

OPTICAL PROPERTIES OF Eu^{3+} IONS IN BORO-TELLURITE GLASS

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Abstract. *Boro-tellurite (BTe) glass doped with concentrations of 1.0 mol% of Sm^{3+} ions was prepared by melting method. Their excitation, emission spectra and lifetime have been investigated. Sideband phonon spectrum have recorded three peaks at 865, 1375 and 1763 cm^{-1} . The electron-phonon coupling strength (g) has been calculated. The value of Ω_λ parameters were calculated from the emission spectra using Judd-Ofelt theory. These parameters were used to predict radiative properties such as transition probabilities (A_R), calculated branching ratios (β_R) and stimulated emission cross-sections ($\sigma_{\lambda p}$) for ${}^5D_0 \rightarrow {}^7F_J$ transitions. The results have shown that the ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions in BTe glass is very promising for laser emission and optical amplification.*

Keywords: Boro-tellurite glass, Judd-Ofelt theory.

Classification numbers: 74.25.nd, 74.25.Gz.

I. INTRODUCTION

The optical properties of trivalent rare-earth (RE^{3+}) ions doped glasses have attracted the attention of scientists due to their wide applications in many optical devices like lasers, light converters, sensors, high-density memories and optical amplifiers [1–4]. The borate glasses offer excellent heat stability and lower melting temperature compared with other glasses but the pure borate based glasses possess high phonon energy in the order of 1300-1600 cm^{-1} [3, 4]. Tellurite oxide (TeO_2) is a conditional glass former and forms glass only with modifiers such as alkali/alkaline earth and transition metal oxide or other glass formers, for example, B_2O_3 , SiO_2 . The

tellurite glass exhibits some outstanding features as low melting points, slow crystallization rates, good thermal and chemical stability, low cut off phonon energy in the order of $600\text{-}800\text{ cm}^{-1}$ and high refractive index, which favors high spontaneous transition rate. The presence of an amount of TeO_2 in the borate glass matrix decreases its hygroscopic nature, reduces the cut-off phonon energy, improves glass quality with an enhancement in transparency and refractive index [3–5].

Among the RE^{3+} ions used to optically active materials, Eu^{3+} ions are mostly chosen due to Eu^{3+} ions emit narrow-band, almost monochromatic light and have long lifetime at the optically active states. Further, Eu^{3+} ions have often been used as probes for estimation of local environment around the Ln^{3+} ions in different matrices [3-6]. In this work, the optical properties of Eu^{3+} ions in borotellurite ($44\text{TeO}_2\cdot 30\text{B}_2\text{O}_3\cdot 20\text{ZnCl}_2\cdot 5\text{Al}_2\text{O}_3\cdot 1\text{Eu}_2\text{O}_3$) have been studied, moreover the Eu^{3+} ions are used as an optical probe for studying the local symmetry of the surroundings of these ions.

II. EXPERIMENT

Eu^{3+} -doped borotellurite (BTe) glasses were prepared by conventional melt quenching. The starting materials are B_2O_3 , TeO_2 , ZnCl_2 , Al_2O_3 and Eu_2O_3 with the following molar compositions: $44\text{TeO}_2\cdot 30\text{B}_2\text{O}_3\cdot 20\text{ZnCl}_2\cdot 5\text{Al}_2\text{O}_3\cdot 1\text{Eu}_2\text{O}_3$. All the above weighed chemicals were well-mixed and heated for 120 min in a platinum crucible at $1300\text{ }^\circ\text{C}$ in an electric furnace, then cooled quickly to room temperature. The BTe glasses were annealed at $350\text{ }^\circ\text{C}$ for 12 h to eliminate mechanical and thermal stress. The photoluminescence (PL) and excitation spectra were recorded by Fluorolog-3 FL3-22 Spectrometer (Horiba Jobin Yvon). Luminescence lifetime was measured using a Varian Cary Eclipse Fluorescence Spectrophotometer.

III. RESULTS AND DISCUSSION

Excitation and phonon-sideband spectra

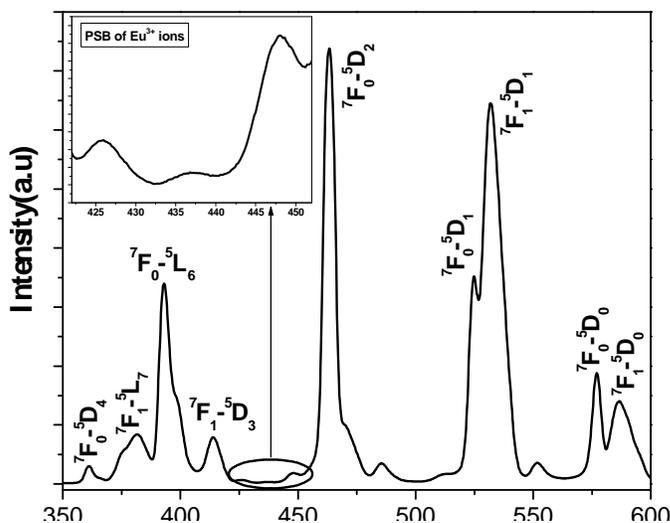


Fig. 1. The excitation spectrum at room temperature of the BTe:Eu³⁺ glass.

The excitation spectrum of BTe:Eu^{3+} was recorded in the spectral region 320-600 nm by monitoring at emission wavelength of 613 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition) as shown in Fig. 1. The excitation spectrum consists of the sharp bands (peaks at 361, 375, 394, 414, 464, 525, 532, 577 and 587 nm) due to the $f-f$ transitions from ${}^6\text{F}_{0,1}$ to the excited levels of Eu^{3+} ions [7]. The intense bands at wavelength of 394, 463 and 532 nm, these bands are often used in fluorescence excitation for Eu^{3+} ions. It is noted that the excitation bands of Eu^{3+} ions coincide with the active spectral region of some lasers and LEDs that provide UV, violet, blue and green light. Thus, they are efficient pump sources to obtain the emission of red band (613 nm) of Eu^{3+} ions in the borotellurite glass.

The local structure of the Eu^{3+} ion can be explored using the phonon sideband (PSB) spectra of the Eu^{3+} ions at the high energy side of the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition peaking at 464 nm wavelength. The PSB of Eu^{3+} ions in borotellurite glasses is clearly observed and is shown in the inset of Fig. 1, for which the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ excited transition is the pure electronic transition (PET). The difference in energy between the PSB and the PET bands corresponds to the energy of one phonon, associated with the maximum energy vibrational mode coupled to the Eu^{3+} ions [8]. The phonon energy expressed through wavenumber is given by [3,4]:

$$\text{Phonon energy} = 10^7(1/\lambda_{PSB} - 1/\lambda_{PEB}) \quad (1)$$

where λ_{PSB} and λ_{PEB} are the wavelength (nm) of the phonon sideband and pure electronic band, respectively. The electron-phonon coupling strength (g) relates the covalency of Eu^{3+} -ligand bond and can be calculated from the intensity ratio between PSB and PET using the following equation [3,4]:

$$g = \frac{\int I_{PSBs} d\lambda}{\int I_{PET} d\lambda} \quad (2)$$

where I_{PSBs} and I_{PET} is intensity of PSB and PET, respectively.

For Eu^{3+} ions in borotellurite, the PSB spectra are grouped in three bands peaking at 865, 1375 and 1763 cm^{-1} , which are abbreviated as PSB1, PSB2 and PSB3, respectively. The assignment of these three bands is correlated with the Raman and FTIR spectra of the boro-tellurite glasses [9], that is, the PSB1, PSB2, and PSB3 are assigned to the Te-O-Te bending vibrations in $[\text{TeO}_4]$ units [4], the vibrations of B-O⁻ non-bridging bonds of the $[\text{BO}_3]$ units [10], and the B-O vibrations associated with the $[\text{BO}_3]$ units in the borate rings and their NBO^- [4], respectively. The electron-phonon coupling strength g of total vibrational modes for the BTe glass are found to be 0.04. This value is lower than that in lead fluoroborate glasses [4], borotellurite glasses [3] and lead tungstate tellurite glass [5], i.e. the electron-phonon coupling and the ionic in Eu^{3+} -O bond in BTe glass are weaker than that in lead fluoroborate (LFB) glasses and borotellurite glasses.

Emission spectra

Fig. 2 illustrates the emission spectrum of Eu^{3+} ions in borotellurite using the 464 nm excitation wavelength of a xenon lamp source.

The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{2,4,6}$ transitions induced electric dipole (ED) transitions, so its intensity depends strongly on the local symmetry around Eu^{3+} ion, polarizability of ligand and energy separation between initial and final level. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition is magnetic dipole (MD) which splits into three components, indicating that the crystallographic site of the Eu^{3+} ions in the present glass is as low as orthorhombic, monoclinic or triclinic in a crystalline lattice [3,4,6]. The intensity of

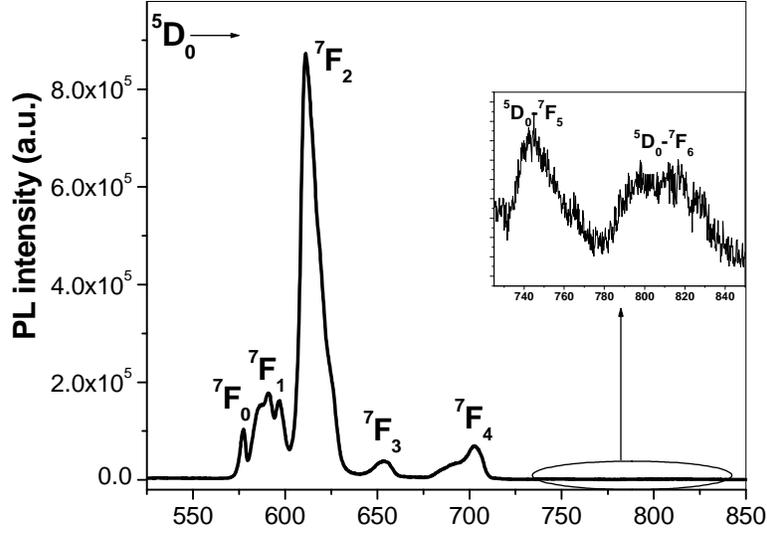


Fig. 2. The emission spectrum of Eu^{3+} in BTe glass.

${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition depends on the host but it is independent local symmetry and reduced matrix elements, so this transition is often used as an internal standard to evaluate the asymmetry of ligand and fluorescent efficiency of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition through the ratio $R = I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)/I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$. For BTe: Eu^{3+} glass, $R = 3.88$, this value is much larger than that in lead fluoroborate glasses [4], borotellurite glasses [3] and lead tungstate tellurite glass [5]. Thus, the fluorescent efficiency of red band and the covalency of Eu^{3+} -ligand bond are higher than those of some other glasses [3–5]. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0,3,5}$ transitions are strict forbidden under selection rules, so their intensity are often very weak.

Judd-Ofelt analysis

The Judd-Ofelt (JO) theory [11, 12] was shown to be useful to characterize radiative transitions for RE-doped solids, as well as aqueous solutions, and to estimate the intensities of the transitions for rare-earth ions. This theory defines a set of three intensity parameters, Ω_λ ($\lambda = 2, 4, 6$), that are sensitive to the environment of the rare-earth ions.

Commonly, Judd-Ofelt (JO) intensity parameters are usually derived from absorption spectrum. However, owing to the special energy level structure of Eu^{3+} ion, these Judd-Ofelt parameters could be estimated from the emission spectra. Three main emission peaks ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ are used to calculate JO parameters. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ is a magnetic-dipole transition and its spontaneous emission probability A_{md} is given by [3, 4, 13, 14]:

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

where h is the Planck constant, ν is the wavenumber of the transition in interest, J is the total angular momentum of the excited state, and n is the refractive index, S_{md} is the magnetic-dipole line strength, which is a constant and independent from the host material. 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 [4].

The ${}^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions are an ED partially allowed. The spontaneous emission probabilities A_{ed} of ED transition is given using the following expression [3, 4, 13, 14]:

$$A_{ed} = \frac{64\pi^4 \nu_J^3 e^2}{3h(2J+1)} \left[\frac{n(n^2+2)^2}{9} \right] \sum_{\lambda=2,4,6} \Omega_\lambda \|U^{(\lambda)}\|^2 \quad (4)$$

where ν_J is the wave number of transition ${}^5D_0 \rightarrow {}^7F_J$, e is the electron charge, $\|U^{(\lambda)}\|^2$ are the squared doubly reduced matrix elements of the unit tensor operator of the rank $\lambda = 2, 4, 6$, and are calculated from intermediate coupling approximation for a transition $|\psi J\rangle \rightarrow |\psi' J'\rangle$. These reduced matrix elements did not nearly depend on host matrix could find from earlier studies [7]. Thus the Ω_λ parameters could be evaluated simply by the ratio of the intensity of the ${}^5D_0 \rightarrow {}^7F_{J=2,4,6}$ transitions to the intensity of ${}^5D_0 \rightarrow {}^7F_1$ transition as follows:

$$\frac{\int I_J d\nu}{\int I_1 d\nu} = \frac{A({}^5D_0 \rightarrow {}^7F_{2,4,6})}{A({}^5D_0 \rightarrow {}^7F_1)} = \left[\frac{e^2}{S_{md1}} \right] \left[\frac{\nu_J}{\nu_1} \right]^3 \left[\frac{(n^2+2)^2}{9n^2} \right] \sum_{\lambda=2,4,6} \Omega_\lambda \|U^{(\lambda)}\|^2 \quad (5)$$

For ${}^5D_0 \rightarrow {}^7F_2$ transition, $U^{(2)} = 0.0033$; $U^{(4)} = U^{(6)} = 0$, ${}^5D_0 \rightarrow {}^7F_4$ transition, $U^{(2)} = 0$; $U^{(4)} = 0.0023$; $U^{(6)} = 0$ and ${}^5D_0 \rightarrow {}^7F_6$ transition, $U^{(2)} = U^{(4)} = 0$, $U^{(6)} = 0.0003$. Using equation (5) and the reduced matrix elements, the JO parameters were calculated for different concentrations. For BTe:1.0 mol% Eu³⁺ glass, $\Omega_2 = 6.08 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.39 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 1.26 \times 10^{-20} \text{ cm}^2$. The characteristic feature of the Ω_2 is that it is sensitive to the local environment of the RE ions and is often related with the asymmetry of the coordination structure and nature of RE³⁺-ligand bond [11, 12]. The values of Ω_2 in BTe glass is equivalent to that of BTLA glass ($6.25 \times 10^{-20} \text{ cm}^2$) [13] but larger than that in B0TN glass ($2.86 \times 10^{-20} \text{ cm}^2$), B2TN glass ($4.28 \times 10^{-20} \text{ cm}^2$) [3], EPbFB glass ($2.48 \times 10^{-20} \text{ cm}^2$) [4] and BTeZnNa ($5.24 \times 10^{-20} \text{ cm}^2$) [14]. These indicate that the asymmetry of crystal field at the Eu³⁺ ions site and covalency of RE³⁺-ligand bond in BTe glass is equivalent in BTLA glass but higher in B0TN, B2TN, EPbFB and BTeZnNa glasses.

Radiative properties

The JO parameters have been used to estimate the radiative properties such as the radiative transition rates (A_R), radiative lifetime (τ_R), stimulated emission cross section $\sigma(\lambda_p)$, branching ratios (β_R) for 5D_0 excited level of Eu³⁺ doped BTe glass by using Eq. (3), (7), (9) and (8) in Ref. [1]. The results are shown in Table 1.

The ${}^5D_0 \rightarrow {}^7F_2$ transition has the highest radiative transition rate in comparison with the other transitions. The predicted branching ratio (β_R) of ${}^5D_0 \rightarrow {}^7F_2$ transition get a maximum value of 69.5 % where as the measured branching ratio (β_{mes}) is 70.7 %. Thus there is a good agreement between experimental and calculated branching ratios. The values of $\sigma(\lambda_p)$ for 5D_0 emission transition are in order of ${}^5D_0 \rightarrow {}^7F_2 > {}^7F_1 > {}^7F_4$. It is found that ${}^5D_0 \rightarrow {}^7F_2$ transition exhibits a maximum $\sigma(\lambda_p)$ ($18.1 \times 10^{-22} \text{ cm}^2$), these results are in agreement with previous reports [3–5]. The measured and calculated lifetime of 5D_0 level is 2.64 ms and 3.50 ms, respectively. The

Table 1. The predicted of radiative transition rates (A_R), branching ratios (β_R) and radiative lifetime (τ_R) of 5D_0 level for BTLA glass doped with 1.0 mol% of Eu^{3+} ions.

${}^5D_0 \rightarrow$	$E(\text{cm}^{-1})$	$A_R (\text{s}^{-1})$	$\beta_R (\%)$	$\beta_{mes} (\%)$	$\sigma(\lambda_P) (10^{-22} \text{ cm}^2)$	$\tau_R (\text{ms})$
7F_0	17,320	0	0	2.7	-	3.50
7F_1	16,944	62.8	17.9	16.3	2.7	
7F_2	16,283	198.2	69.5	70.7	18.1	
7F_3	15,433	0	0	2.8	-	
7F_4	14,464	20.9	7.3	7.5	2.6	
7F_5	13,422	0	0	-	-	
7F_6	12,343	15.2	5.3	-	-	

discrepancy between the measured and calculated lifetime may be due to the additional non-radiative and energy transfer through cross-relaxation [1–5]. The luminescence quantum efficiency of the fluorescent level is defined as the ratio of the measured lifetime to the calculated lifetime by JO theory, $\eta = \tau_{mes}/\tau_R$ [1,2]. In our case, the luminescence quantum efficiency is 75.4 %. The large magnitude of the measured branching ratio (β_{mes}), stimulated emission cross section $\sigma(\lambda_P)$ and luminescence quantum efficiency (η) suggest that the ${}^5D_0 \rightarrow {}^7F_2$ transition in borotellurite glass is very promising for laser emission and optical amplification.

IV. CONCLUSION

From the excitation spectrum, three PSBs were found with the energies about 865, 1375 and 1763 cm^{-1} , which relate to the vibration of the $[\text{TeO}_4]$, $[\text{BO}_3]$ and $[\text{BO}_4]$ units. The small value of electron-phonon coupling strength g shows the low ionic of $\text{Eu}^{3+}\text{-O}^-$ bond in borotellurite glass. The large value of Ω_2 shows that the coordination structure surrounding the Eu^{3+} ions has high asymmetry. By using JO theory, the radiative properties such as branching ratios, the emission cross-section and luminescence quantum efficiency have been calculated. The results show that the ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions in borotellurite glass is very promising for laser emission and optical amplification.

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