



Sm³⁺ Doped Borotellurite Glass: Absorption, Fluorescence and Optical Parameters

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Abstract: Borotellurite glasses doped with Sm³⁺ ions were prepared by a melt–quenching technique. The studies on optical characterization of Sm³⁺ ions have been carried out through absorption, emission and decay spectra. Judd-Ofelt (JO) intensity analysis has been presented and JO parameters were calculated for Sm³⁺ ions in borotellurite glasses. Radiative properties such as transition probabilities, branching ratios, radiative lifetime of ⁴G_{5/2} level and quantum efficiency were estimated by using JO parameters.

Keywords: Borotellurite glasses, Judd-Ofelt theory.

1. Introduction

Glasses doped with various rare earth ions are important materials for making fluorescent display devices, optical detectors, lasers, optical fibers, waveguides and fiber amplifiers [1-4]. Spectral properties of rare earth ions in glasses vary in a wide range depending on the chemical composition of glass former and modifier [3, 4]. Among lanthanides, the Sm³⁺ ion is one of the most interesting ions for analyzing the fluorescence properties because it is widely used in the fields such as undersea communications, high-density memories, colour displays and solid-state laser [2, 5-8].

Boric oxide (B₂O₃) is one of the representative glass former and flux material among the characteristic networks former [2]. Borate glasses have been extensively investigated due to intriguing properties such as good transparency in the infrared, low melting point, high solubility of rare earth [2-4, 8]. The disadvantage of these glasses is that high phonon energy (around 1300-1500 cm⁻¹) results in strong occurrence of multi-phonon and reduces the luminescence efficiency of the material [3, 4, 6, 7]. The phonon energy of TeO₂ is about 750 cm⁻¹ [4]. Thus, when TeO₂ is added to the borate glass, the phonon energy of the new glass would decrease significantly [2, 4]. This minimizes multi-phonon

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decay processes between energy levels which are very close to those of the lanthanide ions, and leading the increase in the quantum efficiency of the fluorescent processes.

Due to the advantages of the telluro-borate glass as well as the technological importance of Sm^{3+} ions, the following composition is chosen to fabricate the studied samples: $\text{B}_2\text{O}_3\text{-TeO}_2\text{-Na}_2\text{O-Al}_2\text{O}_3\text{:Sm}_2\text{O}_3$. The addition of the different types of metal oxides like Na_2O , Li_2O_3 , Al_2O_3 to binary telluro-borate glasses improves their chemical durability and alters their physico-chemical properties. Al_2O_3 has received significant consideration as the most likely useful matrix composition due to its high solubility of the RE^{3+} ions. Based on absorption and emission bands of intra-configurational f-f transitions in Sm^{3+} , the optical parameters of Sm^{3+} have been evaluated by using the Judd-Ofelt (JO) theory [9, 10].

2. Experimental

Sm^{3+} doped glasses with various compositions $(65-x)\text{B}_2\text{O}_3+15\text{TeO}_2+10\text{Na}_2\text{O}+10\text{Al}_2\text{O}_3+ x\text{Sm}_2\text{O}_3$, where $x = 0.1; 0.5$ and 1.0 mol% (denoted BTNA0.1, BTNA0.5 and BTNA1.0, respectively) were prepared by a conventional melt quenching technique. All the above weighed chemicals were well-mixed and heated for 60 min in a platinum crucible at 1300°C in an electric furnace, then cooled quickly down to room temperature. The BTNA glasses were annealed at 350°C for 12 h to eliminate mechanical and thermal stresses. The optical absorption spectra were measured between wavelengths 300 and 2000 nm using the Jasco V670 spectrometer. The photoluminescence spectra were recorded by the Fluorolog-3 spectrometer, model FL3-22, Horiba Jobin Yvon. Luminescence lifetime was measured using the Varian Cary Eclipse Fluorescence Spectrophotometer. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Absorption spectra

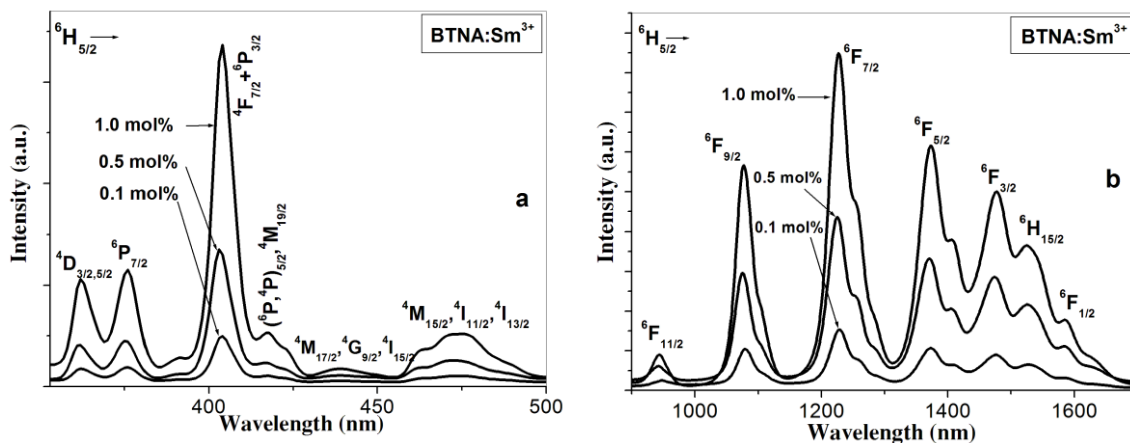


Figure 1. The absorption spectra of BTNA: Sm^{3+} glasses: (a) in the range of UV-Vis and (b) in the range of NIR.

The absorption spectra of BTNA:Sm³⁺ glass samples with some concentrations are shown in Fig.1a and Fig.1b for UV-Vis and NIR regions, respectively. There are 13 absorption bands appearing at the wavelengths of 1585, 1527, 1478, 1374, 1223, 1075, 944, 473, 439, 417, 402, 375 and 362 nm. These are the characteristic wavelengths in the absorption spectrum of Sm³⁺ ions, which are attributed to transitions from the ⁶H_{5/2} ground state to excited levels [11]. In NIR region, the transitions from ⁶H_{5/2} to ⁶H_J and ⁶F_J are allowed by the spin selection rule ($\Delta S = 0$), so the intensity of these transitions is often quite strong. The ⁶H_{5/2}→⁶F_{1/2} and ⁶H_{5/2}→⁶F_{3/2} transitions obey the selection rule $|\Delta J| \leq 2$, $|\Delta S| = 0$ and $|\Delta L| \leq 2$, thus these are hypersensitive transitions [9, 10]. Usually, the position, shape and intensity of hypersensitive transitions in RE³⁺ ions are very sensitive to the ligand coordination [9, 10]. However, there is not very big difference in hypersensitive transitions of the Sm³⁺ ion between hosts [2, 3, 5, 12]. In the UV-Vis regions, the various ^{2S+1}L_J energy levels are very close to each other. Therefore, the absorption transitions are overlapped and that creates broad bands. The strongest intensity in this region corresponds to ⁶H_{5/2}→⁶P_{3/2} transition (at the wavelength of 402 nm). This transition is a spin allowed transition which is normally used for fluorescence excitation.

3.2. Emission spectra

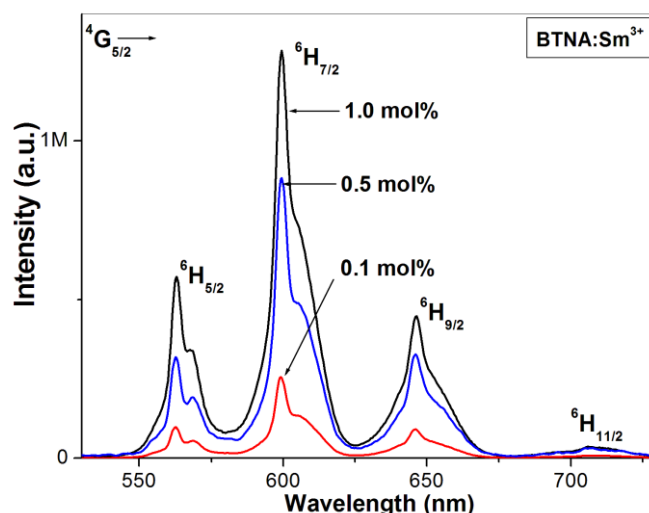


Figure 2. The emission spectra of the BTNA:Sm³⁺ glasses.

The emission spectra of the BTNA:Sm³⁺ glasses are recorded in the wavelength region 500-850 nm using the 402 nm excited wavelength and are shown in Fig.2. The emission spectra consists of 4 observed emission bands at wavelengths of 560, 600, 645 and 710 nm which correspond to the ⁴G_{5/2}→⁶H_J (J = 5/2, 7/2, 9/2, 11/2) transitions, respectively [11]. Among emission transitions, the ⁴G_{5/2}→⁶H_{7/2} transition has the most intense intensity whereas the ⁴G_{5/2}→⁶H_{11/2} transition is very weak in intensity. Two emission bands with an average intensity corresponding to ⁴G_{5/2}→⁶H_{5/2} and ⁴G_{5/2}→⁶H_{9/2} transitions which are usually used in high-density optical memory, color display and diagnostics in medicines [2, 6]. The ⁴G_{5/2}→⁶H_{9/2} and ⁴G_{5/2}→⁶H_{11/2} transitions are purely electric dipole (ED) transitions, whereas the ⁴G_{5/2}→⁶H_{5/2} and ⁴G_{5/2}→⁶H_{7/2} transitions include both electric and magnetic dipole (MD) transitions but the magnetic dipole is dominant mechanism in ⁴G_{5/2}→⁶H_{7/2} transitions. Thus, the intensity of the ⁴G_{5/2}→⁶H_{9/2} transition (red) strongly depends on the nature of ligand such as asymmetry and covalency of RE³⁺-ligand bond whereas the ⁴G_{5/2}→⁶H_{7/2} transition (orange) is less dependent on those [2, 12]. Therefore, the intensity ratio O/R (orange/red) can be used

to evaluate the characteristics of the local environment around the RE³⁺ ions [12, 13]. The O/R ratios increase slightly from 2.15 to 2.29 when the concentration of Sm³⁺ increases from 0.1 to 1.0 mol%. The small change of these ratios indicates that the asymmetry of ligand and covalency of RE³⁺-ligand bond nearly does not depend on the Sm³⁺ concentration. However, the values of the O/R ratios in BTNA glass are higher than those of the zinc potassium fluorophosphate (PKAMZF) and borotellurite (BTS) glasses [12, 13]. This indicates the asymmetry of crystal field at the RE³⁺ ions site and the covalency of RE³⁺-ligand bond for BTNA glass is lower in the PKAMZ and BTS glasses.

3.3. Optical parameters of Sm³⁺ ion in BTNA:Sm³⁺ glasses

The Judd-Ofelt (JO) theory [9, 10] was seen to be useful to evaluate the radiative parameters of RE³⁺-doped solids, as well as RE-doped aqueous solutions. According to the JO theory, the electric dipole oscillator strength of a transition from the ground state to an excited state is given by:

$$f_{cal} = \frac{8\pi^2 mc\nu}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_{\lambda} \|U^{(\lambda)}\|^2 \quad (1)$$

where n is the refractive index of the material, J is the total angular momentum of the ground state, Ω_{λ} are the JO intensity parameters and $\|U^{(\lambda)}\|^2$ are the squared doubly reduced matrix of the unit tensor operator of the rank $\lambda = 2, 4, 6$, which are calculated from intermediate coupling approximation for a transition $|\Psi J\rangle \rightarrow |\Psi' J'\rangle$. These reduced matrix elements are nearly independent of host matrix as mentioned in earlier studies [11].

On the other hand, the experimental oscillator strengths, f_{exp} , of the absorption bands are experimentally determined using the following formula [2, 5]:

$$f_{exp} = 4.318 \times 10^{-9} \int \alpha(\nu) d\nu \quad (2)$$

where α is molar extinction coefficient at energy ν (cm⁻¹). The $\alpha(\nu)$ values can be calculated from absorbance A by using Lambert-Beer's law

$$A = \alpha(\nu)cd \quad (3)$$

where c is RE³⁺ concentration [dim: L⁻³; units: mol/dm³], d is the optical path length [dim: L; units: cm].

By equating the measured and calculated values of the oscillator strength (f_{cal} and f_{exp}) and solving the system of equations by the method of least squares, the JO intensities parameters Ω_{λ} ($\lambda = 2, 4$ and 6) can be evaluated numerically. The calculated results Ω_{λ} ($\times 10^{-20}$ cm²) for BTNA:Sm³⁺ are shown in Table 1. Ω_4/Ω_6 ratio (χ) is called as the spectroscopic quality factor that it is important to characterize the quality of optical materials [5]. The values of χ in BTNA:Sm³⁺ is large and comparable to the Sm³⁺-doped other hosts [6-8]. This suggests that the BTNA:Sm³⁺ crystal is a good optical material.

Table 1. The intensity parameters Ω_{λ} of BTNA:Sm³⁺ glasses.

	0.1 mol%	0.5 mol%	1.0 mol%
Ω_2 (10^{-20} cm ²)	2.95	2.88	2.45
Ω_4 (10^{-20} cm ²)	10.99	10.88	10.27
Ω_6 (10^{-20} cm ²)	5.26	4.74	5.68
Ω_4/Ω_6	2.08	2.29	1.81

To understand the lasing and optical amplifier potentialities of a material, the JO theory has been used to determine radiative properties such as: branching ratios (β_{exp} and β_{cal} , %), effective line width ($\Delta\lambda_{eff}$, nm), stimulated emission cross-section ($\sigma(\lambda_p)$, 10^{-22} cm) and gain bandwidth ($\sigma \times \Delta\lambda_{eff}$, 10^{-28} m³). The detail formulas for these parameters have been given in previous reports [2, 5]. The experimental branching ratios (β_{exp}) are obtained by using the relative intensities of individual peaks to that of the total intensity of emission peaks. A radiative transition has potential for laser emission if the experimental branching ratios are higher 50 % [5]. For BTNA:Sm³⁺ samples, the β_{exp} values of ⁴G_{5/2}→⁶H_{7/2} transition are 53.5, 54.6 and 53.2 % for concentrations of 0.1, 0.5 and 1.0 mol% Sm³⁺, respectively. These values are comparable to those in literature [5, 6-8]. Thus, the ⁴G_{5/2}→⁶H_{7/2} transition of Sm³⁺ in BTNA glasses has a promising potential for optical applications. Table 2 shows some radiative parameters of ⁴G_{5/2}→⁶H_{7/2} transition in Sm³⁺ ion.

The stimulated emission cross-section - $\sigma(\lambda_p)$ is an important parameter which has been used to identify the potential laser transition of rare earth ions in glasses. The values of stimulated emission cross-section are in good agreement with those reported for the other glass hosts [6-8]. The relatively large values of β_{exp} and $\sigma(\lambda_p)$ make BTNA:Sm³⁺ glasses as promising materials for lasing action through the emission channel ⁴G_{5/2} → ⁶H_{7/2} transition. From Table 2, it is clear that among all prepared samples, the BTNA:0.5Sm³⁺ sample possesses larger values of β_{exp} and $\sigma(\lambda_p)$ than other samples. Hence the BTNA:0.5Sm³⁺ glass can be recommended as a good host for lasing emission at 600 nm.

Table 2. Radiative parameters of ⁴G_{5/2}→⁶H_{7/2} transition in Sm³⁺ ion

	0.1 mol%	0.5 mol%	1.0 mol%
β_{cal}	55.3	57.6	56.4
β_{exp}	53.5	54.6	53.2
$\Delta\lambda_{eff}$	14.2	13.1	13.8
$\sigma(\lambda_p)$	13.2	15.3	14.2
$\sigma(\lambda_p) \times \Delta\lambda_{eff}$	18.7	20.2	19.6

3.4. Fluorescence decay

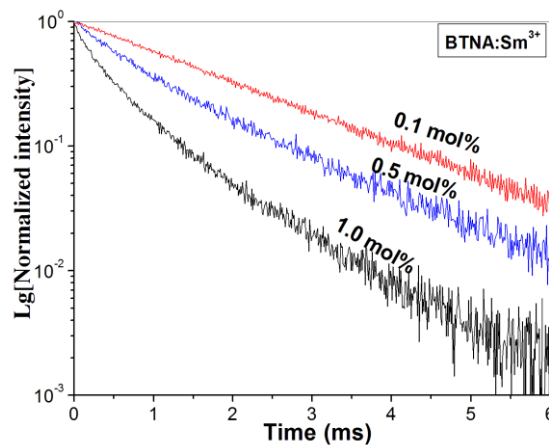


Figure 3. Luminescence decay profiles of the ⁴G_{5/2} of Sm³⁺ ions in BTNA glass.

The fluorescence decay curves for the ${}^4G_{5/2}$ level of Sm^{3+} ions for different concentrations in BTNA: Sm^{3+} glass with an excitation wavelength of 402 nm are shown in Fig.3. The measured lifetimes (τ_{exp}) of samples have been determined by the formula [2, 5]

$$\tau_{exp} = \frac{\int tI(t)dt}{\int I(t)dt} \quad (4)$$

The measured lifetime of ${}^4G_{5/2}$ level are 1.702, 1.301 and 0.689 ms for BTNA:0.1 Sm^{3+} , BTNA:0.5 Sm^{3+} and BTNA:1.0 Sm^{3+} samples, respectively. The lifetime decreases with the increase of the Sm^{3+} concentration. The decrease of lifetime can be related to the concentration quenching mechanism [2, 5, 8].

The lifetime obtained from JO theory (τ_{cal}) are 1.895, 1.757 and 1.879 ms for BTNA:0.1 Sm^{3+} , BTNA:0.5 Sm^{3+} and BTNA:1.0 Sm^{3+} samples, respectively. With a certain concentration, the τ_{exp} is smaller than the τ_{cal} . The discrepancy between the measured and calculated lifetime may be due to the nonradiative transfer processes which consists multi-phonon relaxation and energy transfer through cross-relaxation between the pairs of Sm^{3+} ions and the migration of the excitation energy [5-8]. The luminescence quantum efficiency of the fluorescent level is defined by the ratio of the measured lifetime to the calculated lifetime by JO theory [5, 6]: $\eta = \tau_{mes}/\tau_{cal}$. The quantum efficiency for BTNA:0.1 Sm^{3+} , BTNA:0.5 Sm^{3+} and BTNA:1.0 Sm^{3+} samples are 89.82, 74.05 and 56.67 %, respectively. The large values of quantum efficiency show the ability to use BTNA: Sm^{3+} glasses for optical amplifier. It is found that the quantum efficiency decreases with increase of concentration of Sm^{3+} ions. In addition, the decay curve is the single exponential with concentration of 0.1 mol% and becomes non-exponential with the higher concentrations (0,5 and 1,0 mol%). The causes of these phenomena is due to the increase of energy transfer rate with increase of Sm^{3+} concentration [2, 5, 8].

4. Conclusions

The optical properties of Sm^{3+} -doped borotellurite glasses have been investigated. By using JO theory, the radiative properties such as branching ratios and the stimulated emission cross-section have been predicted. The large values of the branching ratios, the stimulated emission cross-section and quantum efficiency show that BTNA: Sm^{3+} glass is the promising materials for lasing action and optical amplifier through the emission channel ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition

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