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A Study on the Effect of Eu^{3+} dopant on Physical and Photoluminescence Properties of Zinc Phospho-Sulfo-Tellurite Glasses

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Abstract

In this paper, the effect of substituting europium (Eu^{3+}) ion on physical and photoluminescence properties of zinc phosphor-sulfo-tellurite glasses is reported for the first time. The glass matrices with novel compositional range of $10ZnO–40TeO_2–10SO_3–(40-x)P_2O_5– xEu_2O^3$ were synthesized by convectional melt-quenching route and characterized via density and photoluminescence (PL) measurements. The non-linearity properties of these glasses was ascertained and dependence of red emission performance under λex= 394 nm excitation wavelengths disclosed bright red emission at λem. = 612nm. The concentration quenching phenomenon was observed after a particular value of europium ions (beyond 2 mol %). Thus, 2 mol% of Eu^{3+} in the glass composition was identified as the optimized concentration for the design and development of solid state red laser and color display devices.

Keywords: Phospho-Sulfo-Tellurite Glasses; Europium ion; Physical and Photoluminescence properties; Excitation Wavelength

I. Introduction

Over the past few decades, the spectroscopic properties of rare earth (RE) doped glass materials have received a lot of attention due to their potential applications in optical devices such as planar optical waveguides, solid state lasers, optical amplifiers, optical memories, optoelectronics and magneto-optical devices, etc. [1, 2]. Physical and photoluminescence analysis reveals that the non-linear and emission features of RE ions in glasses strongly depend on host matrix and can be modified by proper selection of network forming and modifying ions [3].

While, many researchers have tried to focus their attention on Eu^{3+} doped glasses such as boro-tellurite [4], sulpho borophosphate [5], tellurofluroborate [6] and flurophosphate glasses [7], the search for novel glass host with optimized concentration of rare earth ions that can be customized for the fabrication of new optical device is an ongoing issue in the field of material science and engineering.

Phospho-sulfo-tellurite glass matrix has been chosen in this study as a host due to its unique characteristics such as low dispersion, good transparency, and low refractive indices from the ultraviolet to near-infrared regions, good rare earth ion solubility, better chemical stability and durability.

Tellurium oxide (TeO_2) based glass consist of three-dimensional network structure in which the trigonal bipyramid units are connected to the edge and share random orientations. These structural changes usually occur because of the chosen chemical composition, involvement of various types of modifiers and conditions applied during glass preparation.

Conversely, phosphate network might provide many sites for rare earth dopants allowing relatively higher RE ion solubility [8].

However, incorporation of sulfate (intermediate) into tellurite and phosphate networks is expected to enhance the glass quality with an improvement in transparency, refractive index, density, thermal stability, moisture resistance, high gain coefficient, wide band width capability and IR transmission [5]. Addition of ZnO is essential to improve the moisture resistance of these glasses. The strong interaction of easily polarisable valence shells of Zn^{2+} ions with highly polarisable O^{2-} ions present in the zinc oxide may also be of particular interest for non-linear optical materials. For these reasons, this work aim to investigate the dominant role of europium oxide (Eu_2O_3) on the physical and photoluminescence properties of zinc phospho-sulfo-tellurite glass system.

II. MATERIALS AND METHODS

A. Sample preparation

A series of Eu^{3+} doped zinc phospho-sulfo-tellurite glasses with chemical composition of $10ZnO–40TeO_2–10SO_3–(40-x)P_2O_5– xEu_2O_3$, (where x = 0.5, 1.0, 1.5 and 2.0 mol %) labelled as 0.5Eu, 1.0Eu, 1.5Eu and 2.0Eu were prepared by the melt quenching technique. Appropriate amounts of the raw materials, $ZnCO_3$, TeO_2, H_2SO_4, H_3PO_4 and Eu_2O_3 of 99.9 % purity, were thoroughly mixed and ground in an agate mortar in 25 g batches. The prepared batches were heated in alumina crucible at 500℃ for 2 hours to ensure decarbonisation of the zinc carbonate. The temperature was then raised and maintained at 1100℃ for about one hour. The mixture was occasionally stirred to ensure homogeneous mixing of all constituents and to obtain bubble-free samples. Finally, the mixture was poured into a preheated brass mould and annealed at 300℃ in order to eliminate internal mechanical stress. Samples of good optical quality were selected and polished in order to study their luminescence properties. The chemical compositions of the samples are summarized in Table I.

Table I. Nominal composition of $ZnO–TeO_2–SO_3–P_2O_5$ glasses doped with different concentrations of Eu_2O_3 (in mol %)

S/N0	Sample code	ZnO	TeO_2	SO_3	P_2O_5	Eu_2O_3
1	0.05Eu	10	40	10	39.5	0.5
2	1.00Eu	10	40	10	39.0	1.0
3	1.50Eu	10	40	10	38.5	1.5
4	2.00Eu	10	40	10	38.0	2.0

B. Measurements

First, the density of glass sample were measured at room temperature using the Archimedes principle with toluene used as the immersion liquid. The weight of glass sample in the air and toluene were measured using a digital weighing machine with an accuracy of $\pm 0.0001g$.

Thereafter, the bulk glass samples were crushed and grinded in order to obtain fine powder. The fine powder of the sample with optimum concentration ($2.0\ mol\ \%$) was placed on the aluminium holder in the X'PERT PRO PW304 with Cu Kα radiation. The instrument was connected to a computer in order to generate the XRD pattern and also to record data at 2θ angles in the range of $80° \geq \theta \geq 0°$ for 30 minutes with the step of $0.02°$ during the scanning process.

Finally, the Perkin Elmer LS55 luminescence spectrophotometer was employed to characterize the luminescence analysis of Eu^{3+}-doped samples. The excitation and emission spectra of the samples were examined at 612 nm emission and 394 nm excitation wavelengths, respectively.

C. Fundamental Equations

Using Archimedes principle, the density of the glass samples can be computed using (1) [8]:

$$\rho = \frac{w_a}{w_a - w_l} \times 0.865\ gcm^{-3} \quad (1)$$

Where, w_a is the weight of glass in air, w_l is the weight of glass in toluene, and $0.865\ gcm^{-3}$ is the room temperature density of toluene. While, the molar volume (V_m) can be computed using the value of density as (2) [9]:

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

Where M is the molecular weight of the glass sample.

From the density measurement, other physical parameters such as neodymium ion concentration (N_i), polaron radius (r_p), inter-nuclear distance (r_i) and field strength (F) can be determined using the standard relations (3), (4) and (6) [10, 11].

The ion concentration of the dopant (Eu^{3+}) ions N_i is given as:

$$N_i = \frac{x\rho N}{M_a} \quad (3)$$

Where x is the mole fraction of dopant in mol%, N is the Avogadro's number and M_a is the average molecular weight of the prepared sample.

Polaron radius

$$r_p(\text{Å}) = \frac{1}{2}\left(\frac{\pi}{6N_i}\right)^{1/3} \quad (4)$$

Inter-nuclear distance

$$r_i(\text{Å}) = \left(\frac{1}{N_i}\right)^{1/3} \quad (5)$$

Field Strength (F)

$$\text{F} = \frac{Z}{r_p^2} \quad (6)$$

Where Z is the atomic number of the dopant

III. RESULTS AND DISCUSSION

A. XRD Analysis

X- ray diffraction is a useful method to readily detect the presence of crystals in a glassy matrix if their dimensions are

typically greater than 100 nm. The X-ray diffraction pattern of an amorphous material is distinct from that of crystalline material and consists of a few broad diffuse halos rather than sharp rings. The doped samples were tested, and the results showed the absence of crystalline characteristics. Fig. 1 depicts the typical X-ray diffraction pattern of zinc phospho-sulfo-tellurite glass containing 2.0 $mol\%$ Eu_2O_3. As seen from Fig. 1, the diffraction pattern of the prepared sample does not exhibit any sharp peak. This pattern indicates that the synthesized sample is amorphous in nature.

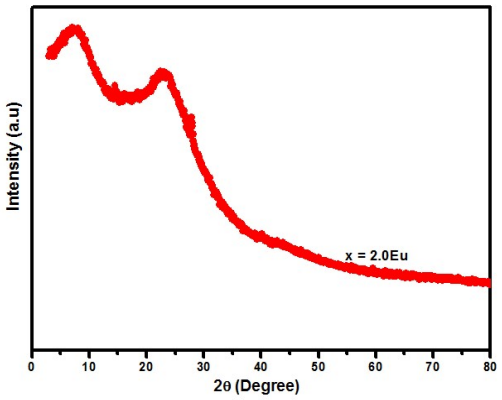

Fig. 1 XRD pattern of zinc tellurosulfo-phosphate glass sample containing 2.0 $mol\%$ Eu_2O_3

B. Physical properties Analysis

A summary of measured and computed values of density (ρ) along with other physical parameters such as molar volume (v_m), Ion concentration (N_i), Polaron radius (r_p), inter-nuclear distance (r_i), field strength (F) are are presented in Table II. While Fig. 2 depicted the variations of density and molar volume of neodymium doped zinc borosulfo-phosphate glass samples. It can be seen from Fig. 2, that density increases non-linearly while molar volume decreases when Eu_2O_3 composition in the glass samples varies from 0.5 to 2.0 mol %. This can be attributed to the addition of Eu_2O_3 which led to the modification of the P_2O_5 glass network. However, the molar volume was observed to vary between $51.126\ cm^3mol^{-1}$and $46.354\ cm^3mol^{-1}$ which depends primarily on the presence of phosphate units in the network structure of glass. The increase in density is attributed to the high relative molecular mass of Eu_2O_3 $(151.9640\ g/mol)$ compared to P_2O_5 $(141.94\ g/mol)$.

Furthermore, a rearrangement of the atoms was also observed as a result of the insertion of Eu_2O_3. The Eu^{3+} in the host network breaks the phosphate double bond, giving rise to the creation of more bridging oxygen. Thus, explaining the role of Eu^{3+} in transforming PO_3 to PO_4 in the glass network. On the contrary, the decrease in molar volume entails a decrease in bond length and inter-atomic distance between the atoms. Therefore, the compactness of the glass will increase and more bridging oxygen (BO) will be created which in turn increase the rigidity of the glass.

It is observed from Table II that the europium concentration N_i increases where as the polaron radius and internuclear distance of rare earth ions are found to decrease with the increase in europium oxide content in the compositions. This considerable decrease in the inter-nuclear distance from 6.576 to 4.261 Å and Polaron radius from 2.650 to 1.717 Å with the increase of dopant concentration is ascribed to the congestion of Eu^{3+} in the glass host. Consequently, the significant enhancement in the observed field strength $(8.869 - 21.137\ cm^2)$ is due to the occurrence of strong link between the Eu^{3+} and P- ions.

Table II. Physical properties of $10ZnO–40TeO_2–10SO_3–(40-x)P_2O_5– xEu_2O_3$ glasses

Physical Property	0.5Eu	1.0Eu	1.5Eu	2.0Eu
Average Molecular Weight (g)	102.042	102.150	102.258	102.420
$\rho\ (gcm^{-3})$	1.996	2.117	2.119	2.210
$v_m\ (cm^3mol^{-1})$	51.126	48.241	48.205	46.354
$Eu^{3+}N_i \times 10^{21}ionscm^{-2}$	03.534	06.242	08.730	12.991
$r_p(\AA) \times 10^{-8}$	2.650	2.193	1.961	1.717
$r_i(\AA) \times 10^{-8}$	6.576	4.540	4.464	4.261
$F \times 10^{16}cm^{-2}$	08.969	13.105	16.389	21.137

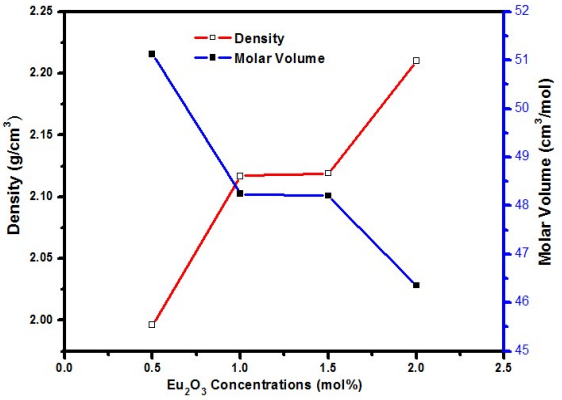

Fig. 2 Eu_2O_3 concentration dependent density and molar volume of zinc tellurosulfo-phosphate glasses

C. Photoluminescence Analysis

Fig. 3 displays the excitation spectra of $10ZnO–40TeO_2–10SO_3–(40-x)P_2O_5–xEu_2O_3$ glasses recorded from $320–560\ nm$ at an emission wavelength of $612\ nm$. These spectra have been analyzed in similar manner to those of other Eu^{3+} -doped glasses [12, 13]. Five excitation bands were noted originating from intra - 4f forbidden transition of Eu^{3+} ions at 358, 377, 394, 411 and 462 nm attributed to the electronic

transition of $^7F_0 \rightarrow {}^5D_4$, $^7F_0 \rightarrow {}^5L_7$, $^7F_0 \rightarrow {}^5L_6$, $^7F_0 \rightarrow {}^5D_3$ and $^7F_0 \rightarrow {}^5D_2$ transitions respectively. From these bands, the transition ($^7F_0 \rightarrow {}^5L_6$) at 394 nm exhibited prominent excitation intensity. Therefore, this prominent excitation wavelength has been used to excite the studied glass samples for emission spectra profiles.

Fig. 4 demonstrates the emission spectra of 10ZnO–40TeO$_2$–10SO$_3$–(40-x)P$_2$O$_5$–xEu$_2$O$_3$ glasses at 394 nm excitation. The emission peaks were observed at 587, 612, 650 and 698 nm corresponding $^5D_0 \rightarrow {}^7F_b$, (b = 1, 2, 3, and 4) electronic transition of Eu^{3+} ion. The $^5D_0 \rightarrow {}^7F_1$ transition defined as magnetic dipole transition (independent of host matrix) gives orange emission and is allowed by the selection rule $\Delta J=1$. Among all the transition, $^5D_0 \rightarrow {}^7F_2$ has been a super-sensitive transition (highly hypersensitive to the environment of Eu^{3+} ions) obeying the selection rule of $\Delta J = 2$ and hence gives bright red emission at 612 *nm*. 5D0$\rightarrow {}^7F_{2,4,6}$ are electric dipole in nature and their existence is ascribed to the absence of center of symmetry and mixing of 4f orbitals with opposite orbitals. However, $^5D_0 \rightarrow {}^7F_6$ transition which found to occur in the near infrared region was not observed. This could be due to the experimental deficiencies. In accordance with parity selection rule, $\Delta J = 0, 0 \leftrightarrow 0$ ($^5D_0 \rightarrow {}^7F_0$) transition is forbidden when Eu^{3+} occupies an inversion symmetry environment in the crystal lattice field. The current findings attest that the emission intensity of zinc-tellurosulfo-phosphates glasses is Eu^{3+} concentration dependent. In other word, the emission intensity increase proportionally with Eu$_2$O$_3$ content. The energy level diagram for excitation and emission transitions of Eu^{3+} doped zinc phospho-sulfo-tellurite glasses is presented in Fig. 5. As seen in Fig. 5, Eu^{3+} ions were pumped by 394 nm from the ground state ($^7F_0$) to the excited energy levels. A fast non radiative (NR) multiphonon relaxation from excited states ($^5L_6$) to the $^5D_0$ level results in emission transitions corresponding to $^5D_0 \rightarrow {}^7F_b$ (b = 1, 2, 3, 4).

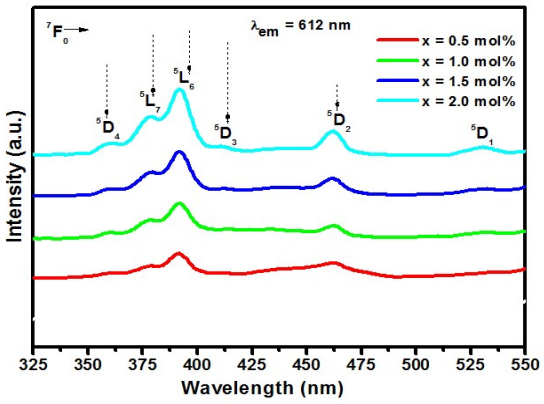

Fig. 3 Excitation spectra of 10ZnO–40TeO$_2$–10SO$_3$–(40-x)P$_2$O$_5$– xEu$_2$O$_3$ glasses

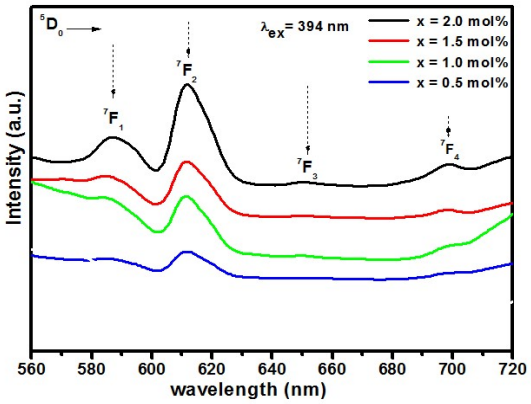

Fig. 4 Emission spectra of 10ZnO–40TeO$_2$–10SO$_3$–(40-x)P$_2$O$_5$– xEu2O3 glasses

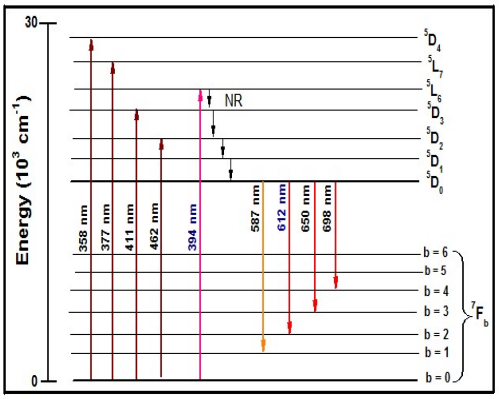

Fig. 5 Energy level diagram of all the observed excitation and emission transitions of 10ZnO–40TeO$_2$–10SO$_3$–(40-x)P$_2$O$_5$– xEu$_2$O$_3$ glasses.

IV. Conclusion

A study on the physical and luminescence features of Eu$_2$O$_3$ doped zinc phospho-sulfo-tellurite glasses was successfully carried out with results indicating the influence of different concentrations of Eu$_2$O$_3$ on the physical and photoluminescence properties of the glass samples. The study on the Physical properties revealed micro changes within the glass network. The non-linear behavior of density and molar volume suggests the existence of non-bridging oxygen as Eu$_2$O$_3$ is incorporated to the zinc phospho-sulfo-tellurite. However, the non-linear features observed from the physical properties of the synthesized glasses suggest their suitability for non-linear optical device applications. The photoluminescence analysis revealed the emission intensity increased with increase in Eu$_2$O$_3$ concentration from 0.5 to 2.0 *mol%*; while the quenching effect was observed beyond 2.0 *mol%*. Hence, 2.0 *mol%* (optimum concentration) contained sample of Eu^{3+} doped zinc phospho-

sulfo-tellurite glass could be suggested as promising luminescent host material for red lasers applications.

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