Thermal and Physical properties of Lu^{3+} ions doped Zinc Lithium Tungsten Antimony Molybdate Glasses

S.L.Meena

Ceremic Laboratory, Department of physics, Jai Narain Vyas University, Jodhpur 342001(Raj.) India

Abstract

Zinc lithium tungsten antimony molybdate glasses containing Lu^{3+} in (45- x): Mo_2O_3: 10 ZnO: 10Li_2O:10 WO_3:25Sb_2O_3:xLu_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 Lu_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: *Molybdenate based glass; Electrical Susceptibility; Metallization criterion.*

I. INTRODUCTION

Molybdenate glasses containing alkaline earth oxides along with Li_2O, ZnO, WO_3 and Sb_2O_3 as glass modifiers are promising materials for their probable applications in the fields of optical fibres, laser hosts, optical filters, , photonic devices [1-5]. Physical properties of rare-earth ions in glasses vary in a wide range that depends on the chemical composition of glass former and glass modifier. Molybdenate are chemically durable, thermally stable and optically transparent at the excitation and lasing wavelength. Glass is not only easy to prepare but also a reasonably good variation in the refractive indices can be achieved. A variety of glasses are available where the refractive index would be anywhere in the range of 1.4-1.7. Molybdenate is a well-known glass former and Lead can act as both former and modifier [6-8]. Molybdenate glasses have high refractive index, good physical and chemical stability and large transmission windows in the near infrared regions [9, 10].

Recently, molybdate 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 Lu^{3+}doped zinc lithium tungsten antimony molybdate glass with different Lu_2O_3concentrations and to study the effect of Lu_2O_3content on the various physical parameters such as density, refractive index, molar refractivity.

II. EXERIMENT TECHNIQUES

Preparatin of glasses

The following Gd^{3+} doped zinc lithium tungsten antimony molybdate glass samples (45- x): Mo_2O_3:10ZnO: 10Li_2O:10WO_3:25Sb_2O_3:xLu_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 Mo_2O_3, Li_2O, ZnO, WO_3, $Sb_2O_3$and Lu_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 1070^0C, for preparation of zinc lithium tungsten antimony molybdate 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 380^0C 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 %)
ZLTAM (UD)	45 Mo_2O_3:10ZnO: 10Li_2O:10WO_3:25Sb_2O_3
ZLTAM (LU 1)	44 Mo_2O_3:10ZnO: 10Li_2O:10WO_3:25Sb_2O_3:1Lu_2O_3
ZLTAM (LU 1.5)	43.5 Mo_2O_3:10ZnO: 10Li_2O:10WO_3:25Sb_2O_3:1.5Lu_2O_3
ZLTAM (LU 2)	43 Mo_2O_3:10ZnO: 10Li_2O:10WO_3:25Sb_2O_3:2Lu_2O_3

ZLTAM (UD) -Represents undoped zinc lithium tungsten antimony molybdate glass specimens

ZLTAM (LU) -Represents Lu $^{3+}$ doped zinc lithium tungsten antimony molybdate glass specimens

III. RESULT AND DISCUSSION

A. 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 within the resolution limit of XRD instrument.

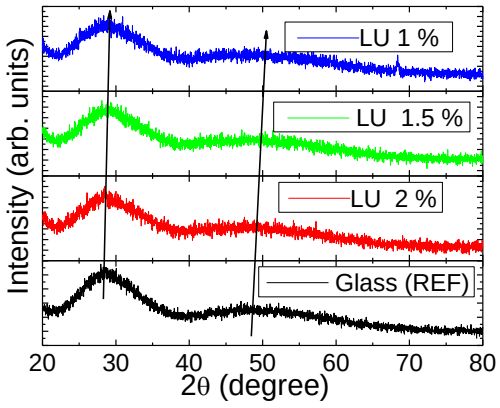

Fig.1: X-ray diffraction pattern of ZLTAM (LU) glasses.

B. Thermal Studies

Fig. 2 depicts the DTA thermogram of powdered ZLTAM 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, 580^{0}C and 600^{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 64^{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.

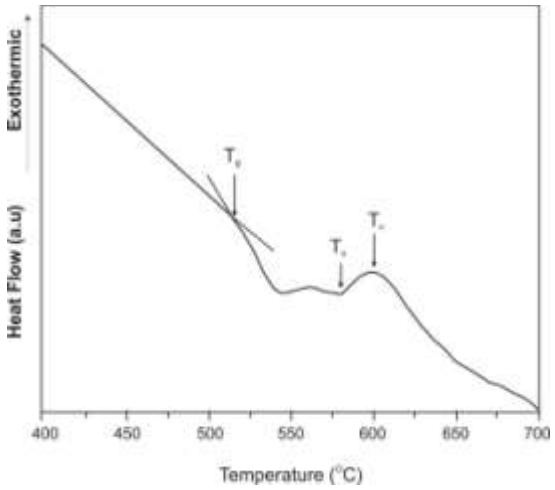

Fig.2. DTA thermogram of powdered ZLTAM sample.

C. Physical properties

Density measurement

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

$$\rho(gm/cm^3) = \frac{W_a}{W_a - W_b} \times \rho_b \qquad (1)$$

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:

$$V_m=\frac{M_T}{\rho} \quad (2)$$

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

$$M_T=X_{Mo2O3} Z_{Mo2O3} + X_{ZnO} Z_{ZnO} + X_{Li2O} Z_{Li2O} + X_{WO3} Z_{WO3} + X_{Sb2O3} Z_{Sb2O3} + X_{Lu2O3} Z_{Lu2O3} \quad (3)$$

Where X_{Mo2O3}, X_{ZnO}, X_{Li2O}, X_{WO3}, X_{Sb2O3}, X_{Lu2O3} are the molar fraction of the constituent oxides and Z_{Mo2O3}, Z_{ZnO}, Z_{Li2O}, Z_{WO3}, Z_{Sb2O3}, Z_{Lu2O3} 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 [11]

$$R_L = \left[\frac{(n-1)}{(n+1)}\right]^2 \quad (4)$$

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 [12]

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

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 [13]

$$E_g= 20\left(1-\frac{R_m}{V_m}\right)^2 \quad (6)$$

Molar electronic polarizability

The molar electronic polarizability of the material can be calculated from following expression [14]

$$\alpha_{m=} \frac{R_m}{2.52} \quad (7)$$

Dielectric constant

The dielectric constant was calculated using refractive index of the glass [15]

$$\varepsilon = n^2 \quad (8)$$

Where n is the refractive index.

Optical dielectric constant

The optical Dielectric Constant refractive index of the glass [16]

$$p\frac{dt}{dp} = (\varepsilon -1) = n^2-1 \quad (9)$$

Where ϵ is the dielectric constant.

Electronic polarizability

The electronic polarizability was cal calculated using the formula [17]

$$\alpha_e = \frac{3(n^2-1)}{4\Pi A_V(n^2+2)} \quad (10)$$

Where A_V is the Avogadro number.

Ionic concentrations

The ionic concentrations of the glass samples are determined using the following relation [18]

$$N\ (ions/cm^3) = \frac{(Avogadro's\ number)(glass\ density)}{(Average\ molecular\ weight)} \times (mol\%\ of\ rare\ earth) \quad (11)$$

Polaron radius

The polaron radius was calculated using the formula [19]

$$R_p = \frac{1}{2} \times \left(\frac{\Pi}{6N}\right)^{\frac{1}{3}} \quad (12)$$

Where N is the ionic concentrations.

Inter-ionic distance

Inter-ionic distance of the glass samples is given as [20]

$$R_i = \left(\frac{1}{N}\right)^{\frac{1}{3}} \quad (13)$$

Where R_i is the ionic concentrations.

Field strength

The field strength was calculated using the formula [21]

$$F\ (cm^3) = \left(\frac{Z}{R_p^{\ 2}}\right) \quad (14)$$

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 [21]

$$O.P.D. = n\left(\frac{\rho}{M}\right) \times 1000 \quad (15)$$

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.

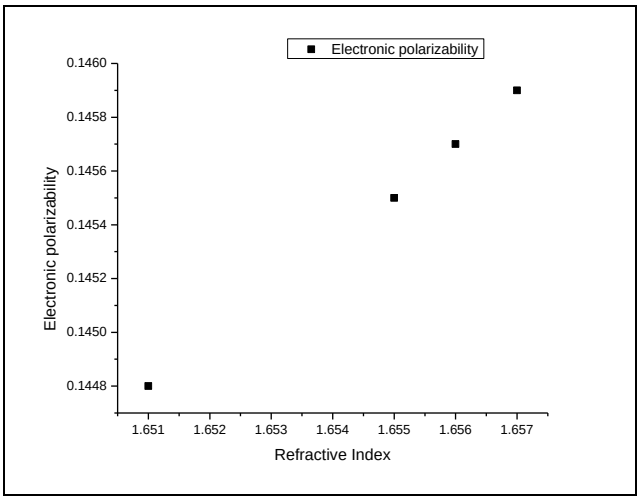

Fig.3. Varation of Electronic polarizability with Refractive Index.

Table 2: The physical and optical properties of Mo_2O_3: ZnO: Li_2O: WO_3: Sb_2O_3 glasses

Physical properties	**ZLTAM (UD)**	**ZLTAM (LU 01)**	**ZLTAM (LU 1.5)**	**ZLTAM (LU 02)**
Refractive Index (n)	1.651	1.655	1.656	1..657
Density (ρ) $\left(gm/cm^3\right)$	3.248	3.542	3.642	3.732
Thickness(Z)	0.245	0.245	0.245	0.245
AveragemolecularweightM (g)	215.1317	216.7175	217.5078	218.2980
Rare earth ions concentratio(N)	--	0.984	1.513	2.059
Dielectric Constant (ϵ)	2.726	2.739	2.742	2.746
OpticalDielectricConstant $p\frac{dt}{dp}$	1.726	1.739	1.742	1.746
MolarVolume (V_m) $\left(gm/cm^3\right)$	66.24	61.19	59.72	58.49

Reflection losses(R_L)	6.030	6.086	6.100	6.114
Molar refractivity ($R_{m)}$	24.190	22.454	21.941	21.515
Polaron radius R_p $\left(A^0\right)$	--	4.052	3.511	3.169
Interionic distance(R_i) $\left(A^0\right)$	--	1.0054	0.8712	0.7862
Electronic polarizability (α_e)	0.1448	0.1455	0.1457	0.1459
Field strength (F)	--	0.1492	0.1487	0.2440
Molarpolarizability(α_m) $\times 10^{-24} cm^3$	9.5992	8.9103	8.7067	8.5377
Oxygen packing density(OPD)	39.251	42.491	43.537	44.452
Metallization criterion (M)	0.6348	0.6330	0.6326	0.6322
Energy gap(E_g)	8.0597	8.015	8.004	7.993
Electrical susceptibility (χ)	0.1374	0.1385	0.1387	0.1390

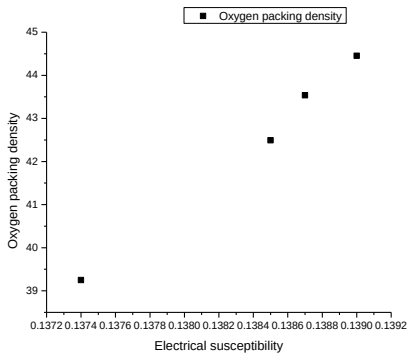

Fig.4. Variation of oxygen packing density with electrical susceptibility.

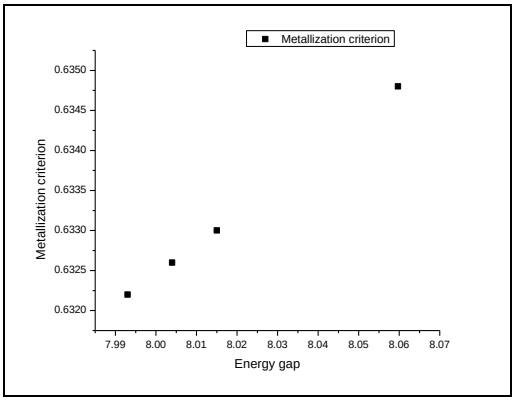

Fig.5. Variation of metallization criterion with energy gap.

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

$$M=\left(1-\frac{R_m}{V_m}\right) \quad (16)$$

Electrical susceptibility (χ)

The Electrical susceptibility was calculated using the formula [23]

$$\chi=\left(\frac{n^2-1}{4\pi}\right) \quad (17)$$

IV. Conclusions

The Lu^{3+} doped zinc lithium tungsten antimony molybdate gasses were prepared at various doping concentration of Lu_2O_3 and characterized for their physical properties. The density and refractive index

increases with an increase in concentration of Lu_2O_3. The decrease value of metallization criterion indicates that the glass material is metalizing.

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