JUDD OFELT ANALYSIS AND OPTICAL PROPERTIES OF RARE EARTH DOPED TELLURITE GLASSES

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Abstract. In this work, the structural characteristic and photoluminescence properties were investigated in Eu^{3+} ions-doped B_2O_3 - $TeO_2 - ZnO$ - Na_2O glasses. These glasses were prepared by the melting method in air, after that thermal annealed $350 \,^{\circ}$ C, $450 \,^{\circ}$ C and $550 \,^{\circ}$ C for different times. The analysis results of structure on these glasses showed the formation of micro-crystals in host glass after thermal annealed process. The photoluminescence spectra of Eu^{3+} ions in these samples were observed. The local vibration mode around Eu^{3+} ions was investigated by the phonon side band associated with 7F_0 - 5D_2 transition of Eu^{3+} . Judd-Ofelt parameters have been evaluated from photoluminescence spectra and were to predict the luminescence intensity ratios of ${}^5D_0 \rightarrow {}^7F_J$ (J=2, 4 and 6) to ${}^5D_0 \rightarrow {}^7F_1$ transition. The obtained results have been used for calculating Ω_2 , Ω_4 , Ω_6 parameters by using Judd-Ofelt theory. These Ω_2 , Ω_4 , Ω_6 parameters allow to derive radiative properties of Eu^{3+} ions in glass material such as transition probabilities, radiative lifetimes and peak stimulated emission cross-section for the ${}^5D_0 \rightarrow {}^7F_J$ transitions.

I. INTRODUCTION

Oxide glasses are the most stable host matrices for practical applications due to their high chemical durability and thermal stability. Among the oxide glasses, tellurite glasses have proved to be interesting host for lanthanide ions, both from a fundamental and an applied point of view. It is well-known, the non-radiative loss is dominated by the highest energy phonon available in the matrix. Therefore, it is meaningful to select a host material for which the maximum phonon energy is as low as possible. In silica, this phonon energy is reasonably large (about 1100 cm⁻¹). It is quite low for chalcogenide glasses (about 300 cm⁻¹), which, however, lack many of the desirable features of silica-based glasses, including mechanical strength and chemical durability. Tellurite glasses represent a compromise between the desire for a low phonon energy (650-750 cm⁻¹) [1–3] host couple with the need to retain mechanical strength and process temperatures... However, less spectroscopic study on Borate-tellurite-zinc-sodium based glass was reported.

Among the Ln^{3+} ions used to optically activate the glass matrices, the trivalent europium ion Eu^{3+} is the mostly used choice due to the fact that Eu^{3+} (4f⁶) ions emit narrow band, almost monochromatic light and have long lifetimes of the optically active states. Eu^{3+} is usually the rare earth ion of choice for several studies due to its simple electronic energy level scheme. Eu^{3+} ions exhibit pure magnetic and electric dipole transitions which make it a very sensitive probe for the rare earth ion site structure symmetry. The transition probability of hypersensitive transition (${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$) of Eu^{3+} ion is depressed under higher symmetric environment whereas the magnetic dipole transition are not affected by the environment and their emission intensities are often used as internal standard [4,5].

II. EXPERIMENTS

Using the melting method, $40B_2O_3$. $40TeO_2$. 10ZnO. $10Na_2O$ glasses containing Eu₂O₃1 mol % concentrations were prepared with two process (melting and heated-treatment). The starting components B_2O_3 , TeO_2 , ZnO, Na_2CO_3 and Eu₂O₃ were used. At first, the all components were mixed and dried at $100^{\circ}C$ for 3h. After that the mixture was melted at $1200^{\circ}C$ in air for 2 h in a Pt crucible. The fining temperature was 1150 °C for about 15min. The glass samples was obtained by cooling the melt down to room teperature slowly. Then, the glasses was heated-treatment in oven at $350^{\circ}C$, $450^{\circ}C$ and $550^{\circ}C$ for 10 h, 15 h and 24 h, respectively. The resulting glass, which was transparent colorless. Followed, the sample was cut and polished for optical measurements.

X –ray diffraction measurement by on a XRD-D5000 SIEMENS diffractometer. Excitation and emissition spectra of the samples were measured using Horiba FluoroLog Spectrophotometer FL3-22 using a 450W xenon lamp source, monochromator (f/3.6 Czeny-Turner, double grating, all reflective optics) and R928P photomultiplier and recorded under computer control software FluorEssence 2.0 (powered by Origin 7.5). All the measurements were carried out at room temperature.

III. RESULTS AND DISCUSSION

III.1. Structural characterization

Generally, melting is a strongly method to prepare the glass materials. Beside, heated-treatment for as-prepared glasses is an important process which produce stable structure of glass. During this process, the micro-crystals can be formed in host glass which is called glass-ceramic materials.

To identify crystallization phase, XRD analysis was performed on a X-ray powder diffractometer (XRD-D5000) with CuK α radiation. The XRD spectra of glass samples are compared in Fig,1a-c in the range of $2\theta = 20^{\circ}$ to 70°. Show the XRD diagram of the glass samples heated-treatment at 350°C-10 h (a), 450°C -15 h (b) and 550°C -24 h (c). The structural analysis results exhibit that the amorphous phases of the glass sample heated-treatment 350°C-10 h, while the heated sample at 450°C-15 h and 550°C-24 h exhibits both amorphous and crystaline phase. As we know, the glass crystallization process strongly

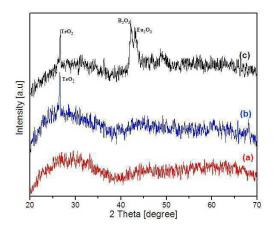


Fig. 1. XRD patterns of 1 mol % Eu^{3+} doped $40B_2O_3.40TeO_2.10ZnO.10Na_2O$ glass samples heat-treatment $350^{\circ}C-10$ h(a), $450^{\circ}C-15$ h(b) and $550^{\circ}C-24$ h (c)

depend on the conditions of thermal annealing as temperature, time and host components. Therefore, these initial result suggest to allow preparation glass-ceramic materials [6,7].

III.2. Optical properties

A. Excitation spectrum

The excitation spectrum for 612 nm red emission of 1 mol % Eu³⁺ doped the samples is shown in Fig. 2. The transitions of excitation spectra are assigned (originating from $^{7}F_{0}$ and $^{7}F_{1}$) based on free-ion energy level structure and by taking into account both the electric and magnetic dipole contributions. There are fifteen obvious excitation peaks parking at 299 nm, 304 nm, 319 nm, 327 nm, 361 nm, 365 nm, 377 nm, 382 nm, 394 nm, 400 nm, 414 nm, 465 nm, 472 nm, 526 nm, 533 nm. Among them the intensities of 394 nm excitation peak is strongest.

The PSB of the ${}^{5}D_{2}-{}^{7}F_{0}$ transition of the Eu³⁺ ion was observed in the excition spectrum as shown in Fig.2. The PSB of the B₂O₃- base glass is due to the stretching vibration modes of B-O⁻ and B-O of B₂O₃ and BO₄⁻ units in tetra-and diborate groups [8], where $-O^{-}$ and -O stand for the non-bridging oxygen (NBO) and bridging oxygen (BO), respectively. In fact, PSB is influenced both by the stretching vibration mode of NBO in the neighborhood of the Eu³⁺ ion and by the stretching vibration modes of NBO and BO which are apart from the Eu³⁺ ion.

The energy level diagram (Fig. 3) of Eu^{3+} shows the energy gaps among the levels of ${}^{5}G_{2}$, ${}^{5}L_{6}$, ${}^{5}D_{3}$, ${}^{5}D_{2}$, ${}^{5}D_{1}$ and ${}^{5}D_{0}$. The emission efficiencies of ${}^{5}D_{3}$, ${}^{5}D_{2}$ and ${}^{5}D_{1}$ levels are related with the non-radiative rates W_{NR} tightly. W_{NR} can be expressed by:

$$W_{NR} = W_P + W_{ET} \tag{1}$$

Where W_P is the multiphonon decay rate and W_{ET} is the relaxation rate by energy transfer. For the lower concentration of Eu³⁺ doping, the contribution of W_{ET} can be ignored temporally, and the factor dominating the quantum efficiency is W_P , which is

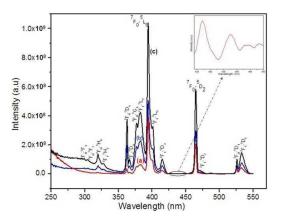


Fig. 2. Room temperature excitation spectrum (λ_{em} =612 nm) of 1 mol% Eu³⁺ doped 40B₂O₃.40TeO₂.10ZnO.10Na₂O glass samples heat-treatment at 350°C-10 h(a), 450°C-15 h(b) and 550°C-24 h (c).

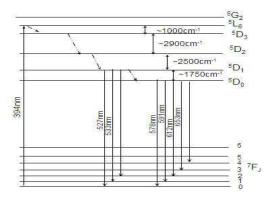


Fig. 3. Energy level diagram of Eu³⁺ in B₂O₃-TeO₂ –ZnO-Na₂O glasses.

associated with the phonon energy, W_P is expressed by

$$W_P = W_0 \exp\left(\frac{-\alpha \Delta E}{\hbar \omega}\right) \tag{2}$$

Where ΔE is the energy gap to the next lower level and is the phonon energy of the matrix glass. W₀ is transition probability extrapolated to zero energy gap, which is independent of the electronic nature of the RE ion. $\alpha = \ln[\Delta E/(\hbar\omega g)]o$, where g is the electron phonon coupling strength [9]. According to Eq. (2), W_{NR} should be much larger in silicate and phosphate with higher maximum-phonon energies ($\hbar\omega \sim 1100 \text{ cm}^{-1}$ and $\sim 1300 \text{ cm}^{-1}$, respectively) than in tellurite glass ($\hbar\omega \sim 750 \text{ cm}^{-1}$) and it is the main reason why the emissions of Eu³⁺ from ⁵D₃, ⁵D₂ and ⁵D₁ levels could not be observed in silicate and phosphate glasses but can be recorded in tellurite (40B₂O₃. 40TeO₂. 10ZnO. 10Na₂O.1Eu³⁺) glasses clearly.

B. Emission spectrum

The emission spectrum of 1mol % Eu³⁺ doped the samples in Fig. 4 which were obtained by exciting in the ${}^{5}L_{6}$ state using a 394 nm wavelength of broad band Xenon lamp source. Emission is mainly observed for ${}^{5}D_{0} \rightarrow {}^{7}F_{J}(J=0, 1, 2, 3, 4)$ transitions (with maximums at 578 nm; 591 nm; 612 nm; 653 nm and 700 nm, respectively) and a weak emission is noticed for ${}^{5}D_{1} \rightarrow {}^{7}F_{0,1,2}$ (with maximums at 527 nm; 534 nm; 553 nm , respectively) which are assigned Fig.4. when increasing the temperature heat- treatment, the intensity spectrum increase significantly.

The emission intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2,4}$ transitions are induced electric dipole allowed and depend strongly on the local symmetry around Eu³⁺ ion. Moreover, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is said to be hypersensitive transition (under the selection rule $\Delta J = 2$) to the surrounding environment, where as the transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ is magnetic dipole allowed and is independent of the local symmetry.

Therefore, the ratio of intergrated emission intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition to that of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition, defined as fluorescence intensity ratio R, is the spectroscopic key to estimate the deviation from the site symmetry of the Eu³⁺ ions. Sometime, Ris defined also as asymmetry ratio. In our experiments, the emission spectra are recorded for the sample 40B₂O₃. 40TeO₂. 10ZnO. 10Na₂O. 1Eu₂O₃ excited by the wavelength 394 nm. The fluorescence intensity ratio R receives the value of 4.1; 3.9 and 3.8 which are given the glass samples heated-treatment at 350°C-10 h; 450°C -15 h and 550°C -24 h, respectively. From Kumar et al. [10], most of the Eu³⁺ doped glasses exhibit the R in the range of 3. 5-4. 2. This indicates the potential of borate-tellurite-zinc-sodium: Eu³⁺ glass as a laser and red luminescence material.

III.3. Judd- Ofelt analysis

The Judd-Ofelt theory was often used to calculate the intensity parameters Ω_{λ} ($\lambda = 2, 4, 6$). The intensity parameters Ω_{λ} could be obtained from absorption spectra. But sometimes the measurement of absorption spectra is difficult. However, the strong luminescence is a characteristic feature for many europium doped materials [11]. Therefore, the Judd-Ofelt analysis by emission spectra is frequently used for the Eu³⁺ doped host matrices.

The emission spectrum of Borate-tellurite-zinc-sodium: Eu^{3+} ion excited by 394 nm light is shown in Fig. 4. Three main emission peaks ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$; ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$; ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ are used to calculate the J.O parameters.

The ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ is magnetic dipole transition and its spontaneous emission probability A_{md} is given using the following expression [4,5]:

$$A_{md} = \frac{64\pi^4}{3h} \frac{\nu^3}{2J+1} n^3 S_{md} \tag{3}$$

where ν is the wave number of transition, h is the Planck constant, J is the total angle momentum of the excited state, n is the refractive index, S_{md} is the magnetic-dipole line strength, which is a constant and independent from the host material.

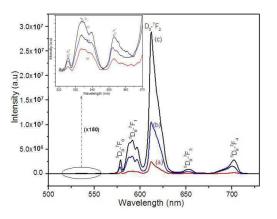


Fig. 4. Room temperature emission spectrum ($\lambda_{ex} = 394$ nm) of 1 mol% Eu³⁺ doped 40B₂O₃.40TeO₂.10ZnO.10Na₂O glass samples with heat-treatments 350°C-10 h(a), 450°C-15 h(b) and 550°C-24 h (c)

The value of A_{md} can be estimated using the reference value of A'_{md} published somewhere and using the relationship $A_{md} = (n/n')^3 A'_{md}$; where A'_{md} and n' are spontaneous emission probability and refractive index of the reference material. For example, with the value of A'_{md} of lithium fluoroborate glass doped by mol 1% Eu³⁺ is 51. 9 s⁻¹, n' = 1.539 [12].

The ${}^{5}D_{0} \rightarrow {}^{7}F_{J=2,4,6}$ transitions are electronic dipole allowed. The spontaneous emission probabilities A_{ed} of electronic transition is given using the following expression:

$$A_{ed} = \frac{64\pi^4 e}{3h} \frac{\nu_J^3}{2J'+1} \frac{n(n^2+2)^2}{9} S_{ed}$$
(4)

where ν_J is the wave number of transition ${}^5D_0 \rightarrow {}^7F_J$; *e* is the electron charge; *h* is Planck constant; *n* is the refractive index; J' is the total angle momentum of excited state; S_{ed} is the electric-dipole line strength of the transition [13].

The emission intensity I of a given transition is proportional to the area S under the emission curve: $I = h\nu A_r N\alpha S$. Where $h\nu$ is transition energy, A_r is radioactive transition rate, N is population of emitting level (⁵D₀). Thus, the Ω_{λ} parameters could be evaluated simply by the ratio of the intensity of the ⁵D₀ \rightarrow ⁷F_{J=2,4,6} transitions to the intensity of ⁵D₀ \rightarrow ⁷F₁ transition as follow:

$$\frac{\int I_J d\nu}{\int I_1 d\nu} = \frac{A_J}{A_1} = \frac{e^2}{S_{md1}} \frac{\nu_J^3}{\nu_1^3} \frac{n(n^2+2)^2}{9n^3} \Omega_J \left\| U^J \right\|^2 \tag{5}$$

As seen from Eq. (5), the Ω_2 and Ω_4 can be evaluated independently from the emission transitions of ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_4$. The Ω_6 can not be evaluated because of limitation of our experimental condition. Since the emission transition ${}^5D_0 \rightarrow {}^7F_6$ at about 810 nm has not been observed from the emission spectra, the Ω_6 parameter could not be determined in our experiment. Because the ${}^5D_0 \rightarrow {}^7F_6$ emission intensity is usually very weak compared with the intensities of the of ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions. The calculated Ω_2 and Ω_4 parameters are presented in Table 1.

Ω_{λ}	The sample	The sample	The sample
	$(350^{\circ}-10 \text{ h})$	$(450^{\circ}\text{C-15 h})$	$(550^{\circ}\text{C-}24 \text{ h})$
Ω_2	4,872	4,718	4,614
Ω_4	1,463	1,487	1,519
Ω_6			

Table 1. Judd-Ofelt parameters $(\Omega_{\lambda} \times 10^{-20} \text{ cm}^2)$

From Table 1, the Ω_2 value is greater than Ω_4 and the value of Ω_6 can not be evaluated in each of samples. Thus, it can conclude that the radiative transition probabilities are mainly dependent on the ${}^5D_0 \rightarrow {}^7F_2$ red hypersensitive emission transition. This result is in agreement with that of the other tellurite glasses [14].

According to Refs. [15, 16] the fluorescence intensity ratio (R) of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions is used to establish the degree of asymmetry in the vicinity of Eu³⁺ ions and Eu-O covalence. Moreover, the R value also depends on the JO parameter Ω_{2} , which is used to explain the short-range effects. Therefore, the variation of R and in turn Ω_{2} gives the information about the short range effect on local structure around Eu³⁺ ions and Eu-O covalent. The higher the value of R, the lower the symmetry around the Eu³⁺ ions and the higher the Eu-O covalent. In table 1, the increase of the heat-treated temperature, the R values and Ω_{2} decrease significantly, but Ω_{4} increase significantly. When the increase of the heat-treated temperature, the degree of symmetry in the vicinity of Eu³⁺ ions increase and rigidity increase.

The Judd-Ofelt theory parameters no only can give the information on local structure and binding state of RE –ions in host matrices, but from the parameters Ω_{λ} , several important optical properties such as branching ratio, relative transition probabilities, life time of the excited states...could be evaluated. The radiative transition probability for transition $\psi J \rightarrow \psi' J'$ is given by: $A(\psi J \rightarrow \psi' J') = A_{ed} + A_{md}$

The calculated radiative life time τ_{cal} of the excited state can be obtained from A_{total} : $A_{total}(\psi J) = \sum_{\Psi'J'} A(\psi J, \psi' J') = 1/\tau_{cal}$ such in order to receive τ_{cal} of ${}^{5}D_{0}$ state, it is necessary to evaluate the radiative transition probability of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transitions. Because the value of the reduced matrix small, the ${}^{5}D_{0} \rightarrow {}^{7}F_{6}$ is negligible, the A_{ed} of this transition can be negligible in τ_{cal} . The branching ratio is given: $\beta_{R}(\psi J, \psi' J') = A(\psi J, \psi' J')/A_{tota} l(\psi J)$.

Table 2. The branching ratio $\beta_R({}^5D_0 \rightarrow {}^7F_2)(\%)$, the life time of the excited τ_{cal} and τ_{exp} of samples

	The sample (350^0-10 h)	The sample $(450^{\circ}\text{C-15 h})$	The sample $(550^{\circ}\text{C-24 h})$
$\tau_{cal}(ms)$	2,984	3,118	3,269
$ au_{exp}(ms)$	1,181	$1,\!235$	$1,\!244$
$\beta_R(^5\mathrm{D}_0 \rightarrow ^7\mathrm{F}_2)(\%)$	72,56	73,32	75,14

The life time τ_{cal} of the excited state (⁵D₀) of this Borate-tellurite-zinc-sodium is longer than the experimental life time τ_{exp} . This is perfectly reasonable, the experimental life time (τ_{exp}) is always the contribution of both conversion: emission and non- emission. Meanwhile, the life time (τ_{cal}) is only emission.

IV. CONCLUSION

Eu³⁺ doped 40B₂O₃.40TeO₂.10ZnO.10Na₂O glasses with 1mol % has been studied. Crystalline phase is formed in dominated amorphous phase for heated glass (at 450°C-15 h and 550°C-24 h). Heat treatment for longer of time is a good condition for glass crystallization process, produces micro-crystals in host glass. The emission and excitation spectra of Eu³⁺ ions in these samples were observed. The PSB of the ${}^{5}D_{2}-{}^{7}F_{0}$ transition of the Eu³⁺ ion was observed in the excitation spectrum. From the emission spectra, the obtained results have been used for calculating Ω_{2} , Ω_{4} parameters by using Judd-Ofelt theory. A relatively higher value of Ω_{2} could be related with higher asymmetry around Eu³⁺ ions in this non-linear optical material. The Ω_{2} value is greater than Ω_{4} and the value of Ω_{6} is negligible in this material. Thus, it can be concluded that the radiative transition. Radiative properties for the ${}^{5}D_{0}$ level of Eu³⁺ ions can be predicted by assuming ${}^{5}D_{0} \rightarrow {}^{7}F_{6}$ is negligible. The high brightness and short lifetime of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission show the good potential application of Borate-tellurite-zinc-sodium glass in photonics.

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