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Investigations on Optical and Physical Properties of Sm_2O_3 , Dy_2O_3 and Eu_2O_3 Doped Zinc Strontium Bismuth Borate Glasses

Kothandan D¹, Chandra Babu Naidu K^{2*}, Jeevan Kumar R^{3*}¹Sreenivasa Institute of Technology and Management Sciences, Chittoor, A.P, India²Srinivasa Ramanujan Institute of Technology, Anantapuramu (A.P), India³Department of Physics, S.K. University, Anantapuramu (A.P), India

*Corresponding authors: Chandra Babu Naidu K (2018) Srinivasa Ramanujan Institute of Technology, Anantapuramu (A.P), India. Tel: +919398426009; Email: chandrababu954@gmail.com

Jeevan Kumar R (2018) Department of Physics, S.K. University, Anantapuramu (A.P), India. Email: rjkskuphy@gmail.com

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Abstract

Borate glasses of stoichiometry $(50-x) \text{H}_3\text{BO}_3-10\text{SrF}_2-10\text{Bi}_2\text{O}_3-20\text{ZnO}-10\text{SiO}_2-\text{Mx}$ ($\text{M} = \text{Sm}_2\text{O}_3, \text{Dy}_2\text{O}_3 \& \text{Eu}_2\text{O}_3$, $x = 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 \& 3.0$) are prepared by melt quenching method by doping various concentrations of rare earth metals (Sm, Dy and Eu). The resultants are characterized using X-ray diffract meter and UV-Visible spectrometer for investigating structural and optical properties respectively. The optical band gap energies (E_g) and refractive indices (n) are found to be varying between 3.39- 3.56 eV and 2.260-2.299. In order to identify the physical stability of glass samples physical properties have been studied. The density of glasses is decreasing with doping item and increasing with composition. In case of Sm^{3+} , Dy^{3+} and Eu^{3+} doped glass, density are varying from 4.02-4.25 g/cm^3 , 3.89-4.13 g/cm^3 & 3.64-3.89 g/cm^3 respectively. The motivation and novelty behind this study is to report the good dense as well as the physical stability of borate glasses.

Keywords: Borate glasses; X-ray diffract meter; Physical Properties; Optical band gap; Melt quenching method

Introduction

Borate glasses pertaining rare earth metal oxides have significant applications for solid state, luminescent applications, laser hosts, lamp phosphors, broad band amplifiers, sensors, optical data storage devices and optical fiber communication systems [1]. Kim et al. [2] investigated the luminescence property of rare earth doped bismuth borate glasses due to 4f-4f and 4f-4d electronic transitions in the visible light range. Padyak et al. [3] also studied luminescence properties of the Samarium doped borate glasses by studying the optical absorption and photoluminescence spectra. Venkata Rao et al. [4] suggested that Dy^{3+} doped borate glasses are the candidate materials for yellow lighting applications in the visible range by studying optical properties. Shem et al. [5]

demonstrated that Sm^{3+} doped alkaline earth borate glasses are well suited materials for UV to Visible photon conversion layer for solar cell applications. Ivankov et al. [6] revealed that the high content of Eu^{3+} has lead to the disappearance of broad band glass emission at the near UV range. Chimalawang et al. [7] investigated the physical properties of Dy^{3+} doped soda lime glass silicates. But to the best of author knowledge there is no detailed report on the optical and physical properties of Sm, Dy and Eu doped borate glasses. In this investigation an attempt has been made to study the optical properties of present glass materials.

Experimental Procedure

The glasses of general formula $(50-x) \text{H}_3\text{BO}_3-10\text{SrF}_2-10\text{Bi}_2\text{O}_3-20\text{ZnO}-10\text{SiO}_2-\text{Mx}$ ($\text{M} = \text{Sm}_2\text{O}_3, \text{Dy}_2\text{O}_3 \& \text{Eu}_2\text{O}_3$, $x = 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 \& 3.0$) have been prepared by mixing them in appropriate quantity with the help of digital

electronic balance. The chemicals of 99.9 % purity (Sigma Aldrich) are taken. All these compositions are mixed together and stirred in a porcelain crucible. The mixture is melted by placing it in a programmable furnace 1100°C for 30min. The glass samples are taken out from the furnace and pour onto different metal plates. The plate is again annealed for 300°C and as the result the glasses are obtained having transparent, pure and amorphous in nature. The samples are characterized by using XRD (Bruker, Cu_{Kα}=15.418 nm) and UV-Visible spectrometer (UV-Visible-NIR JASCO spectrometer) for studying the structural, absorption spectra and optical band gap energies. Besides, the physical properties have been studied in order to identify the physical stability of glass samples.

Result and Discussions

The recorded XRD profile of Sm³⁺, Dy³⁺ and Eu³⁺ doped zinc strontium bismuth borate glass (ZnSrBiB) as shown in Figure 1 have confirmed the amorphous nature without exhibiting any single or polycrystalline phases.

Optical Properties

The optical absorption spectra of (50-x) H₃BO₃-10SrF₂-10Bi₂O₃-20ZnO-10SiO₂-Mx (M = Sm₂O₃, Dy₂O₃ & Eu₂O₃, x= 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 & 3.0) is recorded and is shown in (Figure 1)

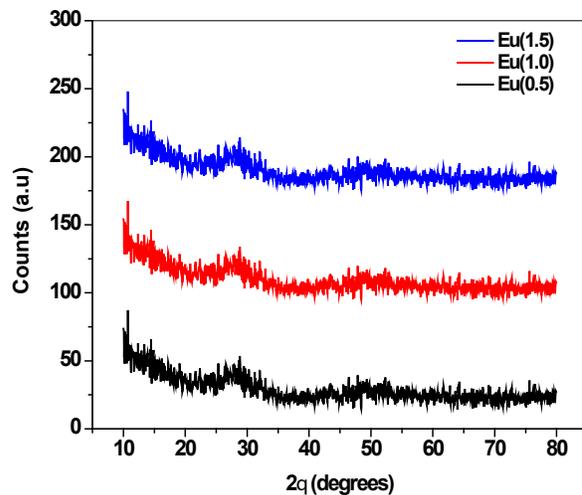
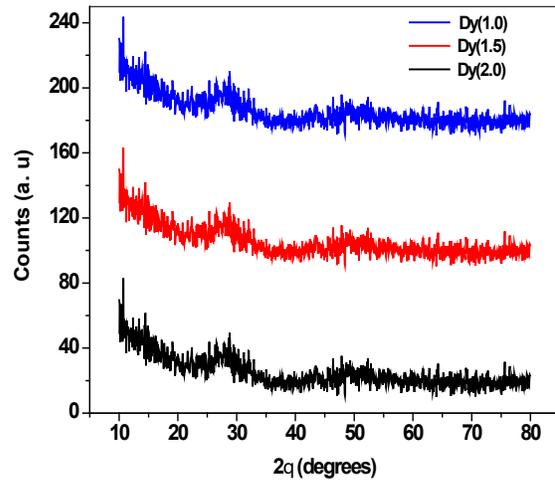
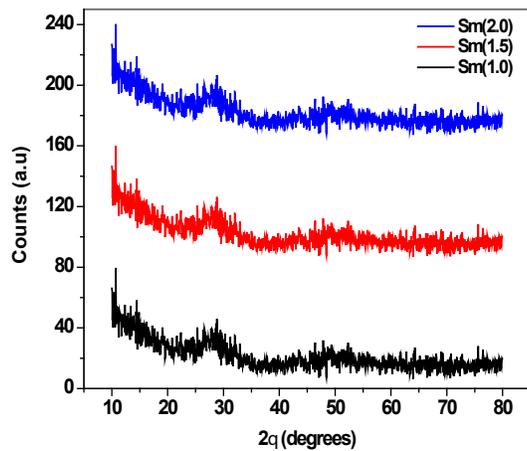


Figure 1: The XRD spectra Sm (1.0, 1.5, and 2.0) (b) Dy (1.0, 1.5, and 2.0) & (c) Eu (0.5, 1.0, and 1.5) doped glass matrix.

In the absorption spectra of present amorphous materials maximum absorption wavelength (λ_m) is observed and is tabulated in (Table 1).

S.No	Sample	E _g (Ev)	N	λ _m (Nm)	A
1	Sm _{1.0}	3.46	2.283	296	0.888
2	Sm _{1.5}	3.42	2.292	301	1.761
3	Sm _{2.0}	3.39	2.299	301	2.647
4	Dy _{1.0}	3.56	2.26	301	0.882
5	Dy _{1.5}	3.51	2.271	301	1.781
6	Dy _{2.0}	3.51	2.271	290	2.667
7	Eu _{0.5}	3.49	2.276	301	0.868
8	Eu _{1.0}	3.48	2.278	301	1.761
9	Eu _{1.5}	3.47	2.281	301	2.681

Table 1: Data for optical parameters of Sm, Dy & Eu doped borate glasses.

From (Figure 2) (a) it is evident that low concentration of Sm, λ_m is decreased to 296 nm while the rest high Sm contents show the similar λ_m values (301 nm).

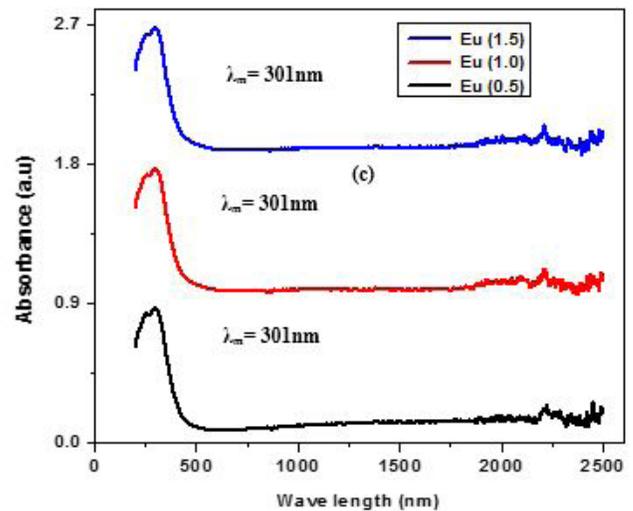
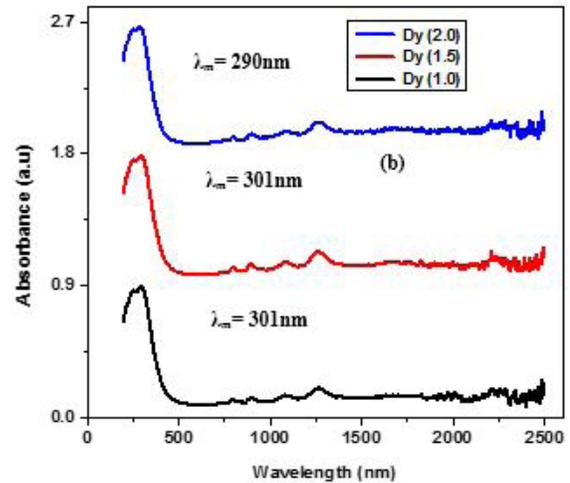
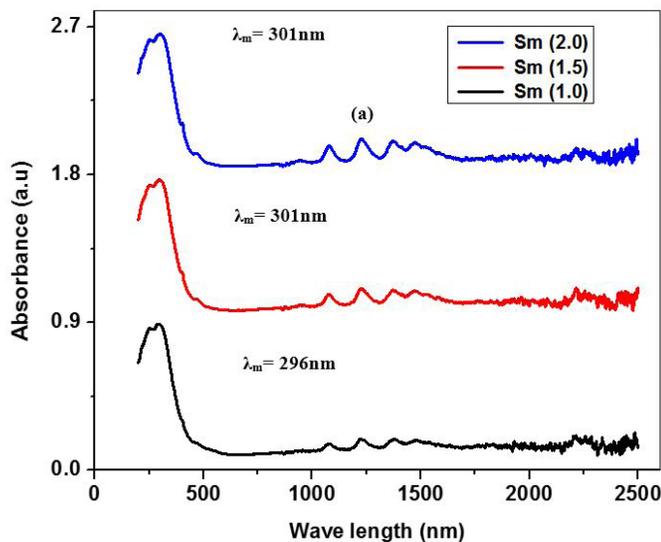


Figure 2: Absorption spectra of (a) Sm (1.0, 1.5, and 2.0) (b) Dy (1.0, 1.5, and 2.0) & (c) Eu (0.5, 1.0, and 1.5) doped borate glasses.

(Figure 2) (b) Reveals that at the high concentrations of Dy, λ_m decreases to 290 nm. On the other hand the rest compositions exhibit the identical λ_m values (301 nm).

But, interestingly (Figure 3) (c) shows for all contents of Eu doped borate glasses perform the similar λ_m values of 301 nm. Comparatively, Sm doped glass shows few absorption peaks between wavelength range 1100-1400 nm

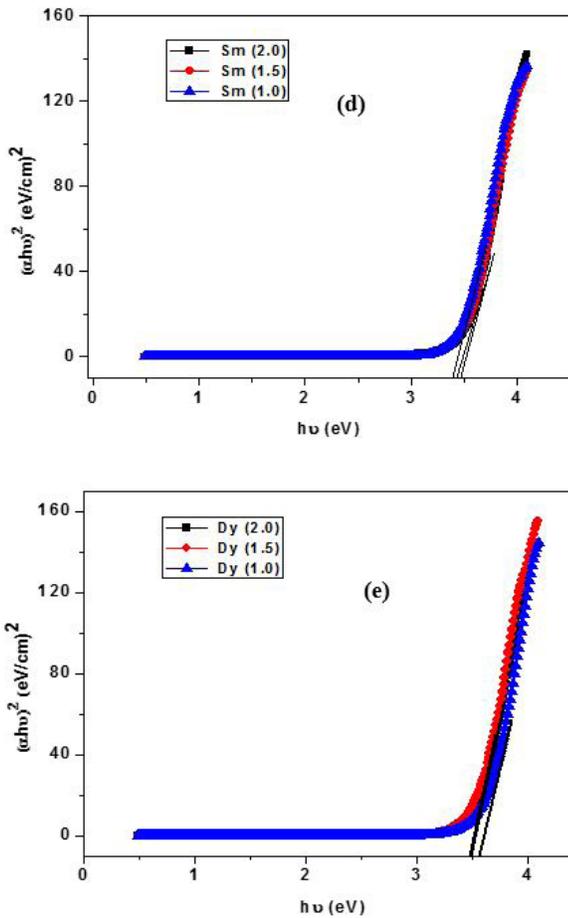


Figure 3: $(\alpha hv)^2$ Vs photon energy plots of (a) Sm (1.0, 1.5, and 2.0) (b) Dy (1.0, 1.5, and 2.0) & (c) Eu (0.5, 1.0, and 1.5) doped borate glasses.

While Dy-doped glass showed the absorption, peaks possessing the left shift over the wavelength range 750-1400nm. These absorption peaks may be due to the presence of few impurities. The diffuse reflectance spectra are recorded in wavelength range of 200-2500 nm in order to determine the optical band gaps for the glass samples. Using the following equation Kubelka- Munk function of reflectance $F(R)$ can be calculated [8, 9].

$$F(R) = \frac{(1-R)^2}{2R} \quad (1)$$

The absorption coefficient α is directly proportional with $F(R)$ and hence an equation for determining the band gap can be written as follows.

$$(\alpha hv)^n = A (hv - E_g) \quad (2)$$

Where A = Energy- independent constant that depends on transition probability, E_g = optical band gap, n = the kind of transition i.e. $n=2$ for direct transition, $2/3$ for direct forbidden transition, $1/2$ for indirect allowed transition, $1/3$ for indirect forbidden transition and $h\nu$ = photon energy [8]. In the present study $n = 2$ is taken for direct transition. E_g values are determined and tabulated in table.1 by plotting $(\alpha hv)^2$ against the photon energy $h\nu$ (eV) as shown in (figure 2) and the slope of α tends to zero. The obtained band gaps are found to be varying between 3.39- 3.56 eV. The refractive index (n) is calculated using the optical band gap energies (E_g) with the help of following formula.

$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_g}{20}} \quad (3)$$

In the present investigation for all the dopants of borate glasses the optical band gap energies are decreasing with increase of doping contents while refractive indices and absorbance (A) values are showing increasing trend with doping contents. This establishes a fact that there exists an inversely proportional relationship between E_g & n , A .

Physical Properties

In respect of the physical properties refractive index (n), density (ρ), molar refractivity (R_m), concentration (mol/lit & ion/cm³), polaron radius (r_p), intermolecular distance (d), field strength (F), molar volume (V_m), electric polarizability (α), reflection losses (dB) and metallization factors (M_f) are determined. These properties can show the mechanical stability of glass composition and are shown in (Table 2).

Sm ₂ O ₃	0.01	0.05	0.1	0.5	1	1.5	2	2.5	3
concentration(mol/lit)	0.00501	0.0335	0.06955	0.35431	0.70909	1.06801	1.41494	1.75491	2.0748
concentration(ion/cc)	3.29E+18	2.04E+19	4.22E+19	2.14E+20	4.27E+20	6.44E+20	8.53E+20	1.06E+21	1.25E+21
inter-molecular distance	5.74E-07	3.24E-07	2.49E-07	1.32E-07	9.72E-08	8.03E-08	7.00E-08	6.27E-08	2.54E+01
molar volume	24.7611	24.75337	24.61374	24.8421	24.8971	24.9273	25.0383	25.1821	9.21653
molar refractivity	8.32318	8.38595	8.36496	8.48106	8.86139	8.94E+00	9.00065	9.07725	6.52E-23
electric polarizability	1.70E-20	2.60E-21	1.80E-21	3.41E-22	1.85E-22	1.24E-22	9.64E-23	7.89E-23	5.36E+00
reflection losses	4.65952	4.72723	4.75437	4.79513	5.17861	5.24763	5.27529	5.30297	5.35841
metallization factors	0.52326	0.52093	0.51999	0.5186	0.50573	0.50346	0.50256	0.50166	0.49985

Table 2: The data of physical parameters of Sm³⁺ doped glass matrix.

Sm₂O₃ Doped Glass Matrix

These glasses in general are moisture insensitive and capable of accepting large concentration of rare earth ions without losing transparency. It is interesting to note that the increase in the Sm₂O₃ composition in the glass matrix enhances various optical parameters such as refractive index, polaron radius, inter-ionic distance, molar refractivity, electronic polarizability, dielectric constant and density [10]. Concentration and field strength values show the decreasing trend with increase of samarium content. The measured density, molar volume, refractive index and other related physical properties of Sm³⁺-doped ZnSrBiB glass samples for different Sm₂O₃ concentrations are shown in (Table 2) it is seen from the (Figure 6).

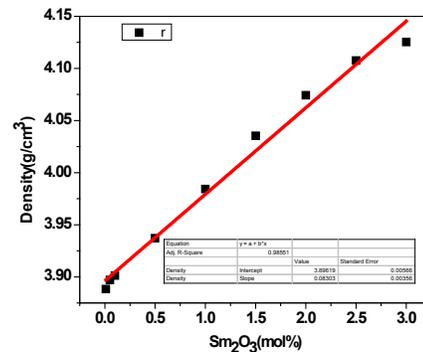


Figure 6: The refractive index of Sm³⁺ doped glass matrix.

The density increases with an increase in samarium content. Since samarium has high relative molecular mass, therefore, it is an expected result. The change in molar volume depends on the rates of change of both density and molecular weight. However, the rate of increased molecular weight is greater than the rate of increase in density. This would be accompanied by molar volume, as can be seen from (Table 3).

Dy ₂ O ₃	0.01	0.05	0.1	0.5	1	1.5	2	2.5	3
concentration(mol/lit)	0.00732	0.03581	0.07186	0.35662	0.7114	1.07032	1.41725	1.75722	2.07711
concentration(ion/cc)	4.41E+18	2.16E+19	4.33E+19	2.15E+20	4.28E+20	6.45E+20	8.54E+20	1.06E+21	1.25E+21
Inter-molecular distance	6.10E-07	3.59E-07	2.85E-07	1.67E-07	1.33E-07	1.16E-07	1.05E-07	9.81E-08	9.28E-08
molar volume(g/cc)	27.9759	27.9682	27.8286	28.0569	28.0569	28.1421	28.2532	28.3969	28.6436
molar refractivity	9.3366	9.39937	9.37838	9.49448	9.87481	9.94924	10.0141	10.0907	10.22995
electric polarizability	1.81E-20	3.72E-21	1.86E-21	3.76E-22	1.96E-22	1.31E-22	9.92E-23	8.02E-23	6.82E-23
metallization factors	0.66626	0.66393	0.663	0.6616	0.64873	0.64646	0.64556	0.64466	0.64285

Table 3: The data of physical parameters of Dy³⁺ doped glass matrix.

The molar volume of the glass system increases with the increase in samarium content, which is attributed to the increase in the number of non-bridging oxygen (NBOs). It may be assumed that the increase in samarium content at the expense of SiO₂ causes the opened glass network structure [11]. The variation of refractive index, polaron radius (r_p) & field strength (F) of Sm³⁺ doped glass matrix is clearly shown in (Figure 4 &5) respectively

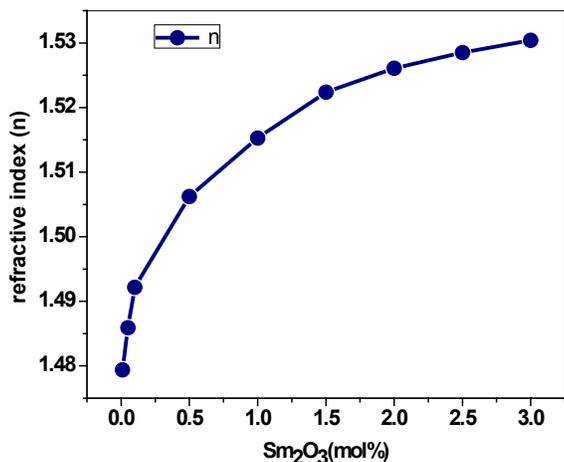


Figure 4: The refractive index of Sm^{3+} doped glass matrix.

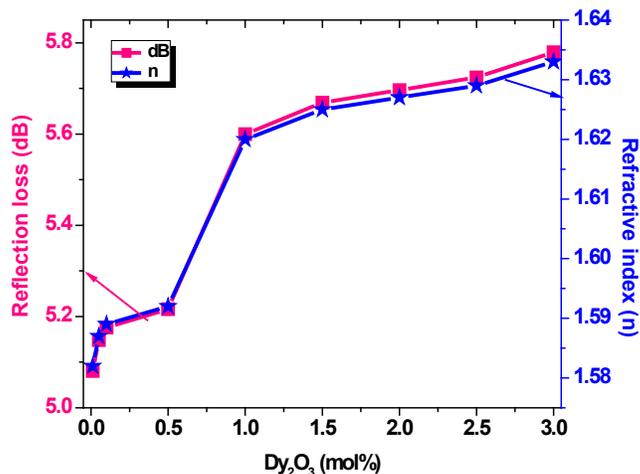


Figure 7: The variation of reflection loss refractive index of Dy^{3+} doped glass matrix.

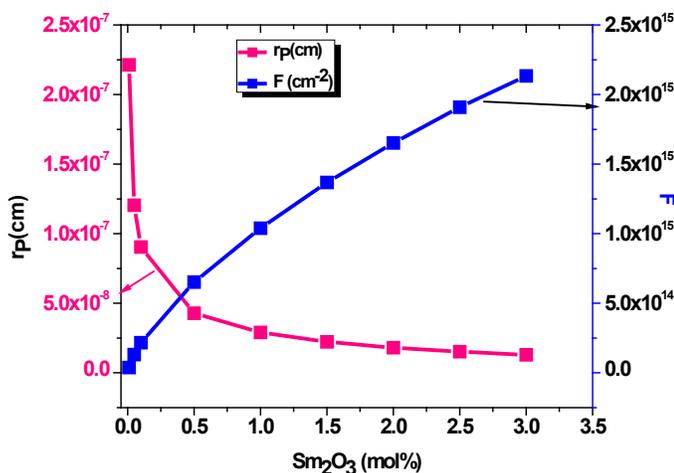


Figure 5: The variation of polaron radius (r_p) & field strength (F) of Sm^{3+} doped glass matrix.

Dy_2O_3 Doped Glass Matrix

It is interesting to note that the increase in the Dy_2O_3 composition in the glass matrix enhances various optical parameters such as refractive index, polaron radius, inter-ionic distance, molar refractivity, electronic polarizability, dielectric constant and density. Concentration and field strength values show the decreasing trend with increase of dysprosium content. From (Figure 7&9)

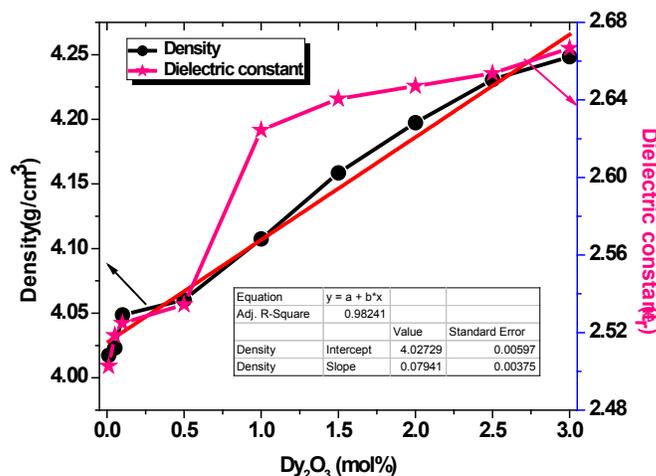


Figure 9: The variation of density and dielectric constant of Dy^{3+} doped glass matrix.

It has been found that the refractive index, dielectric constant and density values are increasing for all the glasses with the substitution of dysprosium oxide in the place of SiO_2 . Due to higher molecular weight of Dy_2O_3 compared to that of SiO_2 . Theoretically, the molar refraction, which depends on the refractive index, is a function of density and mean polarizability of

the medium [12]. The variation of polaron ionic radius and field strength is shown in (Figure 8) and are following the similar trend as that of samarium doped glass matrix

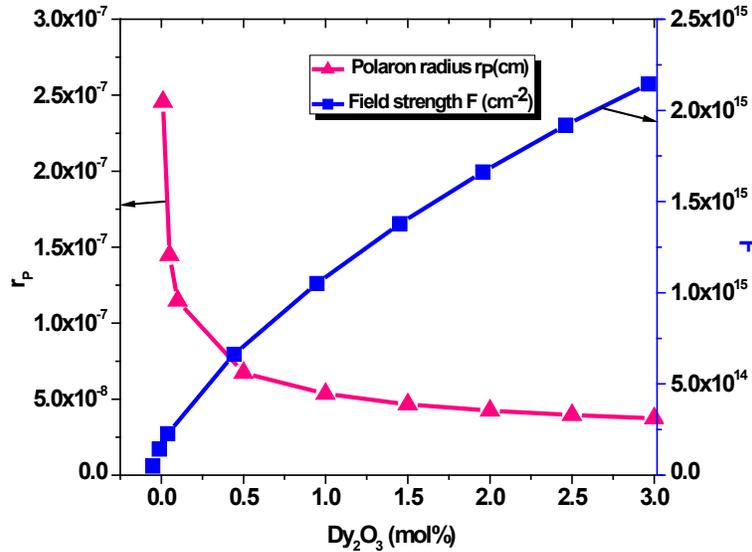


Figure 8: The variation of polaron radius (r_p) & field strength (F) of Dy³⁺ doped glass matrix.

Eu₂O₃ doped glass matrix

The increase in the Eu₂O₃ composition in the glass matrix enhances various optical parameters such as refractive index, polaron radius, inter-ionic distance, molar refractivity, electronic polarizability, dielectric constant and density. Concentration and field strength values show the decreasing trend with increase of europium content. It is observed the (Table 4).

Eu ₂ O ₃	0.01	0.05	0.1	0.5	1	1.5	2	2.5	3
concentration(mole/lit)	0.00288	0.03137	0.06742	0.35218	0.70696	1.06588	1.41281	1.75278	2.07267
concentration(ion/cc)	3.17E+18	2.03E+19	4.20E+19	2.14E+20	4.27E+20	6.43E+20	8.52E+20	1.06E+21	1.25E+21
inter-molecular distance	5.23E-07	2.72E-07	1.98E-07	8.01E-08	4.57E-08	2.89E-08	1.85E-08	1.12E-08	5.90E-09
molar volume(g/cc)	22.2822	22.2745	22.1348	22.3632	22.4182	22.4484	22.5594	22.7032	22.9499
molar refractivity	8.07422	8.13699	8.116	8.2321	8.61243	8.68686	8.75169	8.82829	8.96757
electric polarizability	1.59E-20	2.43E-21	1.69E-21	3.12E-22	1.70E-22	1.12E-22	9.26E-23	7.66E-23	6.33E-23
reflection losses	4.44502	4.51273	4.53987	4.58063	4.96411	5.03313	5.06079	5.08847	5.14391
metallization factors	0.39876	0.39643	0.39549	0.3941	0.3941	0.37896	0.37806	0.37716	0.37535

Table 4: The data of physical parameters of Eu³⁺ doped glass matrix.

That the concentration increases with increasing Eu₂O₃ composition in the glass matrix. It should be mentioned that the europium ions are assumed to be uniformly distributed in the glass matrix. Also, observed from (Figure 11).

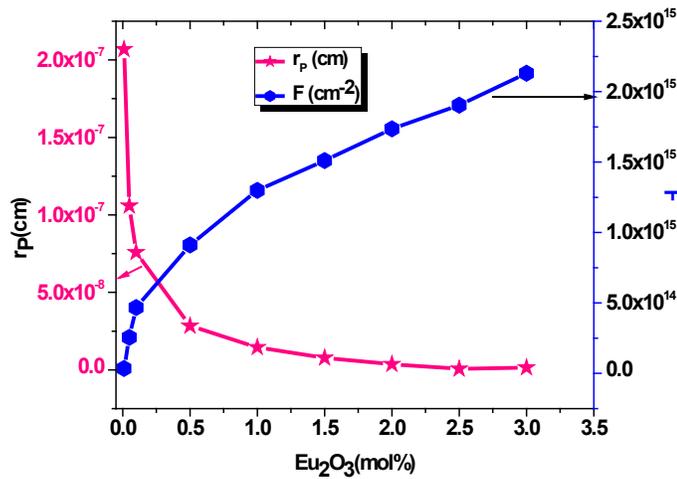


Figure 11: The variation of polaron radius (r_p) & field strength (F) of Eu^{3+} doped glass matrix.

That the decrease of polaron radius with increasing Eu^{3+} content is most likely related to the increased value of ionic concentration (N) of europium. The RE (rare earth) ions are situated between the layers and thus the average RE– oxygen distance decrease. As a result of that, the Eu-O bond strength increase, producing a stronger field around the Eu^{3+} ions. The variation of refractive index and density is shown in (Figure 10 & 12) respectively.

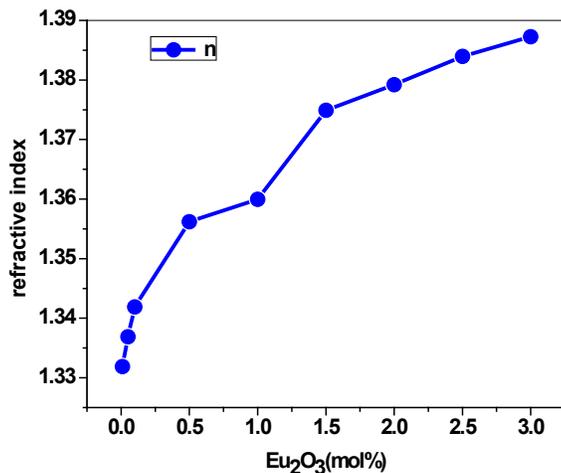


Figure 10: The refractive index of Eu^{3+} doped glass matrix.

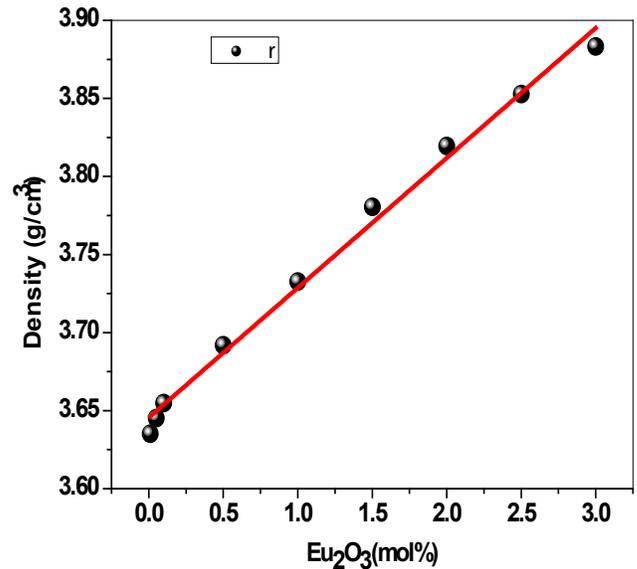


Figure 12: The density of Eu^{3+} doped glass matrix.

The current study pointed out a thing that the glass ceramic materials with good dense and physical stability like samarium doped borate glasses are well suited for potential optical transparent materials in bio processing and bio techniques. Therefore, these kinds of materials will have some attractive importance in optical transparent materials or glass slides which are being used in biomedical treatments. The present glass ceramics have showed good density and physical stability than the reported literature [1].

Conclusions

The values of optical band gaps of the glass sample are due to direct transitions. Decreasing of E_g values confirms the extension of localized states into band gap. The observed variations in band gap are due to oxide ion polarizability and hence the structural changes may occur in the glass network with the replacement of rare earth oxides. Hence, these materials can act as glass network modifier (GNM). The decrease of band gap energy in turn causes to increase of refractive index with doping content. The density of glasses is decreasing with doping item and increasing with composition i.e. in case of Sm^{3+} Dy^{3+} and Eu^{3+} doped glass, density are varying from 4.02-4.25 g/cm^3 , 3.89-4.13 g/cm^3 & 3.64-3.89 g/cm^3 respectively. It is interesting to note that the increase in the rare earth doped composition in the glass matrix enhance various

optical parameters such as refractive index, polaron radius, inter-ionic distance, molar refractivity, electronic polarizability, dielectric constant and density. The motivation and novelty behind this study is to report the good dense as well as the physical stability of borate glasses.

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