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Structural and Spectroscopic Studies on Eu³⁺ doped Boro-tellurtie glasses

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Abstract

 Eu^{3+} - doped boro-tellurite glasses have been prepared by melt quenching technique with the chemical composition $(69-x)B_2O_3+xTeO_2+15Na_2CO_3+15NaF+1Eu_2O_3$ (where x = 0, 10, 20, 30 and 40 wt %). Structural and optical behavior of the prepared Eu^{3+} doped boro-tellurite glasses were studied and reported. The FTIR spectral studies reveal the $O_3B-O-BO_3$ bending vibrations and Te-O bending vibrations in the TeO_3 and TeO_6 units. Through the optical absorption spectra, bonding parameters ($\overline{\beta}, \delta$) were calculated and the covalent nature of the prepared glasses could be identified. The Judd–Ofelt (JO) parameters and Luminescence intensity ratio (R) values have been calculated using the luminescence spectra. The JO parameters ($\Omega_{\lambda}, \lambda = 2$, 4 and 6) have been used to calculate the radiative properties for the ${}^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3 and 4) transitions of the Eu^{3+} ions.

Keywords: FTIR, Absorption, Photoluminescence, Judd-Ofelt analysis, Stimulated emission crosssection

1.0 INTRODUCTION

Oxide based glasses such as silicates, phosphates, borates, germanate, vanadates and tellurites are found to be promising for photonic applications. Tellurite glasses are useful in areas such as lasers, optical communication, optical fiber, non-linear devices, switching and semiconducting devices due to their low melting temperature, high refractive index, high dielectric constant and good infrared transmission [1]. TeO_2 does not readily form a glass on its own. But when it is mixed with other oxides like B₂O₃, P₂O₅ or SiO₂ it forms glasses. Atomic network in the tellurite based glasses is more open than the silica based glasses. Because of this fact the Te-O bond in the tellurite glasses can be easily broken and it is useful to accommodate rare earth (RE) ions in these glasses. Borate based glasses are suitable for photonic applications due to their high transparency, high thermal stability and good RE ion solubility. Boro-tellurite glass is an excellent material for optical communication. The presence of TeO₂ in the alkali borate glass matrix decreases its hygroscopic nature, improves the glass quality and enhances the IR transmission [2]. Among the lanthanides, the trivalent europium ion Eu³⁺ has been chosen as a probe to explore the optical behavior of the boro-tellurite glasses due to the fact that Eu³⁺ (4f⁶) ion possess narrow band emission, almost monochromatic light and longer lifetime of the optically active state. The Judd-Ofelt (JO) theory has been used to calculate the JO parameters Ω_{λ} (λ =2,4,6) and inturn used to derive the radiative properties of the prepared glasses in the present work.

2.0 EXPERIMANTAL

The Eu^{3+} doped boro-tellurite glasses were prepared by conventional melt quenching technique with the high purity analytical grade chemicals H₃BO₃, TeO₂, Na₂CO₃, NaF and Eu₂O₃. About 15 gm of the batches were thoroughly mixed and crushed in an agate mortar to obtain a homogeneous mixture. The ingredients were taken into a porcelain crucible and kept in an electrical furnace at 900°C for 1hr. The melt was poured on to a preheated brass plate and pressed by another brass plate to obtain a uniform thickness. The glass samples were annealed for 7 hrs at

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300°C to remove strain and to improve the mechanical strength. The structural analysis were carried out using Perkin-Elmer Paragon 500 FTIR spectrometer. The absorption spectra have been recorded using CARY 500 UV-VIS spectrometer in the range 350–600 nm. The luminescence spectra were measured between 550–725 nm using Perkin-Elmer LS55 spectrophotometer. All these measurements were recorded at room temperature only.

3.0 RESULTS AND DISCUSSION

3.1 Strectural Analysis

The FTIR spectra of the Eu^{3+} doped boro-tellurite glasses recorded in the region 400–4000 cm⁻¹ is shown in figure 1. The FTIR spectra exhibit several peaks at around 3363, 2929, 2860, 2370, 1642, 1385, 1023, 944, 763, 613 and 477 cm⁻¹. The absorption band at around 3363 cm⁻¹ is attributed to the fundamental stretching of O–H group.



Fig. 1: IR spectra of the Eu³⁺ doped boro-tellurite glasses

The bands observed around $2860-2929 \text{cm}^{-1}$ indicates the hydrogen bonding. The peak at 1642 cm^{-1} is assigned to the B–O⁻ bond in the isolated pyroborate group. The absorption band at 1385 cm^{-1} indicate the B–O stretching vibration of BO₃ units in the metaborate, proborate and ortoborate groups. The band around 1023 cm^{-1} is attributed to the B–O stretching vibration of BO₄ units in tri–, tetra– and pentaborate groups. The band observed at 944 cm⁻¹ is assigned to the B–O–B bending vibrations in the BO₄ units. The band observed around 763 cm^{-1} is assigned to the O₃B–O–BO₃ bond bending vibrations and the Te–O bending vibrations were observed due to TeO₃ and TeO₆ units. The sharp peak at 477 cm^{-1} is attributed to the Te–O–Te or O–Te–O linkage bending vibrations [3,4].

1.2 Absorption Spectra

The absorption spectra of the Eu³⁺ doped boro-tellurite glasses were recorded at room temperature in the

wavelength range 350–600 nm and as a representative case the absorption spectrum of the Eu^{3+} :B4TN glass is shown in figure 2.



Fig. 2: Absorption spectrum of the Eu³⁺:B4TN glass

Table 1. Observed band positions (cm⁻¹), bonding parameters ($\bar{\beta}$ and δ), JO parameters ($\Omega_{\lambda} \times 10^{-20}$ cm²) and luminescence intensity ratio (R) of the Eu³⁺ doped boro-tellurite glasses

Transitions	BOTN	B1TN	B2TN	B3TN	B4TN
$^{7}F_{1} \rightarrow {}^{5}D_{0}$	16949	16978	16949	16967	16976
$^{7}F_{0}\rightarrow ^{5}D_{0}$	17275	17269	17254	17261	17268
$^{7}F_{1} \rightarrow {}^{5}D_{1}$	18781	18739	18718	18728	18726
$^{7}F_{0}\rightarrow ^{5}D_{1}$	19022	19018	19017	19005	19013
$^{7}F_{0}\rightarrow ^{5}D_{2}$	21534	21552	21510	21532	21536
$^{7}F_{1}\rightarrow ^{5}D_{3}$	24086	24077	24080	24066	24091
$^{7}F_{1}\rightarrow ^{5}L_{6}$	24952	24926	24945	24938	24899
$^{7}F_{0}\rightarrow ^{5}L_{6}$	25381	25377	25367	25377	25376
$^{7}F_{0}\rightarrow ^{5}G_{2}$	26216	26185	26072	26168	26227
$^{7}F_{0}\rightarrow ^{5}G_{4}$	26554	26512	26564	26591	26599
$^{7}F_{0}\rightarrow ^{5}D_{4}$	27625	27611	27638	27622	27620
$\overline{\beta}$	0.9999	0.9994	0.9988	0.9994	0.9997
δ	0.0107	0.0570	0.1170	0.0622	0.0317
Ω_2	3.285	4.920	5.260	3.982	3.335
Ω_4	0.207	0.308	0.286	0.315	0.277
Ω_6	0.000	0.000	0.000	0.000	0.000
R	2.86	3.80	4.29	3.05	2.28

The absorption spectra originates from the ${}^{7}F_{0}$ and ${}^{7}F_{1}$ level of the Eu³⁺ ions. The band positions and their assignments are presented in table 1. From absorption spectra, eleven absorption bands were observed namely

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 ${}^{7}F_{1} \rightarrow {}^{5}D_{0}, {}^{7}F_{0} \rightarrow {}^{5}D_{0}, {}^{7}F_{1} \rightarrow {}^{5}D_{1}, {}^{7}F_{0} \rightarrow {}^{5}D_{1}, {}^{7}F_{0} \rightarrow {}^{5}D_{2}, {}^{7}F_{1} \rightarrow {}^{5}D_{3}, {}^{7}F_{1} \rightarrow {}^{5}L_{6}, {}^{7}F_{0} \rightarrow {}^{5}L_{6}, {}^{7}F_{0} \rightarrow {}^{5}G_{2}, {}^{7}F_{0} \rightarrow {}^{5}G_{4}$ and ${}^{7}F_{0} \rightarrow {}^{5}D_{4}$ with energies at 16985, 17275, 18781, 19022, 21558, 24086, 24952, 25381, 26256, 26554 and 27625 cm⁻¹ respectively. The ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ absorption band is found to be more intense than all the other transitions, even though it is forbidden by the ΔS and ΔL selection rules but allowed by the ΔJ selection rule. The intensity of the ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ induced electric dipole transition is stronger than the ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$ magnetic dipole allowed transition for all the studied glasses. The ${}^{7}F_{0} \rightarrow {}^{5}D_{3}$ transition is not observed because it is forbidden by the selection rule $\Delta J=3$. The Nephelauxetic ratios and the bonding parameters ($\overline{\beta}$ and δ) have been calculated to find the nature of Eu^{3+} -ligand bond. The bonding will be covalent or ionic depending on the positive or negative sign of $\delta.$ The bonding parameters ($\overline{\beta}$ and δ) of the prepared Eu^{3+} doped boro-tellurite glasses are presented in table 1 and it is observed from table that, the Eu–O ligand is of covalent in nature.

3.3 Emission Spectra and JO analysis

The luminescence spectra of the $Eu^{3+}:BxTN$ glasses recorded in the wavelength region 550–725 nm with 393 nm excitation is shown in figure 3. The spectra contains



Fig. 3:Emission spectra of the Eu³⁺:BxTN boro-tellurite glasses

five transitions such as ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ (581nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (594nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (616nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ (656nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ (705nm) respectively. Due to the experimental limitations the ${}^{5}D_{0} \rightarrow {}^{7}F_{6}$ (lies in the infrared region) transition could not be observed. The narrow emission bands are due to the shielding effect of the 4f^{6} electrons by 5s and 5p electrons in the outer shells of the Eu³⁺ ions. Among the five transitions ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ exhibit strong red emission and is hypersensitive in nature which follows the selection rule ΔJ =2. The ${}^{5}D_{0} \rightarrow {}^{7}F_{2,4,6}$ transitions are electric dipole in nature. The magnetic dipole transition

 ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ is allowed by selection rule $\Delta J=1$ which exhibit orange emission. Dejneca et al. [5] reported that, the luminescence spectra could not be observed from the ${}^{5}D_{1,2,3}$ levels in oxide or phosphate hosts because of the fast phonon-assisted depopulation of these levels. The R values of the Eu³⁺:BxTN glasses are found to be 2.86, 3.80, 4.29, 3.05 and 2.28 for the BOTN, B1TN, B2TN, B3TN and B4TN glasses respectively. Among the prepared glasses, Eu³⁺:B2TN glass possess higher R value of 4.29, which is useful in laser applications. The Judd-Ofelt parameters of the prepared glasses are calculated and presented in table 1. The trends of the JO parameters are found to be in the order $\Omega_2 > \Omega_4 > \Omega_6$ for all the prepared glasses. The higher Ω_2 value indicate the higher covalence around the rare earth ions and higher asymmetry, which is further confirmed through bonding parameter values of the prepared glasses. The stimulated emission cross-section value is found to be maximum for ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition for all the Eu³⁺ doped boro-tellurite glasses. The stimulated emission crosssection (σ_p^E) values for the ${}^{5}D_0 \rightarrow {}^{7}F_2$ transition of the B0TN, B1TN, B2TN, B3TN and B4TN glasses are found to be 12.10, 18.34, 21.77, 15.21 and 11.26 respectively. Among the prepared glasses, the σ_p^E values of the B2TN boro-tellurite glass is found to be high, and this glass is suggested for suitable laser applications.

4.0 CONCLUSION

The structural and optical behavior of the Eu³⁺-doped borotellurite glasses were studied through FTIR, UV absorption and luminescence spectra. The FTIR spectra reveal the O₃B–O–BO₃ bending vibrations. The Te–O–Te linkage and Te–O bending vibrations associated with the TeO₃ and TeO₆ units were identified and reported. The bonding parameters of the prepared glasses are found to be covalent in nature. The higher value of the Ω_2 JO parameter indicates the covalent character of the Eu–O bond. The higher R values confirm the higher asymmetry in the prepared glasses which is further confirmed through the bonding parameter values. Among the prepared glasses, Eu³⁺:B2TN glass possess higher stimulated emission crosssection and luminescence intensity ratio values and is suggested for suitable laser applications.

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