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Thermal and Physical Properties of La3+ions doped Yttrium Zinc Lithium Soda lime Borophosphate Glasses

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Abstract

Glass of the system:
(35-x) P_2O_5:10Y_2O_3:10ZnO:10Li_2O:10CaO:10Na_2O:15 B_2O_3:xLa_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 andelectrical susceptibilityhave been evaluated. Dielectric constant,refractive index, electronic polarizability varies with increasing mole% of La_2O_3respectively.Themetallization 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: YZLSLBP Glasses, Electrical Susceptibility, Metallization criterion.

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Introduction

Transparent glass–ceramic as host materials for active optical ions have attracted great interest recently due to their potential application in optical devices such as frequency-conversion materials,lasers,and optical fiber amplifiers [1-5].Phosphate glasses are one of the most important materials for the optical applications among the all other oxide glasses.Phosphate glasses are known to be low melting,optical data transmission, detection,laser technologies,high homogeneity, good corrosion resistance,excellent chemical durability, low glass transition temperature (Tg), better thermal stability, high thermal expansion coefficient, low phonon energy, wide optical transmission regionand high refractive index materials, therefore considered to be potential nonlinear materials [6-8].Recent studies indicate that heavy metal oxide (HMO) glasses have been found to be more affirmative convenient glassymaterials especially for photonic applications with acceptable lowphonon energies [9,10]. Phosphateglass 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 stabilityand crystallization (T_c) temperatures. The thermal stability factor is higher than 60^{0}C.There for phosphate glasses exhibit good thermal stability and is a suitable candidate for fibredrawing [11-13].

Recently, borophosphateglasses 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 La^{3+}doped yttrium zinc lithium soda lime borophosphateglass with differentLa_2O_3concentrations and to study the effect of La_2O_3content on the various physical parameters such as density, refractive index, molar refractivity andthermal properties.

Experimental Techniques

Preparation of glasses

The following La^{3+}dopedYttrium Zinc Lithium Soda lime Boro phosphate glass samples (35-x) P_2O_5:10Y_2O_3:10ZnO: 10Li_2O:10CaO: 10Na_2O:15 B_2O_3: xLa_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,Y_2O_3,ZnO, Li_2O,CaO,Na_2O,$B_2O_3$and La_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 yttrium zinc lithiumsoda lime borophosphateglasses, 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 %)
YZLSLBP (UD)	35 P_2O_5:10Y_2O_3:10ZnO:10Li_2O:10CaO: 10Na_2O:15 B_2O_3.
YZLSLBP (LA1)	34 P_2O_5:10Y_2O_3:10ZnO:10Li_2O:10CaO: 10Na_2O:15 B_2O_3:1La_2O_3.
YZLSLBP (LA1.5)	33.5 P_2O_5:10Y_2O_3:10ZnO:10Li_2O:10CaO: 10Na_2O:15B_2O_3:1.5La_2O_3.
YZLSLBP (LA2)	33 P_2O_5:10Y_2O_3:10ZnO:10Li_2O:10CaO: 10Na_2O:15 B_2O_3:2La_2O_3.

YZLSLBP (UD) - Represents undopedYttrium Zinc Lithium Soda lime Borophosphate
Glass specimens.
YZLSLBP (LA) - Represents La^{3+}dopedYttrium Zinc Lithium Soda lime Borophosphate glass specimens.

Result and Discussion

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.

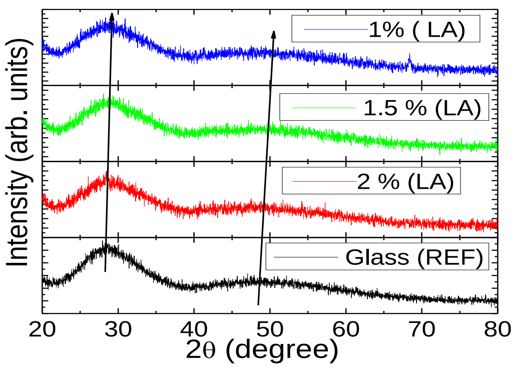

Fig. 1.X-ray diffraction pattern of P_2O_5:Y_2O_3:ZnO:Li_2O:CaO:Na_2O: B_2O_3:La_2O_3glasses.

Thermal Studies

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

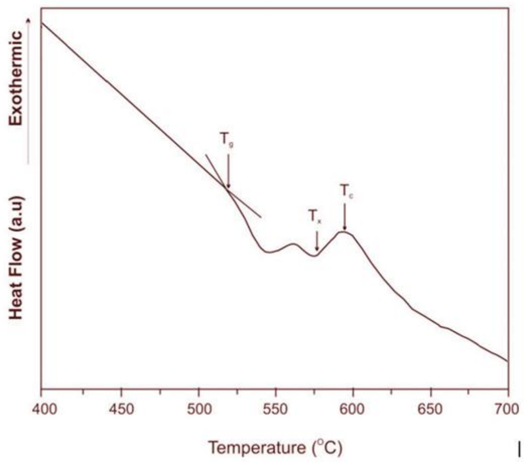

Fig.2. DTA thermogram of powdered YZLSLBP sample.

Obtained results indicate that by increasing the amount of mol% La_2O_3, the $T_g$of thesamples also increases, the small increase of $T_g$in these glasses shows that the structure is strongly and progressively modified.The thermal stabilities ΔTof the YZLSLBP reference glass and La^{+3}doped YZLSLBPglass has been evaluated from their T_g, $T_c$and $T_c$values, the resultsare 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 Hin our glasses increased with the addition of the La_2O_3.Eqs. (2) and(3) present the GS parameter ofWeinberg[14]and Lu and Liu [15], respectively.

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

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

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

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Table 2 Thermal parameters determined from the DTA traces of YZLSLBP(LA) glasses.

Sample Name	% La_2O_3	T_g ^0C	T_X ^0C	T_C ^0C	ΔT	H	K_W	K_{LL}
YZLSLBP (LA1.0)	1	520	588	605	68	4.00	0.1124	0.5227
YZLSLBP (LA 1.5)	1.5	522	591	607	69	4.31	0.1137	0.5235
YZLSLBP (LA02)	2	525	595	610	70	4.67	0.1148	0.5242

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:

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

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

$M_T = X_{P2O5} Z_{P2O5} + X_{Y2O3} Z_{Y2O3} + X_{ZnO} Z_{ZnO} + X_{Li2O} Z_{Li2O} + X_{CaO} Z_{CaO} + X_{Na2O} Z_{Na2O} + X_{B2O3} Z_{B2O3} + X_{La2O3} Z_{La2O3}$

Where X_{P2O5},X_{Y2O3}, X_{ZnO},X_{Li2O}, X_{CaO}, X_{Na2O}, X_{B2O3}, X_{La2O3},are the molar fraction of the constituent oxides and Z_{P2O5},Z_{Y2O3}, Z_{ZnO}, Z_{Li2O}, Z_{CaO}, Z_{Na2O}, Z_{B2O3}, Z_{La2O3}, 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 [16]

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

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 [17]

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

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 [18]

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

Molar electronic polarizability

The molar electronic polarizability of the material can be calculated from following expression[19]

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

Dielectric constant

The dielectric constant was calculated using refractive index of the glass[20]

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

Where n is the refractive index.

Optical dielectric constant

Theoptical Dielectric Constantrefractive index of the glass[21]

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

Whereє is the dielectric constant.

Electronic polarizability

The electronic polarizability was cal (6) calculated using the formula [22]

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

Where $A_V$is the Avogadro number.

Ionic concentrations

The ionic concentrations of the glass samples are determined using the following relation [23]

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

Polaron radius

The polaron radius was calculated using the formula [24]

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

Where N is the ionic concentrations.

Inter-ionic distance

Inter-ionic distance of the glass samples is given as [24]

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

Where R_i is the ionic concentrations.

Field strength

The field strength was calculated using the formula [25]

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

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 [26]

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

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.

Table 3: The physical and optical properties of P_2O_5:Y_2O_3:ZnO:Li_2O:CaO:Na_2O:B_2O_3:La_2O_3glasses.

Physical properties	YZLSLBP (UD)	YZLSLBP(LA 01)	YZLSLBP (LA1.5)	YZLSLBP (LA 02)
Refractive Index (n)	1.650	1.652	1.653	1.654
Density (ρ) (gm/cm^3)	4.345	4.454	4.565	4.648
Thickness(Z)	0.245	0.245	0.245	0.245
Average molecular weight M(gm)	155.32	155.74	155.95	156.16
Rare earth ions concentratio(N)	--	1.722		3.585
Dielectric Constant (ϵ)	2.723	2.729	2.732	2.736
Optical Dielectric Constant (pdt/dp)	1.723	1.729	1.732	1.736
Molar Volume V_m (gm/cm^3)	35.747	34.97	34.16	33.60
Reflection losses(R_L)	6.016	6.044	6.058	6.072
Molar refractivity (R_m)	13.038	12.78	12.51	12.31
Polaron radius R_p(A^0)	--	3.362	2.914	2.633
Interionic distance R_i (A^0)	--	0.8342	0.7231	0.6533
Electronic polarizability (α_e)	0.1447	0.1450	0.1452	0.1453
Field strength(F)	--	0.2168	0.2885	0.3534
Molar polarizability (α_m)	5.174	5.073	4.963	4.886
Oxygen packing density(OPD)	81.126	82.36	84.010	85.125
Metallization criterion (M)	0.6353	0.6344	0.6339	6.335
Energy gap(E_g)	8.0714	8.048	8.037	8.026
Optical basicity	0.5414	0.5493	0.5534	0.5574
Oxideion polarizability	1.697	1.667	1.630	0.5741
Electrical susceptibility (χ)	0.1371	0.1376	0.1379	0.1381

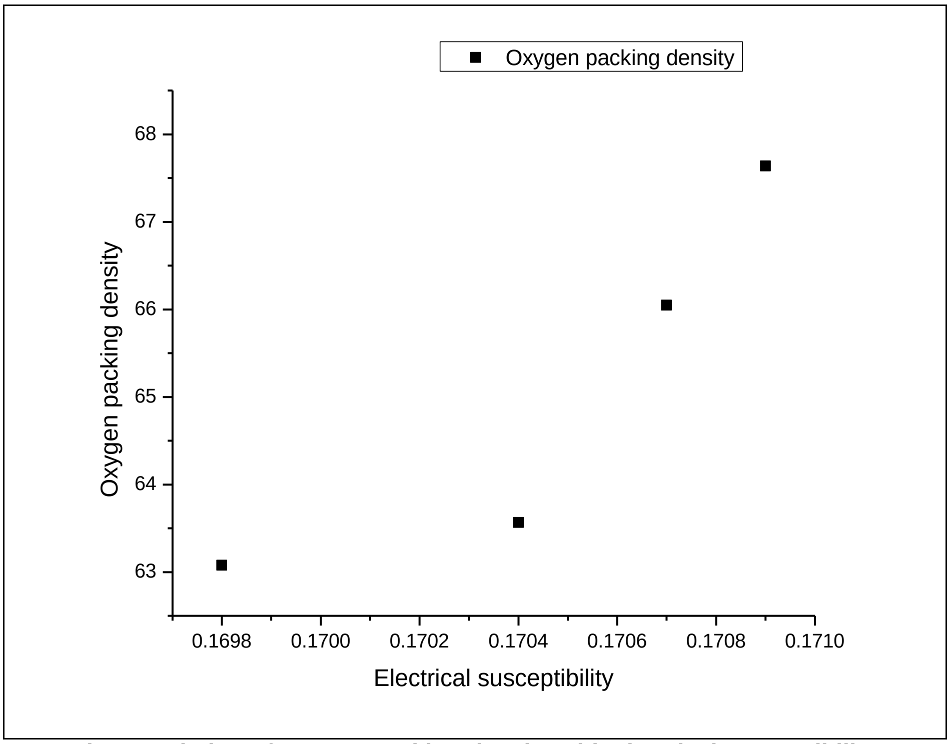

Fig.3. Variation of oxygen packing density with electrical susceptibility

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

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

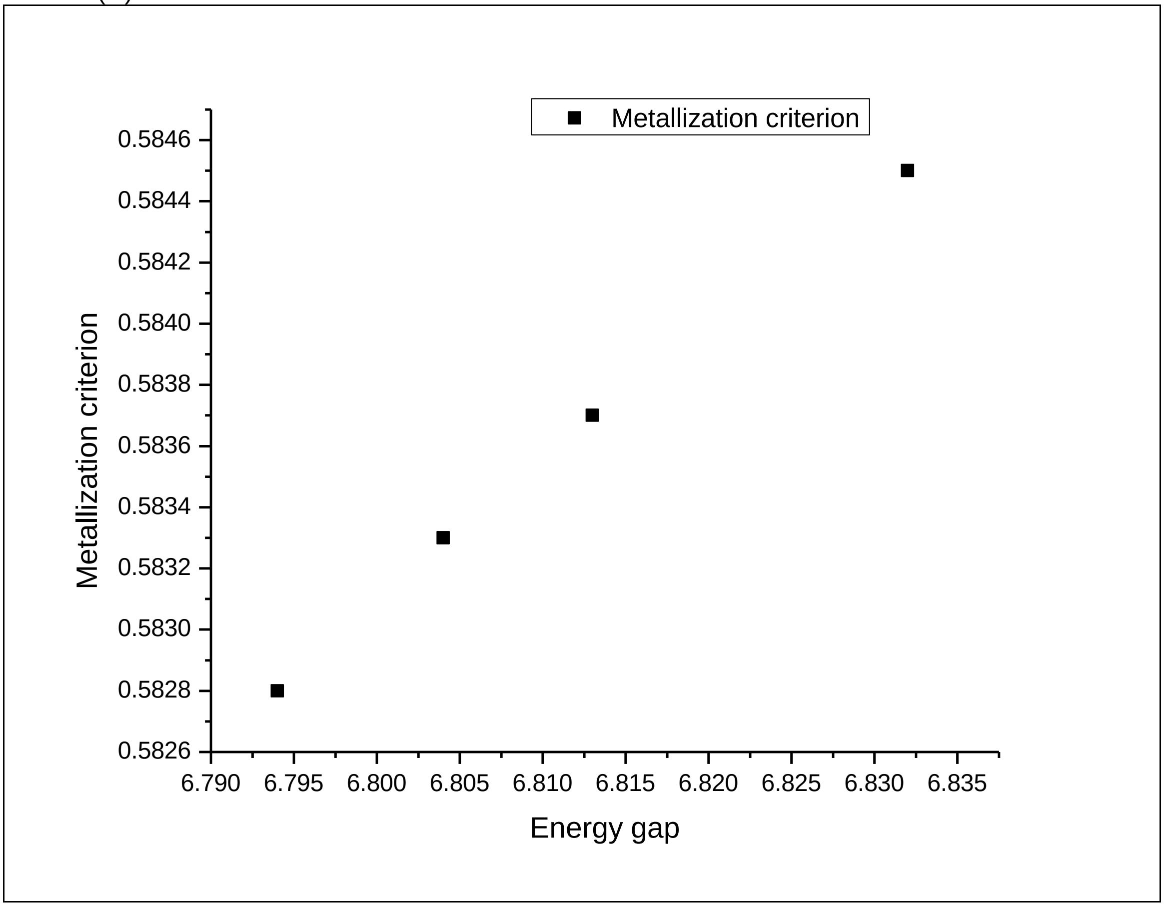

Fig.4 Variation ofmetallization criterion withenergy gap

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 [28]

$$\Lambda_{th}=X_1\Lambda_1+X_2\Lambda_2+X_3\Lambda_3+X_4\Lambda_4+X_5\Lambda_5+X_6\Lambda_6+X_7\Lambda_7+X_8\Lambda_8 \quad (20)$$

Where $X_1,X_2, X_3,X_4,X_5,X_6,X_7,X_8$ are equivalent fraction based on the amount of oxygen each oxide contributes to the overall glass stoichometry and $\Lambda_1,\Lambda_2,\Lambda_3,\Lambda_4,\Lambda_5,\Lambda_6,\Lambda_7,\Lambda_8$. are basicities assigned to the individual oxides. The values of optical basicity of each oxide are:Λ (P_2O_5) =0.93,Λ (Y_2O_3) =0.99,Λ (ZnO) = 0.95,Λ (Li_2O) =1.00,Λ (CaO) =1.00,Λ (Na_2O) =1.11, Λ (B_2O_3) = 0.40, Λ (La_2O_3) = 1.07.

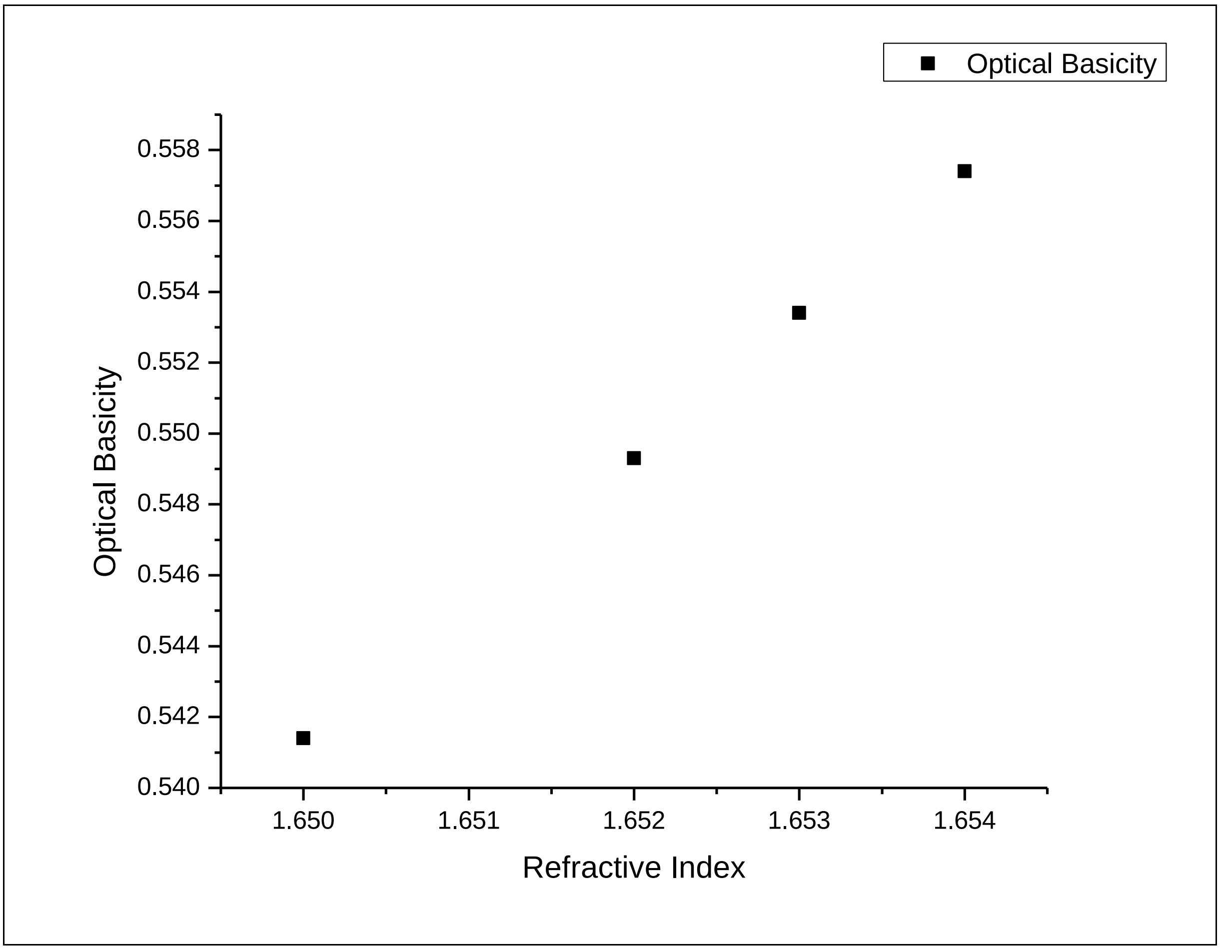

Fig.5 Varation of Optical basicity with Refractive Index

Electronic polarizability of oxide ions

The Electronic polarizability of oxide ions has been calculated using the equation proposed by Dimitrov and Sakka [29]

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

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 α_p=0.04Å^3,α_Y=0.54Å^3,α_{Zn}=0.283Å^3,α_{Li}=0.024Å^3,α_{Ca}=0.47Å^3,α_{Na}=0.179Å^3, α_B=0.003Å^3 andα_{La}=1.052Å^{3}and α_Y =0.54Å^3.

Electrical susceptibility (χ)

The Electrical susceptibility was calculated using the formula [30]

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

Conclusions

The La^{3+} doped yttrium zinc lithium soda lime borophosphate gasses were prepared at various doping concentration of $La_2O_3$and characterized for their physical properties. The refractive indexes of all samples are considerably higher than those obtained for standard optical glasses.The density and refractive index increases with an increase in concentration of La_2O_3. Increase in optical basicity results in increasing ability of oxide ions to donate electrons to surrounding cation. 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 La_2O_3 content.The decrease value of metallization criterion indicates that the glass material is metalizing.

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