphate glasses such as lower melting temperature, high thermal expansion coefficient and biocompatibility guided to use these materials for photonics applications, solid-state lasers and optical fibers [1-8]. Phosphate glass exhibit very important physical, mechanical and chemical properties such as low melting temperature, high thermal expansion coefficient, low glass transition temperature (T_g), low softening temperature, good thermal stability and crystallization (T_c) temperatures, Phosphate glasses have excellent transparency and thermal stability. They act as good hosts for large concentrations of doping RE ions with good homogeneity [9-12].

Recently, borophosphate 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 Tm^{3+}doped lead lithium borophosphate glass with different Tm_2O_3concentrations and to study the effect of Tm_2O_3content on the various physical parameters such as density, refractive index, molar refractivity and thermal properties.

II. Experimental Techniques

Preparation of glasses

The following Tm^{3+} doped lead lithium borophosphate Glasses glass samples (50-x) P_2O_5:10Li_2O: 15PbO:25 B_2O_3: xTm_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 P_2O_5, Li_2O, PbO, $B_2O_3$and Tm_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 1080^0C, for preparation of lead lithium borophosphate 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 360^0C 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 %)
LLBP (UD)	$50P_2O_5$:$10Li_2O$: 15PbO:25 B_2O_3
LLBP (TM 1)	$49P_2O_5$:$10Li_2O$: 15PbO:25 B_2O_3:$1Tm_2O_3$
LLBP (TM 1.5)	$48.5P_2O_5$:$10Li_2O$: 15PbO:25 B_2O_3:$1.5Tm_2O_3$
LLBP (TM 2)	$48P_2O_5$:$10Li_2O$: 15PbO:25 B_2O_3:$2Tm_2O_3$

LLBP (UD) -Represents undoped lead lithium borophosphate glass specimens
LLBP (TM) -Represents Tm^{3+} doped lead lithium borophosphate glass specimens

III. Result and Discussion

3.1. XRD Measurement

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

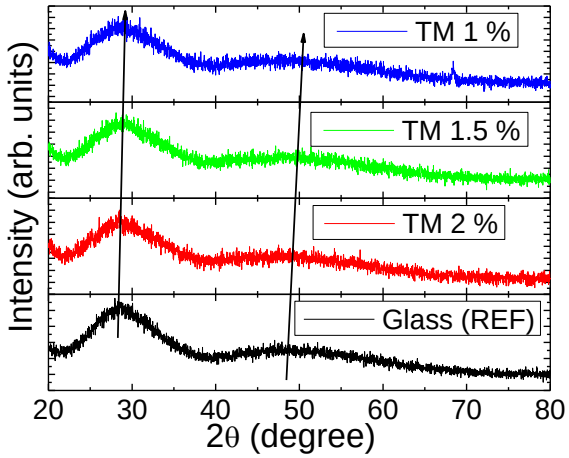

Fig. 1.X-ray diffraction pattern of P_2O_5: Li_2O: PbO: B_2O_3: Tm_2O_3 glasses.

3.2. Thermal Studies

Fig. 2 depicts the DTA thermogram of powdered LLBP 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 516 ^{0}C, 585^{0}C and 601^{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 69^{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.

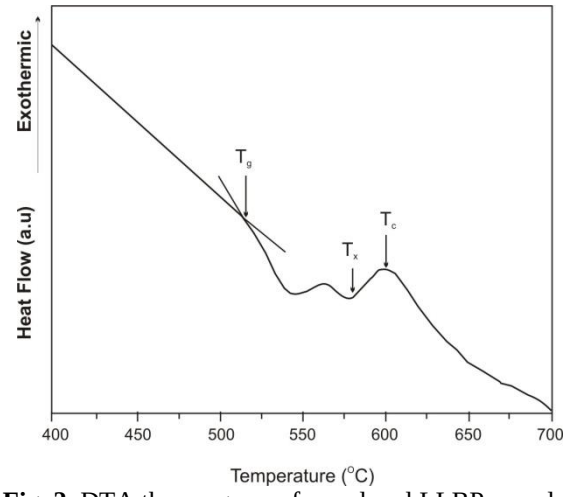

Fig. 2. DTA thermogram of powdered LLBP sample.

Obtained results indicate that by increasing the amount of mol% Tm_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 LLBP reference glass and Tm^{+3} doped LLBP glass has been evaluated from their T_g, T_c and T_m 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 Tm_2O_3.

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

Table 2: Thermal parameters determined from the DTA traces of LLBP (TM) glasses.

Sample Name	% Tm_2O_3	T_g ^0C	T_X ^0C	T_C ^0C	ΔT	H
LLBP (TM 1.0)	1	516	585	601	69	4.31
LLBP (TM 1.5)	1.5	517	587	602	70	4.67
LLBP (TM 02)	2	519	588	603	69	4.60

3.3. Physical properties

Density measurement

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

$$\rho(gm/cm^3)=\frac{W_a}{W_a-W_b}\times\rho_b \quad (2)$$

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:

$$V_m=\frac{M_T}{\rho} \quad (3)$$

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

$$M_T=X_{P2O5}Z_{P2O5}+X_{Li2O}Z_{Li2O}+X_{PbO}Z_{PbO}+X_{B2O3}Z_{B2O3}+X_{Tm2O3}Z_{Tm2O3} \quad (4)$$

Where X_{P2O5}, X_{Li2O}, X_{PbO}, X_{B2O3}, X_{Tm2O3} are the molar fraction of the constituent oxides and Z_{P2O5}, Z_{Li2O}, Z_{PbO} Z_{B2O3}, Z_{Tm2O3}, 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 [13]

$$R_L=\left[\frac{(n-1)}{(n+1)}\right]^2 \quad (5)$$

Where n is the refractive index.

Molar refraction

The molar refractivity of the glass samples were calculated using the formula which is well known as Volf and Lorentz-Lorentz formula [14]

$$R_m=\left[\frac{(n^2-1)}{(n^2+2)}\right]\times V_m \quad (6)$$

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 [15]

$$E_g = 20\left(1 - \frac{R_m}{V_m}\right)^2 \quad (7)$$

Molar electronic polarizability

The molar electronic polarizability of the material can be calculated from following expression [16]

$$\alpha_{m=} \frac{R_m}{2.52} \quad (8)$$

Dielectric constant

The dielectric constant was calculated using refractive index of the glass [17]

$$\varepsilon = n^2 \quad (9)$$

Where n is the refractive index.

Optical dielectric constant

The optical Dielectric Constant refractive index of the glass [18]

$$p\frac{dt}{dp} = (\varepsilon - 1) = n^2 - 1 \quad (10)$$

Where ϵ is the dielectric constant.

Electronic polarizability

The electronic polarizability was cal calculated using the formula [19]

$$\alpha_e = \frac{3\left(n^2 - 1\right)}{4\Pi A_V\left(n^2 + 2\right)} \quad (11)$$

Where A_V is the Avogadro number.

Ionic concentrations

The ionic concentrations of the glass samples are determined using the following relation [20]

$$N\ (\text{ions}/\text{cm}^3) = \frac{(\text{Avogadro's number})(\text{glass density})}{(\text{Average molecular weight})} \times (\text{mol\% of rare earth}) \quad (12)$$

Polaron radius

The polaron radius was calculated using the formula [21]

$$R_p = \frac{1}{2} \times \left(\frac{\Pi}{6N}\right)^{\frac{1}{3}} \quad (13)$$

Where N is the ionic concentrations.

Inter-ionic distance

Inter-ionic distance of the glass samples is given as [21]

$$R_i = \left(\frac{1}{N}\right)^{\frac{1}{3}} \quad (14)$$

Where R_i is the ionic concentrations.

Field strength

The field strength was calculated using the formula [22]

$$F\ (\text{cm}^3) = \left(\frac{Z}{R_p^{\ 2}}\right) \quad (15)$$

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 [23]

$$\text{O.P.D.} = n\left(\frac{\rho}{M}\right)\times 1000 \qquad (16)$$

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.

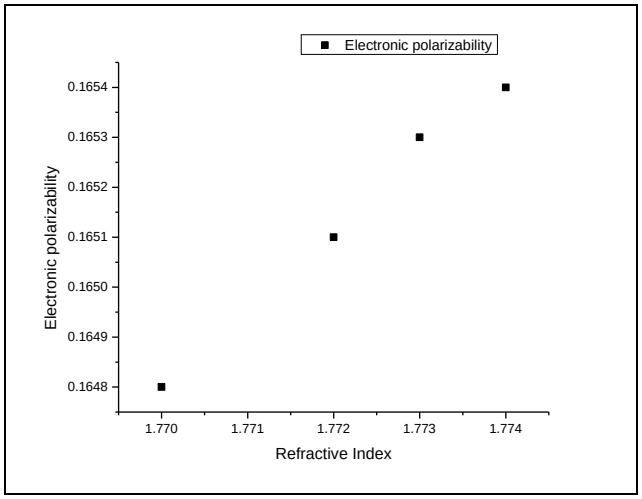

Fig.3. Varation of Electronic polarizability with Refractive Index.

Table 3: The physical and optical properties of P_2O_5: Li_2O: PbO: B_2O_3: Tm_2O_3 glasses

Physical properties	LLBP (UD)	LLBP (TM 01)	LLBP (TM1.5)	LLBP (TM 02)
Refractive Index (n)	1.770	1.772	1.773	1.774
Density (ρ) $\left(gm/cm^3\right)$	2.250	2.325	2.446	2.536
Thickness(Z)	0.225	0.225	0.225	0.225
AveragemolecularweightM $\left(g\right)$	124.8480	127.285	128.5068	129.7263
Rare earth ions concentratio(N)	--	1.100	1.720	2.355
Dielectric Constant (ϵ)	3.133	3.140	3.144	3.147
OpticalDielectricConstant $p\frac{dt}{dp}$	2.133	2.140	2.144	2.147
MolarVolume ($V_{m)}$ $\left(gm/cm^3\right)$	55.488	54.746	52.538	51.154
Reflection losses(R_L)	7.727	7.756	7.771	7.785
Molar refractivity ($R_{m)}$	23.057	22.793	21.895	21.339
Polaron radius R_p $\left(\mathrm{A}^0\right)$	--	3.904	3.364	3.030
Interionic distance(R_i) $\left(\mathrm{A}^0\right)$	--	0.9688	0.8348	0.7518
Electronic polarizability (α_e)	0.1648	0.1651	0.1653	0.1654
Field strength (F)	--	0.1476	0.1988	0.2451
Molarpolarizability(α_m) $\times 10^{-24} cm^3$	9.149	9.045	8.688	8.468
Oxygen packing density(OPD)	63.077	63.566	66.047	67.639
Metallization criterion (M)	0.5845	0.5837	0.5833	0.5828
Energy gap(E_g)	6.832	6.813	6.804	6.794
Electrical susceptibility (χ)	0.1698	0.1704	0.1707	0.1709

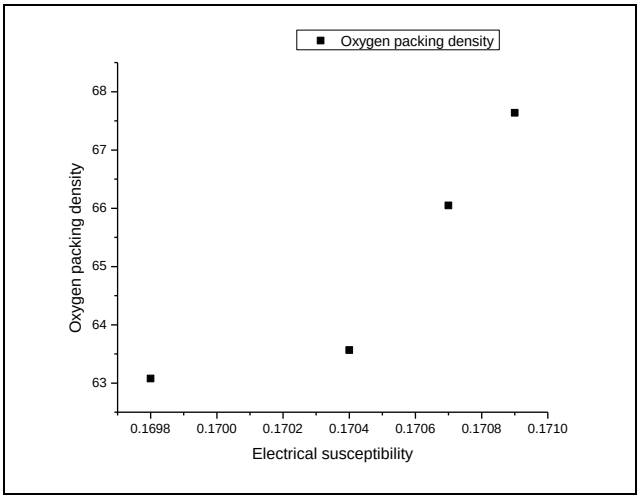

Fig.4. Variation of oxygen packing density with electrical susceptibility.

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 [24]. Subtracting by 1 gives the metallization (M)

$$M=\left(1-\frac{R_m}{V_m}\right) \quad (17)$$

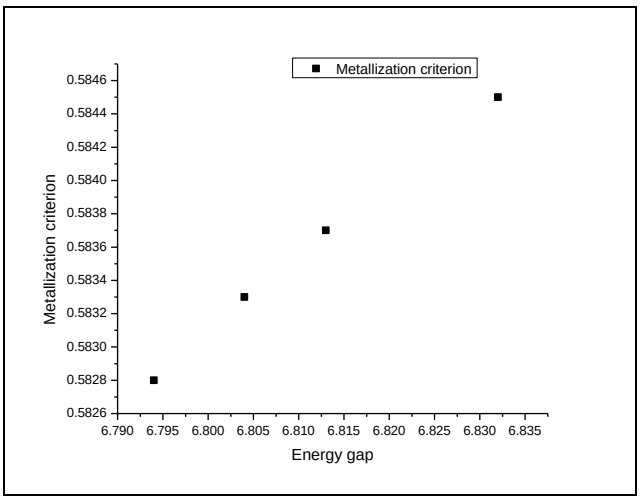

Fig.5. Variation of metallization criterion with energy gap.

Electrical susceptibility (χ)

The Electrical susceptibility was calculated using the formula [25]

$$\chi=\left(\frac{n^2-1}{4\pi}\right) \quad (18)$$

IV. Conclusions

The Tm^{3+} doped lead lithium borophosphate gasses were prepared at various doping concentration of Tm_2O_3 and characterized for their physical properties. The density and refractive index increases with an increase in concentration of Tm_2O_3. Glass stability was calculated by taking the difference of T_c and T_g. Higher the value, higher is the glass stability. The greater values of the Hruby's parameter indicate higher glass forming tendency .The energy band gap found to decrease in glasses with Tm_2O_3 content. The decrease value of metallization criterion indicates that the glass material is metalizing.

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