

Optical Properties of Lithium - Zinc – Boro- MolybdateGlass Doped with Rare Earth Oxides

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Abstract

Rare earth oxides like samarium oxide, neodymium oxide and tellurium oxide doped Lithium –Zinc-Molybdate glass were synthesized by the conventional melt quench technique. In order to understand the role of these rare earth oxides in these glasses, the density, and optical absorption properties were investigated. The density and refractive index were found to be dependent on the molecular mass. The optical absorption spectra were measured in the wavelength range 300-1000 nm and the optical band gaps were determined. The molar refraction shows a consistent increase with increasing rare earth ion content and is found to depend on the refractive index, density and average molecular weight of the glass system and are consistent with all the physical parameters determined.

Keywords: Rare earth oxides, Refractive index, Optical absorption spectra, band gap value

Introduction

The importance of glass in optical applications cannot be over emphasized, particularly as a host for optically active ions. Several applications of optical processes are known, such as inter-ionic electronic transitions, inter-ionic transitions or excitations which takes place within the electronic levels of the same ion, etc. The energy levels of the impurity ions are split by the crystal field of the coordinating ligands and the disorder causes a perturbation to the position of these levels. Those ions with partially filled electronic shells (like transition metal ions, post transition metal ions like Zn^{2+} , Pb^{2+} , Sn^{2+} etc and rare earth ions) generally possess energy levels close to the ground state. The energy separations fall in the useful range of ultraviolet to infrared through the visible range of the electromagnetic spectrum. The electronic transitions between these levels cause absorption in visible regions and impart color to the glass. Doped ions in crystalline or glassy matrices often give luminescence emission on returning from an excited state to the ground state. These transitions are of practical interest, at the same time, the energy intensity of the absorption and luminescence emission of the spectral lines also give useful information on the site of the ion as well as on the properties of the host. In recent times, glasses doped with rare earth ions have drawn considerable interest due to their photonic applications as optical amplifiers and solid state lasers [1]. Wave guide lasers and amplifiers are obtained by doping glasses with rare earth oxides [2]. Optical properties of rare- earth doped glass are found to have applications in the advancement of glass lasers as well as in the production of a wide variety of optical fiber cables, prisms and commercial filter glasses. Neodymium is one of the most studied rare earth ions and is found to have immense applications in photonic devices [3,4]. Neodymium containing glasses are used in halogen lamps to absorb ultra-violet rays, which are harmful to humans. Other rare-earth-doped ions are yttrium (Y^{3+}), samarium (Sm^{3+}), europium (Eu^{3+}), gadolinium (Gd^{3+}), terbium (Tb^{3+}), dysprosium (Dy^{3+}), and lutetium (Lu^{3+}). These are normally not used for laser action but sometimes as a co-dopant,

e.g. for quenching the population in certain energy levels by energy transfer processes, or for realizing saturable absorbers, or as optically passive constituents of crystals. The purpose of the present work is to analyze the structural and optical properties of Lithium –Zinc-Molybdate glasses doped with rare earth oxides like samarium oxide, neodymium oxide and tellurium oxide glasses synthesized by melt quench technique.

Experimental

Glasses were prepared by using the general formula $19.5 \text{ Li}_2\text{O} - 20 \text{ ZnO} - 54\text{B}_2\text{O}_3 - 6 \text{ MoO}_3 - 0.5 x$ (where $x = \text{Gd}_2\text{O}_3, \text{Sm}_2\text{O}_3, \text{Nd}_2\text{O}_3$) by the conventional melt quench technique using analar grade Lithium oxide (Li_2O), Zinc oxide (ZnO), and Molybdenum oxide (MoO_3) doped separately with, gadolinium (Gd_2O_3), samarium oxide (Sm_2O_3) and neodymium oxide (Nd_2O_3) in appropriate proportions in accordance with the above formula. The chemicals were ground together and the grounded mixtures were taken in porcelain crucibles and kept in a muffle furnace. The temperature of the furnace was set to about 1000°C . The melt were stirred in between to ensure homogeneity. Glass was obtained by rapidly quenching the melt between two brass blocks preheated to 100°C to avoid cracking of the samples. The glasses were annealed in a muffle furnace for about 2 hours at 200°C to remove thermal strains that could have developed during quenching and the glasses were preserved in an anhydrous atmosphere (CaCl_2).

Characterization

The density of the glasses free from air bubbles was determined by the Archimedes principle using toluene ($\rho_{\text{toluene}} = 0.860 \text{ gm/cc}$) as the immersion liquid. The densities of the glasses were obtained using the relation

$$\rho = \left(\frac{W_a}{W_a - W_g} \right) \rho_l \quad (1)$$

where W_a is the weight in air, W_b is the weight of the glass sample in buoyant liquid and ρ_l is the density of toluene. All weight measurements were made using a digital balance. The molar volume (M_v) was calculated using the relation $M_v = M / \rho$, where M is the molecular weight. The relative error in the measurement of density was about $\pm 0.005 \text{ g/cm}^3$.

UV–Visible Absorption spectra of the synthesized glasses was recorded using Perkin Elmer (Lambda 35) spectrometer in the UV-Vis-NIR region in the range 200 to 900 nm.

Results and Discussion

Density and molar volume

Composition, code, density (ρ) and packing density (V_t) of $19.5 \text{ Li}_2\text{O} - 20 \text{ ZnO} - 54\text{B}_2\text{O}_3 - 6 \text{ MoO}_3 - 0.5 x$ (where $x = \text{Gd}_2\text{O}_3, \text{Sm}_2\text{O}_3, \text{Nd}_2\text{O}_3$) glasses containing rare earth ions are listed in Table 1. Density and molar volume exhibit molecular mass dependence. Variation of density and molar volume with $\text{Gd}_2\text{O}_3, \text{Sm}_2\text{O}_3$ and Nd_2O_3 mol % is shown in Figure 1.

It can be seen from Figure .1, that density decreases while molar volume increases with the introduction of rare earth oxides like gadolinium, samarium and neodymium oxides. This is due to the fact that the molecular mass of gadolinium oxide is more than samarium oxide which is heavier than neodymium oxide. Also, the substitution of the oxide₃ in the base network increases the density because heavier rare earth oxides is substituted to borate and molybdate network which results in increasing

density. Borate and Molybdenum oxide act as network modifiers and are responsible for the increase in molar volume.

Table 1 Code and Composition of glass system

Compound	Composition in mol%		
Li ₂ O	19.5	19.5	19.5
B ₂ O ₃	54	54	54
ZnO	20	20	20
MoO ₃	06	06	06
Gd ₂ O ₃	0.5	00	00
Sm ₂ O ₃	00	0.5	00
Nd ₂ O ₃	00	00	0.5
Code	LZBM 1	LZBM 2	LZBM 3

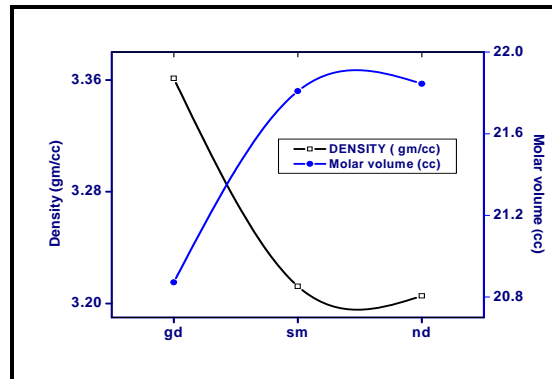


Figure 1 Variation of density and molar volume with Gd₂O₃, Sm₂O₃ and Nd₂O₃ mol %.

The physical properties provide an insight into the atomic arrangements in a glass network. Based on the measured density, molar volume and rare earth ion concentration (N), various physical properties like polaron radius (r_p), inter-nuclear distance (r_i) and field strength (F) were determined using the standard relations (2) - (5) as described below [5].

$$N \text{ (ion/cm}^3\text{)} = (\% \text{ mol of TMO}) \times \frac{(\text{Avogadro's number} \times \text{density})}{(\text{average molecular weight})} \quad (2)$$

$$\text{Polaron radius, } r_p = \frac{1}{2} \left(\frac{\pi}{6} \right)^{1/3} \quad (3)$$

$$\text{Inter nuclear distance, } r_i (\text{\AA}) = \left(\frac{1}{N} \right)^{1/3} \quad (4)$$

$$\text{Field strength, } F(\text{cm}^2) = \left(\frac{Z}{r_p^2} \right) \quad (5)$$

The polaron radius is found to increase with the change in the rare earth ions like Gd₂O₃, Sm₂O₃ and Nd₂O₃. This result agrees with the literature [6]. The inter-nuclear distance also shows an expected increase. All the above mentioned physical properties are listed in Table 2.

Table 2. Concentration ($N \times 10^{22}$ ions/cc), Polaron radius ($r_p \times 10^{10}$ m), inter ionic distance ($r_i \times 10^{10}$ m) and field strength ($F \times 10^{15}$ cm⁻²) of gadolinium, samarium and neodymium ions in LZBM glass samples.

Sample Code	N	r_p	r_i	F
LZBM1	1.4428	1.655	4.107	7.301
LZBM2	1.3802	1.679	4.168	7.094
LZBM3	1.3784	1.680	4.170	7.082

The increase in density observed is attributed to increase in field strength which tends to pull together the oxygen ions, leading to a decrease in the size of the interstices of the glass network.

Optical absorption spectra

Oxide glasses containing rare-earth oxides (REO) in high concentrations have considerable applications in optical data transmission, detection, sensing and laser technologies. The optical absorption spectrum of Gd^{3+} doped glasses is shown in Figure 2.

The transitions of Gd^{3+} start from the $^8S_{7/2}$ ground state of the $4f^7$ configuration of Gd^{3+} . The 6G term in the range 400–500 nm could be seen because of strong absorption by the glass matrix. In comparison with the other lanthanide ions, the absorption bands for Gd^{3+} are very sharp and usually occurs in the range of 200-300nm. Here the shift in the absorption band is due to the addition of molybdenum.

Molybdenum ion in the oxidation state +6 is reported to occur predominantly in four-fold coordination, i.e., as MoO_4 than the six fold coordination as reported in many other glass systems. Mo^{6+} ions in the melted mixtures reduce to Mo^{5+} ions and the absorption band observed in the region of 670–800 nm in the optical absorption spectra of these glass is attributed to transition of Mo^{5+} ($4d^1$) ion.

Figure 3 presents optical absorption spectra for the glass samples doped with samarium ions recorded at room temperature in the wavelength region 400-900 nm.

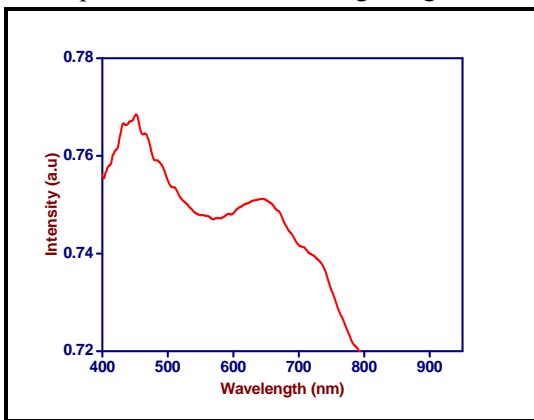


Figure.2. Optical absorption spectra of Gd^{3+} doped glasses

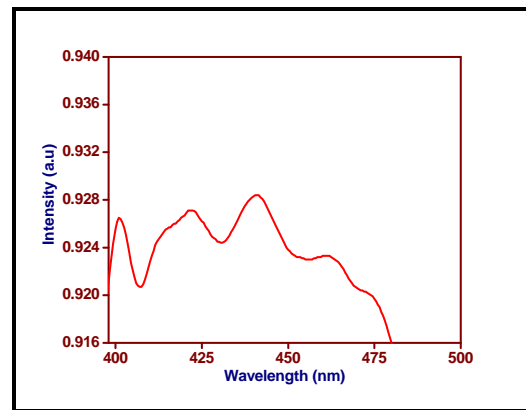


Figure.3. Optical absorption spectra of Sm^{3+} doped glasses

Three absorption bands peaked at 429nm, 440nm, and 452 nm were observed. All absorption band spectra are characteristics of Sm^{3+} doped oxide glasses [7] and the observed absorption bands were assigned to appropriate $f-f$ electronic transitions of Sm^{3+} ions from the $^6H_{5/2}$ ground state to ($^4I_{13/2} + ^4I_{11/2} +$

$^4M_{15/2}$), $^6F_{11/2}$ and $^6F_{9/2}$ respectively but were slightly shifted to lower wavelength due to the effect of Molybdenum ions.

Broad absorption band observed in the region of 670–800 nm in the optical absorption spectra of this glass is attributed to transition of Mo^{5+} ($4d^1$) ion. The optical absorption spectrum of Nd^{3+} doped glass recorded at room temperature in the wavelength region 400-900 nm is shown in Figure 4.

Three absorption bands peaked at 523nm, 581nm, 885nm and 875nm were observed which is characteristic of Nd^{3+} ion.

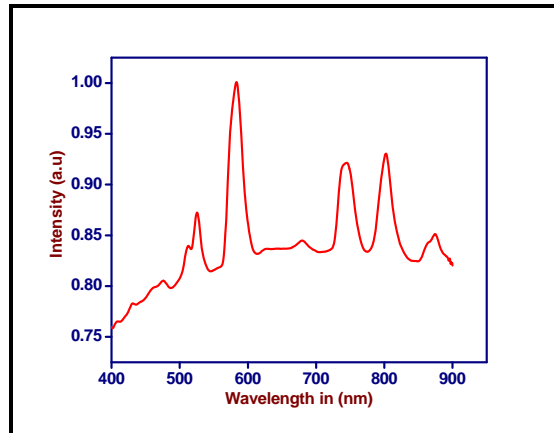


Figure 4 . Optical absorption spectra of Nd^{3+} doped glasses

Again the bands at 672nm and 748 nm are characteristic of transition of Mo^{5+} ($4d^1$) ions which was evident in all the three glass systems analyzed.

The absorption coefficient values corresponding to the absorption bands are dependent on neodymium oxide concentration. The transition $^4I_{9/2} \rightarrow ^4F_{5/2} + ^2H_{9/2}, ^4F_{7/2} + ^4S_{3/2}, ^2G_{7/2} + ^4G_{5/2}, ^2K_{13/2} + ^4G_{7/2} + ^4G_{9/2}, ^4D_{1/2} + ^2L_{15/2}$ between the ground state and higher energy states inside the $4f^3$ electronic configuration of the Nd^{3+} ions are observed in the 400-900 nm spectral region. The assignments of these transitions are made on the basis of Carnell *et al* [8].

According to Mott *et al* [9] and Altafet *et al* [10], the standard method usually employed for investigating optically induced electronic transitions in materials is to measure the optical absorption coefficient (α) near the fundamental absorption edge. Usually two types of transitions namely direct and indirect transitions occur at the absorption edge. The absorption coefficient can be determined for different wavelengths using the relation [11].

$$\alpha(\nu) = \left(\frac{1}{d}\right) \ln \left(\frac{I_0}{I_t}\right) \quad (6)$$

where ' I_0 ' and ' I_t ' are intensities of the incident and transmitted beams and 'd' corresponds to the thickness of the sample. Davis and Mott [12] gave the absorption coefficient $\alpha(\nu)$ as a function of photon energy (hv), for direct and indirect transitions using the relation [13].

$$\alpha(\nu) = B(h\nu - E_{opt})^n/h\nu \quad (7)$$

where the exponent $n = 1/2$ for an allowed direct transition, $n = 2$ for an allowed indirect transition and 'B' is a constant.

The optical energy band gap (E_{opt}) for indirect and direct transitions can be found, by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy (Tauc's plot). The respective values of E_{opt} are obtained by extrapolating $(\alpha h\nu)^{1/2} = 0$ for indirect transitions and $(\alpha h\nu)^2 = 0$ for direct transitions [14].

The Tauc's plot for the glass samples is shown in Figure 5 .

Dimitrovet al [15] proposed that the refractive index of the glasses can be calculated using the relation

$$\left(\frac{n^2-1}{N^2+2}\right) = 1 - \frac{F_0}{\lambda^2} \quad (8)$$

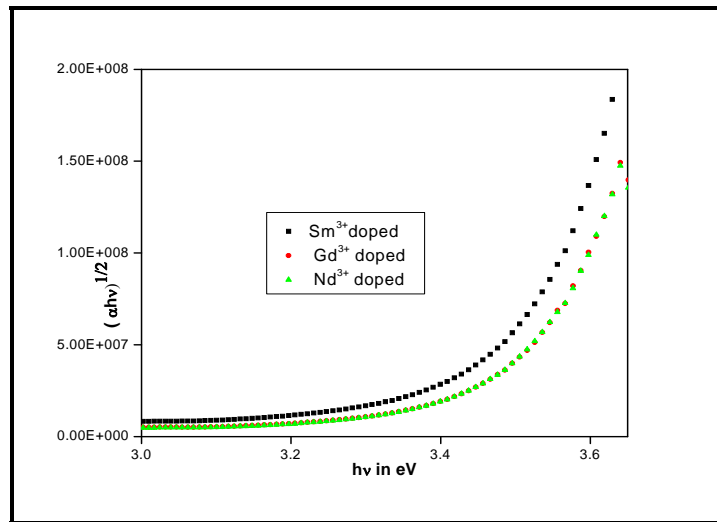


Figure 5. Plots corresponding to indirect band gap for rare earth doped LZBM glass system

According to Klinokowski [16], the electron polarizability α_0 can be calculated using the relation

$$\alpha_0 = \frac{3(n^2-1)}{4\pi N(r_0^3+2)} \quad (9)$$

Duffy and Ingram [17] reported that the optical basicity of an oxide glass which reflects the ability of the glass to donate negative charges to the probe ion can be estimated using the relation $\Lambda_{th} = \sum_{i=1}^n \frac{Z_i r_i}{2V_i}$

(10)

where 'n' is the total number of cations present, 'Z' is the oxidation number of the i^{th} cations, ' r_i ' is the ratio of i^{th} cations to the number of oxides present and ' V_i ' is the basicity moderating parameter of the i^{th} cation. The basicity moderating parameter ' V_i ' can be calculated using the following relation put forth by Duffy and Ingram[17]

$$V_i = 1.36(x_i - 0.26) \quad (11)$$

where ' x_i ' is the Pauling electronegativity [Pauling 1960] of the cation.

The molar refraction (R_m) was calculated by using the equation.

$$\frac{n^2-1}{n^2+2} \left(\frac{M}{\rho} \right) = R_m \quad (12)$$

Molar refraction is related to the structure of the glass and it is proportional to the molar electronic polarizability of the material, through the Clausius–Mossotti relation [18]

$$\alpha_m = \left(\frac{3}{4\pi N} \right) R_m \quad (13)$$

where N is the number of polarizable ions per mole and is assumed to be equal to the Avogadro's number (N_A). The value $4\pi/3$ is a constant in Lorentz function. With α_m in (10^{-24}cm^3), Eq. (13) can be transformed to $R_m = 2.52 \alpha_m$.

The state of polarization of the oxide ions in oxide glasses strongly depends on the polarizing power of the cations. The average electronic polarizability of oxide ions in single component oxides can be calculated using Dimitrov and Sakka [19] on the basis of linear refractive index and energy gap. For multi- component oxide glasses with a general formula $x_1A_nO_m : x_2B_pO_q : x_3C_rO_s$, where x_1 , x_2 and x_3 represents the molar fraction for each oxide, the oxide ion polarizability α_O^{2-} can be calculated using equation:

$$\alpha_O^{2-} = \frac{\left[\frac{N_m}{n^2 n^2} - \sum \alpha_{cat} \right]}{N_O^{2-}} \quad (14)$$

where $\sum \alpha_{cat}$ denotes the molar cation polarizability given by $x_1 n \alpha_A + x_2 p \alpha_B + x_3 r \alpha_C$ and N_O^{2-} denotes the number of oxide ions in the chemical formula given by $x_1 m + x_2 q + x_3 s$.

Electronic polarizability of an ion is related to properties of the material such as refraction, conductivity, optical nonlinearity along with optical basicity and is of significant interest in the study on polarization state of ions in crystalline and amorphous materials [Vesselin Dimitrov [15]. The average electronic polarizability of oxide ions in single component oxides can be calculated using relation (14) on the basis of linear refractive index and energy gap. The molar cation polarizability of the glasses is calculated using data on the polarizability of cations having the following values: $\text{Li}^+ = 0.024 \text{ \AA}^3$, $\text{B}^{3+} = 0.002 \text{ \AA}^3$, $\text{Nd}^{3+} = 2.546 \text{ \AA}^3$, $\text{Gd}^{3+} = 2.381 \text{ \AA}^3$, $\text{Sm}^{3+} = 2.435 \text{ \AA}^3$, $\text{Mo}^{3+} = 0.169 \text{ \AA}^3$ and $\text{Zn}^{2+} = 0.283 \text{ \AA}^3$ [18]. The various optical parameters discussed above are also listed in Table 3. The theoretical optical basicity ' Λ ' was calculated using the relation (10). It is seen that the oxide ion polarizability increases linearly with increase of refractive index. The results show that the refractive index of glass not only depends on the density but also on the electronic polarizability of the glass consistent on the basis of the studies on borate and titanium silicon sodium oxide glass system by Abdel-Baki [13]. This also agrees with the observations of Dimitrov [19] that there is a general trend of an increase of oxide ion polarizability with increasing refractive index and decreasing energy gap which in turn is also consistent with the decreasing density values. The existence of trivalent electrons of samarium ions affects the structure of the glass system by increasing number of free electrons which leads to decreasing number of band gap energy. The non-linear trend of refractive index and polarizability are due to the substitution of ZnO oxides which acts as a modifier and former.

The low values of optical basicity indicates decrease in covalency. It also indicates the increase in NBO's in the network. The refractive index of these glasses are also found to be higher than that of the standard glasses. Lanthanide contraction phenomenon is observed in the optical parameters which can be attributed to the increasing atomic number.

Table 3. Refractive index (n), dielectric constant (ϵ), molar refractivity (R_m) in cm^3 , molar electronic polarizability (α_m) in \AA^3 , glass oxide polarizability (α_G^{3-}) in \AA^3 and optical basicity (A_{eff}) of LZBM glasses.

Code	Band gap	n	R_m	α_m	α_G^{3-}	A_{eff}
LZBM1	3.884	1.989	10.281	8.154	1.799	0.5796
LZBM2	3.901	1.920	10.150	8.051	1.787	0.5797
LZBM3	3.920	1.870	9.9237	7.8711	1.853	0.5799

Conclusions

The glass system were prepared successfully by rapid melt quench method. The concentration of the rare-earth ions is an important variable as it affects lasing of the host material and the physical properties provide an understanding of the atomic arrangements. The molar refraction shows a consistent increase with the increasing rare earth ion content and is found to depend on the refractive index, density and average molecular weight of the glass system are consistent with all the physical parameters determined. The results show that the refractive index of glass not only depends on the density but also on the electronic polarizability of the glass. The optical band gap shows composition dependence.

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