

THE DEVELOPMENT OF Sm^{3+} DOPED BARIUM TITANIUM BISMUTH BORATE GLASS FOR ORANGE EMISSION MATERIAL APPLICATION

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Abstract

Sm^{3+} -doped borate glasses were synthesized using the melt-quenching method, and luminescence characteristics were systematically investigated. Initially, the glass composition was modified by varying the Bi_2O_3 content while maintaining the Sm^{3+} concentration at 1.00 mol%. Optical absorption measurements revealed that BiBaTB1Sm glasses exhibited a prominent peak at 401 nm in the visible region, which was selected as the excitation wavelength for photoluminescence analysis. The emission spectra demonstrated a maximum intensity at 598 nm under 401 nm excitation. Notably, the glass sample without Bi_2O_3 showed stronger emission compared to the Bi_2O_3 -doped counterparts. In a separate study, the Sm^{3+} concentration was varied (0.0, 0.1, 0.5, 1.0, and 2.0 mol%) to examine its effect on luminescence properties. Luminescence intensity enhanced as the Sm content increased to 0.5 mol% before decreasing at higher concentrations due to the concentration quenching effect. Additionally, fluorescence decay time measurements indicated a reduction in lifetime with increasing Sm^{3+} content, attributed to energy transfer via cross-relaxation mechanisms. The CIE diagram confirmed that Sm_2O_3 -doped glass emitted orange light. These findings suggest that Sm^{3+} -doped borate glasses hold promise for applications in orange-emitting photonic devices.

Keywords: Borate Glass, Orange Emission Material, Samarium

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Introduction

Glasses doped with rare-earth (RE) ions have been widely studied for their potential applications in photonic technologies, including laser gain media, fiber lasers, wavelength converters, optical broadband amplifiers, and display devices. These glasses offer several advantages, such as high transparency in the visible spectrum, the ability to incorporate high activator ion concentrations, ease of fabrication into bulk materials, flexibility in shape and size, a straightforward manufacturing process, and cost-effectiveness (Jayasankar *et al.*, 2013; Basavapoornima *et al.*, 2014). Boron trioxide (B_2O_3) is a fundamental glass former and flux, known for its strong bonding, excellent transparency, thermal stability, low melting point, moisture resistance, and ability to effectively dissolve RE ions (Zaman *et al.*, 2016). B_2O_3 glass structures comprise boron atoms in trigonal coordination, forming boroxol rings connected by B–O–B linkages. This network exhibits high phonon energy around 1300 cm^{-1} . The introduction of heavy metal oxides (HMOs) as network modifiers alters the borate structure by converting trigonal BO_3 units into tetrahedral BO_4 units, generating non-bridging oxygens (NBOs) and reducing phonon energy to approximately 980 cm^{-1} (Mariyappan *et al.*, 2016). A lower phonon energy environment enhances the luminescence efficiency of RE ions, which is beneficial for laser applications (Zhou *et al.*, 2008). Among HMOs, bismuth oxide (Bi_2O_3) can function as both a network former and a modifier, depending on its concentration. It exhibits a low melting temperature, high polarizability, excellent thermal stability, and tunable optical properties while reducing the phonon energy of the glass matrix. These properties make Bi_2O_3 -containing glasses suitable for applications such as plasma display panels, lead-free, and high-density radiation shielding windows. However, bismuth alone is not classified as a glass former due to its low field strength of 0.53. Nevertheless, when combined with B_2O_3 , a wide compositional range of stable glass structures can be achieved, leading to an increase in NBOs and refractive indices (Mahamuda *et al.*, 2014; Kirdsiri *et al.*, 2011). Additionally, barium oxide (BaO) plays a role in lowering the melting temperature of borate glass, improving humidity resistance, and enhancing radiation shielding properties (Kirdsiri *et al.*, 2011). Titanium dioxide (TiO_2) contributes to increasing the refractive index (Loiko *et al.*, 2013). Meanwhile, samarium oxide (Sm_2O_3) has been widely investigated in various glass hosts, including borate, tellurite, phosphate, and silicate glasses. The strong

interest in Sm_2O_3 -doped glasses stems from their broad emission bands, particularly those associated with Sm^{3+} transitions from the $^4G_{5/2}$ to 6H_J energy levels. The intensity of these emission bands is highly dependent on both the Sm^{3+} ion concentration and the glass composition (Wantana *et al.*, 2017).

Current work has been focused on the development and optical characterization of samarium doped barium titanium bismuth borate glasses, this research has 2 parts with 2 sets of glass formations glass namely varied Bi_2O_3 and glass varies Sm_2O_3 .

Experiment

This study involves two sets of glass compositions: bismuth barium titanium borate samarium glasses ($xBi_2O_3-15BaO-10TiO_2-(74-x)B_2O_3-1Sm_2O_3$) where x varies from 0 to 5 mol%, and samarium barium titanium borate glasses ($xSm_2O_3-15BaO-10TiO_2-(75-x)B_2O_3$) with x ranging from 0.0 to 2.0 mol%. Both glass types were prepared using the melt-quenching method. A 10 g batch of raw materials was mixed and melted in an alumina crucible at $1200^\circ\text{C}/3$ hours. The molten glass was cast into a preheated brass mold, then annealed at $500^\circ\text{C}/3$ hours. The samples were polished to ensure smooth surfaces for accurate optical measurements. Figures 1 and 2 display the prepared samples.

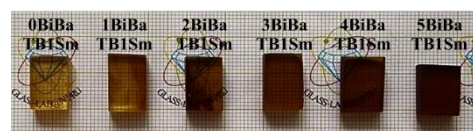


Figure 1. Photograph of borate glasses doped with Bi_2O_3 at varying concentrations

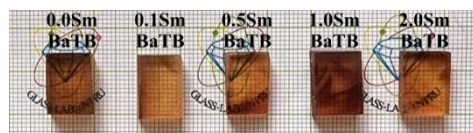


Figure 2. Photograph of borate glasses doped with Sm_2O_3 at varying concentrations

The density of the glass (ρ) was determined using Archimedes' principle, as described in Eq. 1, by measuring the sample's weight in air (w_a) and in water (w_w). The molar volume (V_m) was calculated using Eq. 2, which relates to the glass density. M_T represents the total molecular weight of all components present in the glass composition.

$$\rho = [w_a/(w_a - w_w)] \times \rho_w \quad (1)$$

$$V_m = M_T/\rho \quad (2)$$

Absorption spectra in the 300-2500 nm range were recorded using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. Luminescence spectra were measured with a Cary-Eclipse fluorescence spectrometer and a Quantum Master-300 photoluminescence spectrometer.

Results and Discussion

Bismuth barium titanium borate samarium glasses (Vary Bi₂O₃)

Physical properties (Vary Bi₂O₃)

All BiBaTB1Sm glass samples exhibit a consistent dark yellow appearance. The ρ of the glass increases as the Bi₂O₃ content rises. This is since the higher atomic mass of Bi₂O₃ compared to B₂O₃, meaning that substituting B₂O₃ with Bi₂O₃ at greater concentrations leads to an increase in both the molecular weight and ρ of the glass, as illustrated in Figure 3 (Kirdsiri *et al.*, 2011).

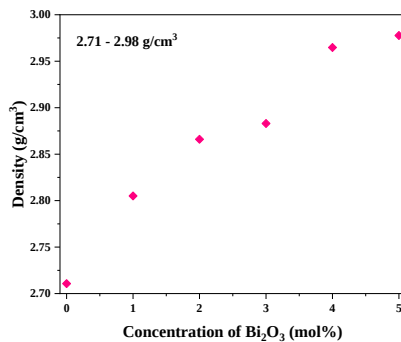


Figure 3. Density of BaTB1Sm glasses doped with Bi₂O₃ at varying concentrations

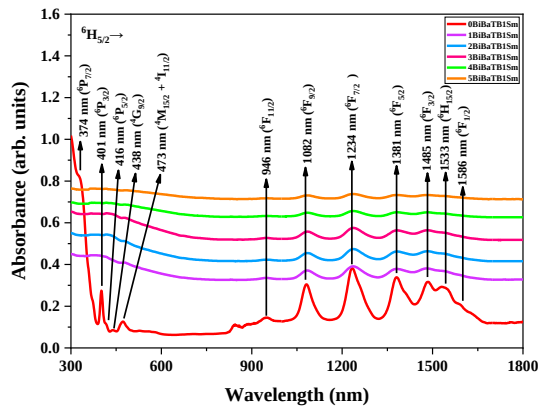


Figure 4. Absorption spectra of BaTB1Sm glasses doped with Bi₂O₃ at varying concentrations

Absorption spectra (Vary Bi₂O₃)

Absorptions spectra of borate 1Sm₂O₃ glasses doped Bi₂O₃ from 0-5 mol% are exhibit in Figure 4. The entire 12 absorption band corresponding to Sm³⁺ absorption was the excitation from the ground state ⁶H_{5/2} to higher energy levels such as ⁶P_{7/2} (374 nm), ⁶P_{3/2} (401 nm), ⁶P_{5/2} (416 nm), ⁴G_{9/2} (438 nm), ⁴M_{15/2} + ⁴I_{11/2} (473 nm), and several ⁶F and ⁶H levels up to 1586 nm. The absorption intensity varied with Bi₂O₃ concentration, influencing the optical properties of the glass (Mariyappan *et al.*, 2016; Wantana *et al.*, 2017).

Excitation and emission spectra (Vary Bi₂O₃)

Figure 5 exhibit the excitation spectra of BiBaTB1Sm glasses measure by monitored the orange emission of Sm³⁺ ion at 598 nm, showing 9 excitation wavelengths at 344, 361, 374, 401, 414, 438, 462, 472, and 500 nm. Among these, the strong excitation peak at 401 nm, corresponding to Sm³⁺, was selected to analyze the emission spectral characteristics of BiBaTB1Sm.

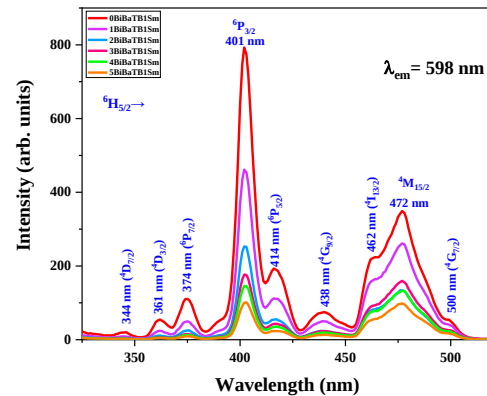


Figure 5. Excitation spectra of BaTB1Sm glasses doped with Bi₂O₃ at varying concentrations

The visible emission spectra of borate 1Sm₂O₃ glasses doped with Bi₂O₃ at concentrations ranging from 0 to 5 mol% were measured by exciting the samples at 401 nm as exhibit in Figure 6. The most intense emission occurs at 598 nm, while other emission peaks are comparatively weaker. The prominent excitation wavelength corresponds to the strong emission observed. It is evident that the undoped glass without Bi₂O₃ exhibits higher emission than the Bi₂O₃-doped samples. This could be due to the opacity induced by Bi₂O₃ doping, which might prevent the laser light from passing through the glass effectively, thus reducing the emission. Additionally, the absorption spectra show that the asymmetry intensity ratio, or R/O ratio, decreases with increasing Bi₂O₃ content, indicating the formation of higher symmetry around the Sm³⁺ ions, which may lead to a decrease in luminescence

intensity (Mariyappan *et al.*, 2016; Wantana *et al.*, 2017).

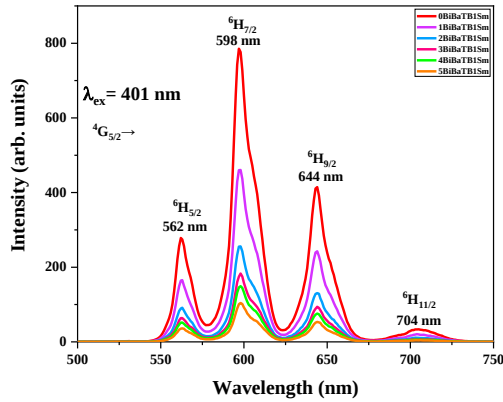


Figure 6. Emission spectra of BaTB1Sm glasses doped with Bi₂O₃ at varying concentrations

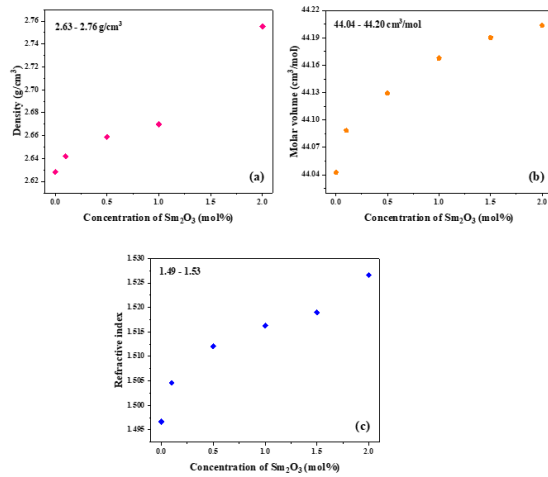


Figure 7. (a) Density (b) molar volume and (c) refractive index of BaTB glasses doped with Sm₂O₃ at varying concentrations

Samarium barium titanium borate glasses (Vary Sm₂O₃)

Physical properties (Vary Sm₂O₃)

Due to the glass sample without Bi₂O₃ doped has a higher emission than Bi₂O₃ doped glass. Therefore, we used a glass formula without Bi₂O₃ to doped Sm₂O₃, is $x\text{Sm}_2\text{O}_3-15\text{BaO}-10\text{TiO}_2-(75-x)\text{B}_2\text{O}_3$, 0.0SmBaTB, 0.1SmBaTB, 0.5SmBaTB, 1.0SmBaTB and 2.0SmBaTB.

All The ρ of glass increase with increasing Sm₂O₃ concentration. This indicates that replacing B₂O₃ with a small number of Sm₂O₃ is since the higher molecular weight of Sm₂O₃ than B₂O₃.

The V_m of glass samples increased with increasing of samarium concentration this is due to Sm₂O₃ acting as a glass modifier, which introduces

more NBOs into the glass network, resulting in bond breakage within the loosely packed structure.

The refractive index of the glass was discover to increase with the addition of Sm₂O₃. This is because the incorporation of Sm₂O₃ into the glass increases its ρ . As the glass becomes denser, it becomes more difficult for light to pass through, leading to an increase in refraction, as displayed in Figure 7(c) (Wantana *et al.*, 2017; Kaewnuam *et al.*, 2016).

Absorption spectra (Vary Sm₂O₃)

Figure 8 present absorption spectra of SmBaTB glasses with varying Sm₂O₃ concentrations. Twelve distinct absorption bands corresponding to transitions of Sm³⁺ ions, which peak is like glass that vary Bi₂O₃. Additionally, an increase in the intensity of these absorption bands was observed with higher Sm₂O₃ concentrations (Wantana *et al.*, 2017).

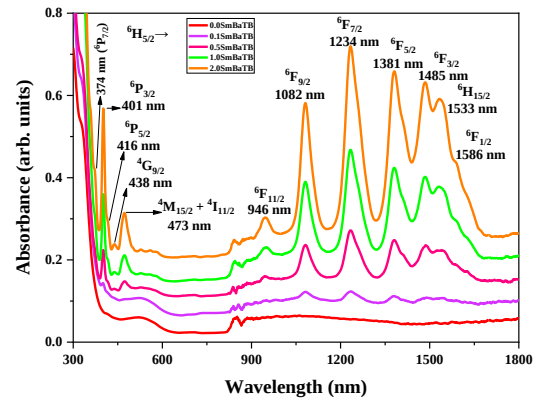


Figure 8. Absorption spectra of BaTB glasses doped with Sm₂O₃ at varying concentrations

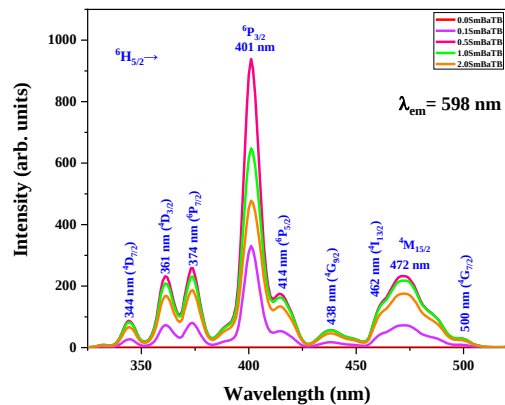


Figure 9. Excitation spectra of BaTB glasses doped with Sm₂O₃ at varying concentrations

Excitation and emission spectra (Vary Sm₂O₃)

Figure 9 present the excitation spectra of SmBaTB glasses, recorded while monitoring the

orange emission of the Sm^{3+} ion at 598 nm. Nine distinct excitation peaks were observed at wavelengths of 344, 361, 374, 401, 414, 438, 462, 472, and 500 nm. Among these, the prominent excitation peak at 401 nm, associated with Sm^{3+} , was chosen for further analysis of the emission spectral properties of SmBaTB glass.

Figure 10 illustrates the partial energy level diagram, highlighting the key emission and non-radiative decay processes. The emitted photons correspond to four wavelengths: 562, 598, 644, and 704 nm (Vijaya *et al.*, 2013; Rao *et al.*, 2012; Li *et al.*, 2007; Souza *et al.*, 2000). Upon excitation at 401 nm, the Sm^{3+} ion initially reaches the $^6\text{P}_{3/2}$ excited state. Subsequently, the energy relaxes non-radiatively (NR) to the lower $^4\text{G}_{5/2}$ state, with energy loss occurring through phonon vibrations. The emission then originates from the $^4\text{G}_{5/2}$ level, with the strongest emission observed at 598 nm, followed by moderate intensity emissions at 644 nm and 562 nm, and a weaker emission at 704 nm.

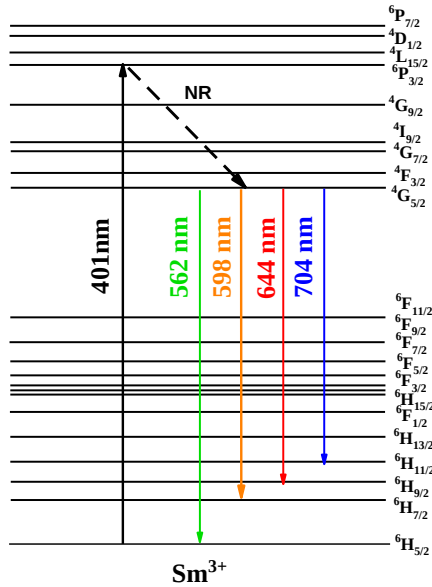


Figure 10. Energy level diagram for emission spectra of Sm_2O_3 doped BaTB glasses

The emission spectra of borate glasses doped with Sm_2O_3 were measured under 401 nm excitation, spanning the wavelength range of 500–750 nm (Figure 11). The most prominent peak appeared at 598 nm, corresponding to the Sm^{3+} ion, with several weaker peaks detected at other wavelengths within this range. A significant increase in emission intensity was observed as the Sm_2O_3 concentration rose up to 0.5 mol%, suggesting efficient excitation of Sm^{3+} ions. However, beyond this concentration, the emission intensity began to decrease, a behavior attributed to

concentration quenching. This decline is linked to non-radiative energy transfer processes e.g. cross-relaxation and resonant energy transfer, which become more pronounced at higher Sm^{3+} ion concentrations. These energy transfer mechanisms interfere with the radiative emission process, thereby reducing the overall emission efficiency (Kaewnuam *et al.*, 2016).

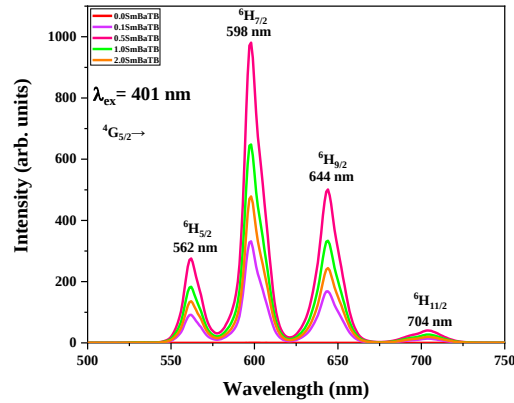


Figure 11. Emission spectra of BaTB glasses doped with Sm_2O_3 at varying concentrations

Lifetime (Vary Sm_2O_3)

Figure 12 illustrates the decay curves of SmBaTB glass, excited at 401 nm and emitting at 598 nm. The lifetimes for SmBaTB glasses with 0.1 to 2.0 mol% Sm^{3+} were 2.266, 1.668, 1.307, and 0.926 ms, respectively, decreasing as Sm^{3+} content increases since non-radiative transitions and concentration quenching (Meejitpaisan *et al.*, 2017). The experimental lifetime (τ_{exp}) for the $^4\text{G}_{5/2}$ level was calculated from the τ_{exp} using the average lifetime formula (Karki *et al.*, 2018).

$$\tau_{\text{exp}} = \frac{\int t I(t) dt}{\int I(t) dt} \quad (3)$$

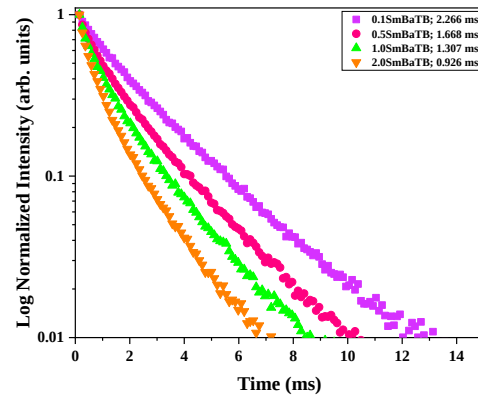


Figure 12. Decay curves of BaTB glasses doped with Sm_2O_3 at varying concentrations

CIE chromaticity diagram (Vary Sm_2O_3)

The CIE 1931 chromaticity diagram's perimeter defines the locus of monochromatic color coordinates, with the interior representing multi-chromatic wavelengths. Figure 13 displays the emission spectra of 0.5SmBaTB glasses under 401 nm excitation, yielding color coordinates (x, y) of (0.59, 0.40), placing the emission in the orange region. This confirms that the glass emits orange light when excited by 401 nm photons, indicating its potential for orange light-emitting applications (Wanta na *et al.*, 2017; Kaewnuam *et al.*, 2016).

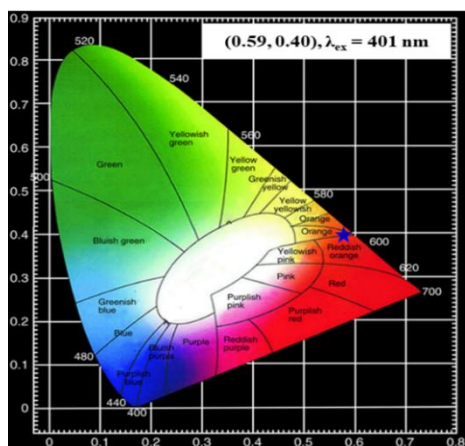


Figure 13. 1931 CIE chromaticity diagram of 0.5SmBaTB glass

Conclusion

In the BiBaTB1Sm glasses, the ρ of glass samples increased with the increasing concentration of Bi_2O_3 . It can be seen that the glass without Bi_2O_3 doped has a higher emission than Bi_2O_3 doped glass. Maybe because the glass is doped with Bi_2O_3 , the glass is opaque. When it's time to bring the glass to measure This causes the laser to measure light, which can't emit through the glass. For SmBaTB glasses, the ρ , V_m , and refractive index increased with higher Sm_2O_3 concentrations. Photons at 401 nm excitation triggered the strongest emission at 598 nm. The optimal Sm_2O_3 concentration for BaTB glass was 0.5 mol %, yielding the highest emission intensity. The CIE chromaticity is the emission in the orange region. The τ_{exp} for different Sm-doped borate glasses were determined using a 401 nm excitation while monitoring the 598 nm emission.

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