Synthesis and structural analysis of trivalent europium (Eu$^{3+}$) ions doped oxyfluoride (ZnBiNaPSr) glasses as prominent host materials for optical devices

D Siva Raju$^{1,2}$, S Hima Bindu$^3$, J Suresh Krishna$^1$, V Vinay Krishna$^4$ and Ch Linga Raju$^{1*}$

1 Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar - 522510, A.P, India
2 Department of Physics, Indian Institute of Science Education and Research Tirupati, Tirupati- 517501, A.P, India
3 Department of Physics, National Institute of Technology Warangal, Warangal-506004, Telangana, India
4 Department of Electronics & Instrumentation Technology, Acharya Nagarjuna University, Nagarjuna Nagar- 522510, A.P, India

*E-mail: drchlraj_phy@yahoo.com

Abstract. A series of trivalent europium (Eu$^{3+}$) ions doped zinc sodium strontium activated bismuth phosphate (P$_2$O$_5$-Bi$_2$O$_3$-Na$_2$CO$_3$-SrCO$_3$-ZnF$_2$-Eu$_2$O$_3$) glasses of different dopant ion compositions have been prepared by conventional melt quenching technique. Physical and optical parameters of the prepared glasses such as density ($\rho$), molecular weight ($M_i$), molar volume ($V_M$), rare-earth ion concentration ($N_{RE}$), polaron radius ($r_p$), inter nuclear distance ($r_i$) field strength ($F$), oxygen to phosphorus (O/P) ratio, refractive index ($n$), dielectric constant ($\epsilon$), reflection losses ($R$), molar refractivity ($R_M$), electron polarizability ($\alpha_M$), susceptibility ($\chi$) oxygen packing density (OPD), metallization (M) and reflection factor (P) have been evaluated using the standard formulae. The amorphous/glassy nature was confirmed by the XRD pattern showing the broad hump centered at $2\theta=28^0$. Surface morphological studies have been carried out using SEM analysis and EDS spectra reveal the successful incorporation of Eu$^{3+}$ ions into the host matrix. Structural information was obtained from FT-IR spectra, recorded in 4000-400 cm$^{-1}$ spectral region which consists of symmetrical, asymmetrical stretching and bending P=O, P-O-P, O-P-O and P-O-H vibrations along with OH$^-$ groups. Furthermore, all the prepared glasses were subjected to study for their optical and luminescence properties in detailed.

1. Introduction
In recent years, extensive research work has been carried out for fabricating optical devices including solid-state lasers, fibre amplifiers, luminescent materials, LEDs, biosensors, solar cells, waveguide lasers, memory storage devices, etc., for their requirement in various fields [1, 2]. Lasers made of glass materials activated with rare earth (RE) ions are present interesting subject for researchers and developing an effective active medium is a challenging task in physics experiments. Oxide glasses have proven the best and suitable host materials for rare earth ions because of the excellent transparency,
compositional variety and easy mass production [3]. Among the oxide glasses, phosphate glasses have grabbed good attention due to their low melting point, refractive index, dispersion and high transparency, electrical conductivity and good thermo-optic properties. The phosphate glasses can have high optical energy storage capacity at greater densities than other hosts. [4, 5]. For the luminescence applications, phosphate glasses were found to be suitable host materials because of high rare earth ions solubility which is 1000 times greater than borate and silicate glasses. The oxygen to phosphorus (O/P) atomic ratio describes the tetrahedral structure of the phosphate having various structural units (Qn, n=0-3), where n represents the number of bridging oxygens for tetrahedron [6]. The fluoride content in the glass matrix can react with OH group leads to decreasing the OH absorption and cut-off edges may be shifted towards the longer wavelengths in the infrared region, make the glass matrix as a suitable host in fibre amplifiers [7]. Fluorophosphate (FP) glasses, have considerable interest because of the wide range transmission, low linear and nonlinear refractive indices, thermal behaviour, low hydroxyl-content, high solubility of rare earth ions with broad absorption as well emission bands and long fluorescence life time [8].

The poor chemical stability, durability and glass forming ability of the phosphate glasses can be improved by the addition of one or more metal oxides. These additives can form relatively M-O-P (M=metal) cross linked bonds and acts like network former, modifier or intermediate etc. It was reported that Bi2O3 occupies both network forming and network modifying positions in oxides glasses when introduced in the network as B2O3 units [9, 10]. In the present system, it is assumed that bismuth oxide (Bi2O3) can form both network forming and network-modifying units conditionally and addition of ZnF2, Na2CO3 and SrCO3 can increase the chemical durability, mechanical strength, fluorescence efficiency and leads to disruption of the glass network which enhances the formation of nonbridging oxygen groups [11, 12]. RE ions doped oxyfluoride glasses have been played a vital role in the application and design of high efficiency photonic devices and solid-state lasers and having good optical properties from ultraviolet to near-infrared regions [13]. The trivalent europium (Eu3+) ion is a prominent material for strongest red emission (612 nm) with narrow emission band (5D0 → 7F2). In this paper the author mainly focuses on preparation and structural characterizations of prepared glasses which serves as a host material for the development of solid state laser applications.

2. Experimental

The molar composition of europium doped oxyfluoride glasses in the present work is (65-x) P2O5 + 15 Bi2O3 + 10 Na2CO3 + 5 SrCO3 + 5 ZnF2 + x Eu2O3 (where x =0, 0.1, 0.5, 1.0, 1.5 and 2.0 mol%). About 15 g batches of each said composition were prepared by adopting the conventional melt quenching technique. In order to prepare the samples, analytical regent (AR) grade chemicals of ammonium dihydrogen phosphate (NH4H2PO4), bismuth oxide (Bi2O3), sodium carbonate (Na2CO3), strontium carbonate (SrCO3), zinc fluoride (ZnF2), and europium oxide (Eu2O3) were weighed using an electrical balance and grounded thoroughly in an agate mortar to get a homogeneous mixture. The mixture is then taken into silica crucible and melted in an electrical furnace for 1 h at 1150 °C. Then the melt is air quenched by pouring on a preheated thick brass plate and pressed against another brass plate. The glasses obtained were annealed about their glass transition temperature i.e. 400 °C for 8 h in an annealing furnace and slowly cooled to room temperature to remove the thermal strains and stress. The obtained coin-shaped white transparent glass samples were polished to measure the optical properties and placed in paraffin liquid to prevent possible atmospheric moisture absorption.

The thickness of the glass sample was measured using digital vernier callipers (Mitutoyo, ± 0.001 cm). The density (ρ) of each prepared glass sample was measured at room temperature by employing the Archimedes principle with an electrical balance (Shimadzu, ± 0.00001 g) using O-xylene (0.879 g/ml) as an immersion liquid. The refractive indices (n) are measured using an Abbe refractometer (ATAGO) at sodium wavelength, 589.3 nm (D line) with 1-Bromonaphthalene (C10H1Br) as a contact liquid. X-ray diffractograms of the powder form of the sample were recorded using RIGAKU X-ray diffractometer (40 kV, 15 mA) with Cu-Kα radiation (1.541852 Å), scan speed, step and range are 10°/ min, 0.02° and 10-90° respectively. The gold coating was performed for the samples for recording the SEM images.
The energy dispersive spectra (EDS) spectra was recorded using Thermo fisher scientific SEM (Apreo LoVac) instrument with an image resolution of 1 nm at 1 kV, magnification of 600000x and EDS spectra resolution of 127 eV on Mn-Kα. The FT-IR transmission spectra were recorded in the 4000-400 cm\(^{-1}\) range at room temperature with FTIR spectrometer (Bruker Alpha –II) of 2 cm\(^{-1}\) resolution at room temperature.

3. Results and discussion

3.1 Physical and optical properties

A few important physical and optical properties of the prepared samples at room temperature were measured/calculated using the below mentioned formulas [14-17] and obtained values are reported in table 1.

The density (\(\rho\)) of the glass samples is determined by:

\[
\rho = \frac{(a-b)}{a} \times \rho_b \tag{1}
\]

where \(a\) & \(b\) are the weight of the sample in air and immersed liquid respectively, \(\rho_b\) is the density of the liquid.

The average molecular weight (\(M_i\)) of the glass system is given by:

\[
M_i = \sum (x_i W_i) \tag{2}
\]

where \(x_i\) and \(W_i\) are the molar fraction and weight fraction of each component of the constituents.

The molar volume (\(V_M\)) of samples was calculated using the following formula:

\[
V_M = \frac{M_i}{\rho} \tag{3}
\]

The Eu\(^{3+}\) ions concentration (\(N_{RE}\)) in the glass system is determined by:

\[
N_{RE} = \frac{(\rho / M_i) \times (y / x) \times 1000 (\text{mol} / \text{lit})}{\text{Avogadro's number} \times \text{Average molecular weight of the glass (ions / cm}^3\text{)}}. \tag{4}
\]

where \(x\) & \(y\) are the total weight of the glass and weight of the Eu\(^{3+}\) ions in (g) in each glass composition \(N_A\) is the Avogadro’s number (\(N_A = 6.023 \times 10^{23} \text{mol}^{-1}\)).

The polaron radius (\(r_p\)) in terms of rare earth ion concentration is determined by:

\[
r_p = \left(\frac{1}{2}\right) \left(\frac{\pi}{6 N_{RE}}\right)^{\frac{1}{3}} \tag{5}
\]

The interionic distance (\(r_i\)) is determined by:

\[
r_i = \left(\frac{1}{N_{RE}}\right)^{\frac{1}{3}} \tag{6}
\]

The field strength (\(F\)) is determined by:

\[
F = \left(z / r_p^2\right) \tag{7}
\]

where \(z\) is the oxidation state of europium ion (+3).

The oxygen to Phosphorus (O/P) is the ratio between no of oxygen atoms (O) to the no of phosphorus atoms (P) in the respective glass compositions.

The dielectric constant (\(\varepsilon\)) is given by:

\[
\varepsilon = n^2 \tag{8}
\]

The optical dielectric constant (\(\varepsilon\)) is given by:

\[
\varepsilon = n^2 - 1 \tag{9}
\]

The reflection loss (R) % is given by:

\[
R = \left(\frac{n-1}{n+1}\right)^2 \times 100. \tag{10}
\]

The molar refractivity (\(R_M\)) is given by:

\[
R_M = V_M \left(\frac{n^2 - 1}{n^2 + 2}\right). \tag{11}
\]

The electron polarizability (\(\alpha_e\)) is given by:

\[
\alpha_e = R_M \left(\frac{3}{4\pi N_A}\right). \tag{12}
\]
The electrical susceptibility (μ) is given by:

\[ \mu = \left( \frac{n^2 - 1}{4\pi} \right). \]  (13)

The oxygen packing density is given by:

\[ \text{OPD} = 1000 \times \text{No. of oxygen atoms} \times (\rho / M_i). \]  (14)

The metallization (M) is given by:

\[ M = \left( 1 - \frac{R_M}{V_M} \right). \]  (15)

The reflection factor (P) is given by:

\[ P = \frac{2n}{n^2 + 1}. \]  (16)

where \( n \) is the refractive index in all the above equations.

**Table 1.** Physical and optical parameters of undoped and Eu\(^{3+}\) doped ZnBiNaPSr glasses.

| Physical and optical parameters | Host | Eu0.1 | Eu0.5 | Eu1.0 | Eu1.5 | Eu2.0 |
|---------------------------------|------|-------|-------|-------|-------|-------|
| Thickness (t), cm              | 0.623| 0.633 | 0.618 | 0.621 | 0.612 | 0.635 |
| Density (ρ), cm\(^3\)          | 3.573| 3.581 | 3.597 | 3.643 | 3.678 | 3.712 |
|Avg. molecular weight (M\(_i\)), g/mol | 242.58 | 242.70 | 243.19 | 243.80 | 244.11 | 245.02 |
| Molar volume (V\(_M\)), cm\(^3\)/mol | 67.893 | 67.775 | 67.609 | 66.923 | 66.452 | 66.007 |
|RE ion concen. (N\(_{RE} \times 10^{21}\)), ions/cm\(^3\) | 0 | 0.888 | 4.454 | 8.999 | 13.595 | 18.249 |
|Polaron radius (r\(_P\)), Å   | 0   | 4.192 | 2.448 | 1.937 | 1.688 | 1.530 |
|Inter nuclear distance (r\(_i\)), Å | 0   | 10.403 | 6.077 | 4.807 | 4.189 | 3.798 |
|Field strength (F \times 10^{15}), cm\(^2\) | 0 | 1.707 | 5.006 | 7.995 | 10.528 | 12.815 |
|Oxygen to phosphorus ratio (O/P) | 4.692 | 4.695 | 4.709 | 4.726 | 4.744 | 4.761 |
|Refractive index (n)            | 1.618 | 1.619 | 1.622 | 1.625 | 1.627 | 1.629 |
|Dielectric constant (ε)        | 2.617 | 2.621 | 2.630 | 2.640 | 2.647 | 2.657 |
|Optical dielectric constant (ε) | 1.617 | 1.621 | 1.630 | 1.640 | 1.647 | 1.657 |
|Reflection loss (R), %         | 5.572 | 5.586 | 5.627 | 5.668 | 5.696 | 5.724 |
|Molar refractivity (R\(_M\)), cm\(^3\) | 23.777 | 23.774 | 23.801 | 23.653 | 23.552 | 23.449 |
|Electron polarizability (α\(_e\) \times 10^{24}), cm\(^3\) | 9.429 | 9.428 | 9.438 | 9.380 | 9.339 | 9.229 |
|Oxygen packing density (OPD)   | 89.846 | 89.929 | 89.944 | 90.402 | 90.666 | 90.898 |
|Metallization (M)              | 0.649 | 0.649 | 0.647 | 0.646 | 0.645 | 0.644 |
|Reflection factor (P)          | 0.894 | 0.894 | 0.893 | 0.892 | 0.892 | 0.891 |

The physical parameters will be played a remarkable role in the development of optical materials and which could be used to predict the structural information of different glasses. The density (ρ) of the prepared glass samples found to be increased from 3.572 to 3.724 g/cm\(^3\) with an increase in Eu\(_2\)O\(_3\) content from 0 to 2.0 mol%. This was expected as the low-density phosphate element (1.8 g/cm\(^3\)) was replaced with the high-density europium element (7.4 g/cm\(^3\)). An increment was observed in the average molecular weight (M\(_i\)) because of the europium has high molecular mass relatively to the phosphate. We may predict that addition of Eu\(_2\)O\(_3\) in glass matrix can form the more nonbridging oxygens by breaking the bond of host network and which results in a compact structure. The decreasing trend in molar volume of the glass network may be due to decreasing inter-atomic spacing among the atoms or decreasing in the bond length with a strong covalent nature [18, 19]. The change in rare earth ion concentration is due to change in Eu\(_2\)O\(_3\) content, therefore, it is an expected result. Polaron radius and inter nuclear distances are found to be decreased with increase in RE ion concentration, it means that the free space decreases as well as the glass structure became more compact. The filed strength is observed to be increased with increase in Eu\(_2\)O\(_3\) content, which is because of strong Eu-O bond strength, can have strong field strength around Eu\(^{3+}\) ions. Based on oxygen to phosphorus (O/P) atomic ratio, the
phosphate glass system can be in ultra-phosphate (2.5 ≤ [O]/[P] < 3) structure with dominated Q\(^2\) and Q\(^3\) structural units, meta-phosphate ([O]/[P] = 3.0) structure consists of rings and/or long chains of Q\(^2\) structural units or poly-phosphate ([O]/[P] > 3.0) structure based on Q\(^2\) chains terminated by Q\(^1\) tetrahedra [20]. The O/P atomic ratio in the present work reveals the presence of polyphosphate structure, further it can be classified into pyrophosphate and orthophosphate structure. The O/P ratio value is close to ortho-phosphate structure with Q\(^0\) represents an isolated (PO\(_4^3\)) units and coexist with small amounts of pyro-phosphate (P\(_2\)O\(_7^4\)) and meta-phosphate units (PO\(_3^–\)) [21-24].

Non bridging oxygens (NBOs) play an important role in determining the refractive index than bridging oxygen because of its more polarizability. The refractive index values are ranging from 1.618 to 1.629 with Eu\(_2\)O\(_3\) concentration, however increasing the values with a high amount of switching of Eu\(_2\)O\(_3\) into phosphate results the breakage of P-O-P bridging units and accumulate a greater number of non-bridging oxygens. Dielectric constant value is ranging from 2.617 to 2.653 however, it depends on chemical composition, the process of preparation and also affected by the type of bonding and crystallinity. The value of dielectric constant in the optical materials may be depends on different factors such as preparation technique, molar composition etc., and high resistance can have the slower transmission because since dielectric constant is larger. The increasing trend of dielectric constant with Eu\(_2\)O\(_3\) content in the present glass system is an indicative of more compact nature. Reflectivity was calculated using Fresnel’s equations. The molar refractivity and electron polarizability values are calculated using Lorentz-Lorentz, Clausius-Mosotti equations respectively. The obtained values are increased for lower concentrations and further decreased for higher concentrations of Eu\(^{3+}\) ion and calculated values following the nonlinear trend. The insulating nature was observed with metallization however, in the present study its average value is ~ 0.646. In general, the value closest to zero indicates the conducting nature and closest to one indicates to the insulating nature. The opposite trend was observed between dielectric constant and the metallization which may be due to the conversation of large number of bridging oxygens to nonbridging oxygens by breaking the P-O-P bonds in phosphate network, which is indicative of close-packed glass structure. The increasing trend was observed in oxygen packing density (OPD), which is an expected result because of the availability of a greater number of oxygen atoms in the Eu\(_2\)O\(_3\) content [25-28]. The variation of obtained parameters w.r.to europium ion content is shown figure 1(a), (b) and (c) and the trends are in good agreement with many Eu\(^{3+}\) doped glass studies (Young et al.[10], Selvi et al.[13], Hima et al.[14], and Chima et al.[16], etc.).

3.2 X-ray diffraction
X-ray diffraction is a quite useful technique to detect the crystal structure and phase purity of prepared samples. The XRD pattern of host and different concentrations of europium doped titled glasses

![Figure 1(a)](image_url)

**Figure 1(a).** Variation of density and molar volume (b) Polaron radius and field strength (c) density and refractive index with Eu\(_2\)O\(_3\) concentration.
recorded at room temperature is shown in figure 2. A broad hunch was observed in $2\theta = 20-35^\circ$ range centred at $2\theta = 28^\circ$, which is a characteristic peak of glass materials and no other crystalline peaks were detected in the entire spectrum. This result confirms the prepared glasses have amorphous nature [29].

![Figure 2](image-url)

**Figure 2.** XRD pattern of ZnBiNaPSr glasses.

3.3 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectra (EDS)
The SEM images of host glass, 1.0 mol% and 2.0 mol% of Eu$^{3+}$ doped glasses scanned at 100 nm are shown in figure 3(a) and (b) respectively. Both images were found to be similar and have not shown any agglomerative structures, which confirm the glassy surface of the prepared glasses [30].

![Figure 3(a)](image-url)

**Figure 3(a).** SEM image of ZnBiNaPSr (a) and ZnBiNaPSr: Eu2.0 glasses.

The energy dispersive spectra allow the elemental composition of the specimen to be measured. The EDS spectra reveal the successful incorporation of europium ion in the host matrix. This spectrum confirms the presence of C, O, Na, P, Zn, Sr, Bi and Eu (except in host) ions in the present glass system and images corresponding to host, 1.0 mol% and 2.0 mol% Eu$^{3+}$ doped glasses are shown in figure 4(a), (b) and (c) respectively. Moreover, the weight percentages are nearly equal to the nominal value of stoichiometry of constituents present in the glass host matrix.

![Figure 4(a)](image-url)

**Figure 4 (a).** EDS spectra of ZnBiNaPSr (b) ZnBiNaPSr: Eu1.0 (c) ZnBiNaPSr: Eu2.0 glasses.
3.4 Fourier Transform Infrared spectroscopy (FT-IR)

Fourier Transform Infrared (FT-IR) spectroscopy is one of the most powerful techniques that provide information about structural components and interactions among various constituents of the glass network. Identification of an absorption peak at a particular frequency of the infrared region will reveal the nature of the bonding with the stretching and bending vibrations of O-H, C-H, C-O and C=C groups. The FT-IR absorption spectra of the prepared glasses were recorded over 4000 - 400 cm\(^{-1}\) at room temperature is shown in figure 5. This spectrum provides the information about phosphate bonds present in the glass network such as P=O, P-O-P, O-P-O and P-O-H. The P-O-H bond can reveal the hygroscopic nature of the prepared samples. No large bands shift was observed in the obtained spectra due to the high amount of phosphate (> 60%) content present in the glass systems.

![Figure 5. FTIR spectra of the ZnBiNaSr glasses.](image)

The diagnostic region (or) functional group region i.e., 4000-1500 cm\(^{-1}\), near to IR region a small broadband centred at 3575 cm\(^{-1}\) assigned to the symmetric stretching vibrations of O-H groups (H-O-H), due to the possibility of absorption of atmospheric moisture. The deplete intensity of this broadband may be due to the existence of metal ions in the glass composition can possibly absorb surface water vapour [31]. The weak absorption bands centred at 2396 cm\(^{-1}\) and 2358 cm\(^{-1}\) are assigned to P-O-H stretching vibrations. The band centred at 1668 cm\(^{-1}\) is due to hydrogen bonding with nonbridging oxygen which was assigned to P-O-H bridge [32]. The weak absorption band centred at 1368 cm\(^{-1}\) is assigned to stretching modes P=O. A very sharp strong band centred at 1287 cm\(^{-1}\) is assigned to asymmetric stretching vibrations of doubly bonded oxygen groups i.e. \(\nu_{as}(P=O)[33]\). The band observed in the region 1170 - 1161 cm\(^{-1}\) is assigned to PO\(_2\) symmetric stretching vibrations. We have observed that the PO\(_2\) symmetric stretching vibrational bands shift towards the lower wavenumber 1161 cm\(^{-1}\) from 1170 cm\(^{-1}\) with increase in Eu\(_2\)O\(_3\) content. This band shifting towards the lower frequencies indicates that the increasing covalent nature with increasing the europium content [34]. The absorption bands in the region 907-912 cm\(^{-1}\) and 764 -780 cm\(^{-1}\) are assigned to asymmetric and symmetric stretching vibrations of P-O-P. The wavenumber of these absorption bands \(\nu_{as}(P-O-P)\) and \(\nu_{s}(P-O-P)\) is shifting towards the higher frequency with the increase in europium content. The symmetric and asymmetric P-O-P bands shifting towards the higher frequencies are due to increasing the covalent nature [35]. The band centred at 618 cm\(^{-1}\) is attributed to the vibrational bands of Bi-O bonds in BiO\(_6\) groups, might be due to the conversion of bridging oxygen (BO) atoms into nonbridging (NBO) atoms. The band centred at 575 cm\(^{-1}\) is assigned to deformation modes of P-O (PO\(_3^3\)). The bands in the very low frequency region of 418-521 cm\(^{-1}\) are attributed due to the deformation vibrations in phosphate groups with the addition of heavy metal oxides used in the preparation of the glass network. The absorption band centred at 521 cm\(^{-1}\) is assigned to P-O deformation and the band centred at 420 cm\(^{-1}\) is assigned to metal-oxygen bond [36].
bands, P-O-P asymmetrical stretching (~ 908 cm$^{-1}$) and P-O-P symmetrical stretching (~ 770 cm$^{-1}$) may indicate the existence of orthophosphate (PO$_4^3-$) units (Q$^0$ tetrahedra) and pyrophosphate (P$_2$O$_7^{4-}$) units (Q$^1$ tetrahedra). The sharp asymmetric stretching vibrational band centred at 1287 cm$^{-1}$ may indicate the existence of meta-phosphate (PO$_3^2-$) units (Q$^2$ tetrahedra) in the glass system. The existence of orthophosphate (PO$_4^3-$) units (Q$^0$ tetrahedra) in addition to the small amount of pyrophosphate (P$_2$O$_7^{4-}$) units (Q$^1$ tetrahedra) and meta-phosphate (PO$_3^2-$) units (Q$^2$ tetrahedra), which is good agreement with the calculated oxygen to phosphorus (O/P) ratio [11, 22, 37]. The observed FTIR bands and corresponding band assignments are listed in table 2.

| Sample/Host | Band assignment | Eu 0.1 | Eu 0.5 | Eu 1.0 | Eu 1.5 | Eu 2.0 | References |
|-------------|----------------|--------|--------|--------|--------|--------|------------|
| O-H$_{\text{(sl)}}$ | 3573 | 3573 | 3575 | 3575 | 3575 | [31] |
| P-O-H$_{\text{(sl)}}$ | 2396 | 2396 | 2396 | 2396 | 2396 | [32] |
| P-O-H$_{\text{(sl)}}$ | 2355 | 2358 | 2355 | 2358 | 2358 | [32] |
| P-O-H$_{\text{(bridge)}}$ | 1665 | 1668 | 1668 | 1667 | 1669 | [32] |
| P=O$_{\text{(as)}}$ | 1286 | 1286 | 1286 | 1287 | 1287 | [32] |
| PO$_2$(as) | 1170 | 1168 | 1166 | 1165 | 1164 | [34] |
| P-O-P$_{\text{(as)}}$ | 902 | 903 | 905 | 907 | 908 | [35] |
| P-O-P$_{\text{O}}$ | 764 | 768 | 771 | 773 | 775 | [35] |
| Bi-O$_{\text{(v)}}$ | 612 | 614 | 616 | 617 | 618 | [11] |
| P-O (PO$_4^{3-}$) | 575 | 574 | 575 | 575 | 576 | [18] |
| M-O (M=metal) | 418 | 418 | 419 | 421 | 420 | [36] |

4 Conclusion

In summary, Eu$^{3+}$ ions doped oxyfluoride glasses were successfully prepared by adopting melt quenching technique. The physical and optical parameters have been evaluated for all the prepared glasses. In physical parameters increasing trend was observed in density, rare earth ion concentration, field strength and oxygen to phosphorus ratio with the increasing concentration of Eu$^{3+}$ ions. In optical parameters increasing trend was observed in refractive index and oxygen packing density with the increasing concentration of dopant ion. The trends are in good agreement with the others reported for europium ions doped phosphate glasses. The amorphous nature of the prepared glasses was confirmed by XRD spectra. No agglomeration was observed in SEM images at 100 nm scale and EDX spectra showed the presence of the ions that are involved in the preparation of glass samples. The structural analysis was carried out with FTIR spectra in which symmetrical, asymmetrical stretching and bending vibrations along with OH groups have been observed. The frequencies of the symmetric and asymmetric P-O-P bands are shifting towards the higher wave number with the increasing concentration of dopant ion are an indicative of the presence of high covalent nature. The bands at ~ 908 cm$^{-1}$ and ~ 770 cm$^{-1}$ corresponding to P-O-P asymmetrical stretching and symmetrical stretching, which may be an indicative of the existence of orthophosphate (PO$_4^3-$) units (Q$^0$ tetrahedra) and pyrophosphate (P$_2$O$_7^{4-}$) units (Q$^1$ tetrahedra). The overall results observed for oxyfluoride glasses have unique identity and followed similar trends to the other reports.

Acknowledgments

One of the authors (D Siva Raju), expressed his gratitude to the UGC, Government of India, for their financial support by awarding Rajiv Gandhi National Fellowship (2016-17).
References

[1] Vijaya N and Jayasankar C K 2012 *J. Mol. Struct.* **1036** 42.

[2] Madhukar Reddy C, Deva Prasad Raju B, John Sushma N, Dhoble N S and Dhoble S J 2015 *Renew. Sustain. Energy Rev.* **51** 566.

[3] Deva Prasad Raju B and Madhukar Reddy C 2012 *Opt. Mater.* **34** 1251.

[4] Linganna K and Jayasankar C K 2012 *Spectrochim. Acta A* **97** 788.

[5] Reza Dousti M, Pozirier G Y and Andrea Simone Strucchi de Camargo 2015 *Opt. Mater.* **45** 185.

[6] Kaushal Jha and Jayasimhadri M 2017 *J. Am. Ceram. Soc.* 1.

[7] Xavier Joseph, Rani George, Sunil Thomas, Manju Gopinath, Sajna M S and Unnikrishnan N V 2014 *Opt. Mater.* **37** 655.

[8] Kesavulu C R, Kiran Kumar K, Vijaya N, Ki-Soo Lim and Jayasankar C K 2013 *Mater. Chem. Phys.* **141** 903.

[9] Bulus I, Isah M, Garba M E, Hussian R and Dalhatu S A 2018 *Niger. J. Technol. Dev.* **15** 121.

[10] Young Hoon NA, Nam Jin KIM, Sang Hyeok CHA and Ki RYU 2009 *J. Ceram. Soc. JAPAN* **117** 1273.

[11] Marzouk M A, ElBatal F H and ElBatal H A 2018, *Silicon* **10** 615.

[12] Deepa Shajan, Priya Murugasen and Suresh Sagadevan 2017 *Optik* **136** 165.

[13] Selvi S, Marimuthu K, Suriya Murthy N and Muralidharan G 2016 *J. Mol. Struct.* **1036** 42.

[14] Hima Bindu S, Siva Raju D, Vinay Krishna V, Rajavardhana Rao T, Veerabrahmam K and Ch. Linga Raju 2016 *Opt. Mater.* **62** 655.

[15] Rajesh M, Reddi Babu M, John Sushma N and Deva Prasad Raju B 2019 *J. Non. Cryst. Solids* **528** 119732.

[16] Chimalawong P, Kirdsiri K, Kaewkhao J and Limsuman P 2012 *Procedia Eng.* **32** 690.

[17] Ali A A, Shaban H M and Abdallah A 2008 *Opt. Mater.* **30** 900.

[18] James Kirkpatrick R and Brow R K 1995, *Solid State Nucl. Magn. Reson.* **5** 49.

[19] Abo-Naf S M, El-Amiry M S and Abdel-Khalek A A 2008 *Opt. Mater.* **30** 900.

[20] Smith C E and Brow R K 2014 *J. Non. Cryst. Solids* **390** 51.

[21] Tiwari B, Dixit A and Kothiyal G P 2007 *Barec Newsletter* **285** 167.

[22] Ramirez R M, Abdelghany A M and Elbatal H A 2018 *Silicon* **10** 891.

[23] Marimuthu K, Karunakaran R T, Surendra Babu S, Muralidharan G, Arumugam S and Jayasankar C K 2009 *Solid State Sci.* **11** 1297.

[24] Ratnakaram Y C, Reddy Prasad V, Babu S and Ravikanth Kumar VV 2016 *Bull. Mater. Sci.* **39** 1065.

[25] Li H S, Lin T S and Yang S W 1997 *Mater. Chem. Phys.* **50** 1.

[26] Coates J *Encyclopaedia of Analytical Chemistry* 1.

[27] Jirak J, Koudelka L, Pospisil J, Montagne P M and Delevoye L 2007 *J. Mater. Sci.* **42** 8592.