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Comparative study of luminescence and optical properties of Sm^{3+} doped glasses with different hosts

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Abstract

The spectoscopic properties of Lithium-gadolinium-borate and Zinc-barium-borate glasses doped with samarium ions had been published in previous studies and metaphorical results were investigated. The samarium-doped lithium-gadolinium-borate glasses [$60Li_2O$:$10Gd_2O_3$:(30-x) B_2O_3:xSm_2O_3] where x = 0.05, 0.10, 0.50, 1.00 and 1.50 mol% and zinc-barium-borate glasses [(60-x)B_2O_3:30BaO:10ZnO: xSm_2O_3] where x= 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 mol% have been prepared by the same method. The absorbtion spectra are similar in transitions from the ground state $^6H_{5/2}$ to the excited states with minor difference. Both glass system gave the emission spectra with peaks at 562, 600, 646, 707 nm arise from the transition $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, and $^6H_{11/2}$ respectively, under 404 nm excitetation ligth. The concentration quenching effect (CQE) was found at 1.0 mol% of the dopant for LGBO: Sm^{3+}, due to not observed for ZBaB: Sm^{3+}. Both glass systems doped with Sm^{3+}.

Keywords: lithium–gadolinium, luminescence spectra, glass, samarium, zinc-barium-borate

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1. Introduction

The potential of rare earth ions, sometimes doped into glasses, as optical devices such as laser in the visible region has inspired an increasing research interests in recent years owing to their highly radiative optical characteristics. Among different glass matrices. Borate glasses stand out as possessing broad range of applications in the fields of optical fiber amplifiers, thermal and mechanical sensors, laser materials, electro-optic switches, optoelectronics and magneto optical devices, reflecting windows, glass ceramics, photonic switches and layers for optical and electronic devices etc., [1- 3].

Of all the rare earth ions, trivalent Samarium (Sm^{3+}) ion is having significance in ongoing research due to its applications in high-density optical storage, color displays different fluorescent devices, undersea communication and bright emission in red-orange regions leads to visible solid-state lasers [4]. High quantum efficiency and a range of populating and quenching emission channels are possible with ground state of ($^4G_{5/2}$) Sm^{3+} ions [5]. Earlier, several authors reported physical, optical and photoluminescence studies on Sm^{3+} doped with different host glass matrices. Samarium exhibit promising characteristics for spectral hole burning studies [6]. Sm^{3+} ions are important activators for inorganic lattices, giving rise to the emission of reddish orange light due to electronic transitions $^6G_{5/2}$, $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ [7]. Borate glasses containing high concentrations of rare earth ions have more advantages than any other oxide glasses [8].

It is well known that the boric oxide, B_2O_3, acts as one of the most important glass formers. Borate glasses have high transparency, low melting point, high thermal stability, different coordination numbers, and good solubility of rare-earth ions [9, 10]. Important applications of borate glasses in laser and photonic devices for development of optical technologies make them interesting materials to study. On the other hand, ZnO can enter in the glass network either as glass former or as a modifier or both [11]. Glasses containing ZnO give rise to good non-linear optical properties [12]. Also, the addition of alkaline earth oxide, like BaO, improves the

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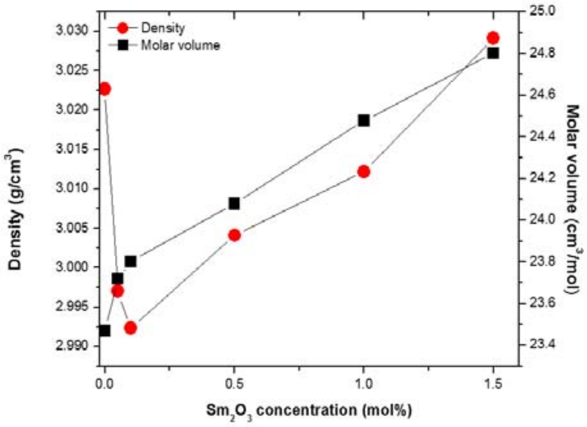

Figure 1. Densities and molar volumes for different concentration of Sm_2O_3 in LGBO glasses.

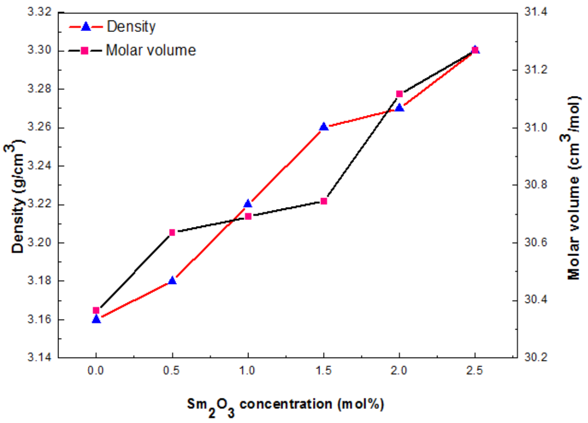

Figure 2. Densities and molar volumes for different concentration of Sm_2O_3 in ZBaB glasses.

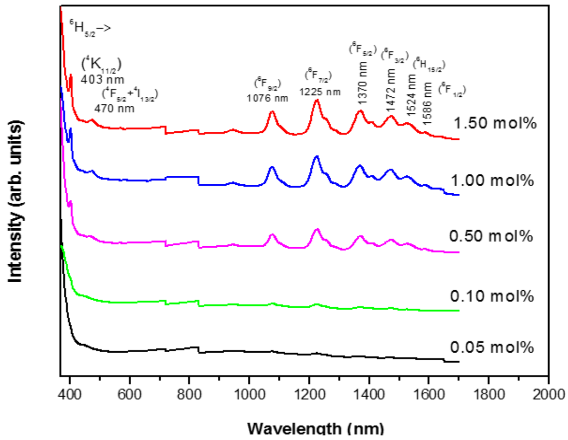

Figure 3. The absorbance spectra for LGBO:Sm^{3+} glasses in UV-VIS- NIR range.

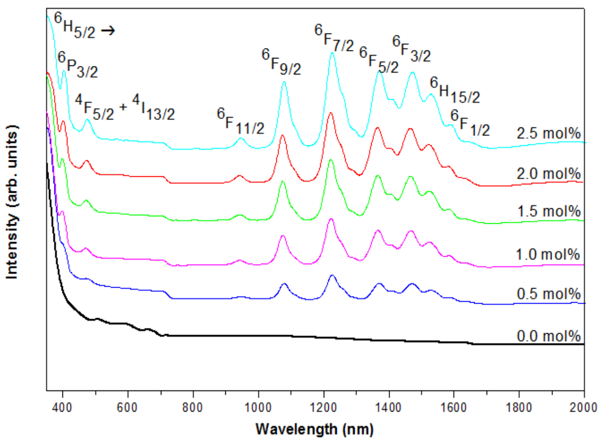

Figure 4. The absorbance spectra for ZBaB:Sm^{3+} glasses in UV-VIS- NIR range.

optical properties of the glasses [13] and can be used as low cost optical connectors [14].

Two glass systems had been studied in previous works: samarium-doped lithium-gadolinium-borate glasses [$60Li_2O$:$10Gd_2O_3$:(30-x) B_2O_3:xSm_2O_3] where x = 0.05, 0.10, 0.50, 1.00 and 1.50 mol% [15] and zinc-barium-borate glasses [(60-x)B_2O_3:30BaO:10ZnO: xSm_2O_3] where x= 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 mol% [16]. The purpose of the present work is to compare the physical, optical and photoluminescence properties of these glass systems named LGBO: Sm^{3+} and ZBaB: Sm^{3+} respectively.

2. Materials and methods

Two works have presented the similar procedures in preparing glass samples. The first study used Li_2O, Gd_2O_3, B_2O_3 (LGBO) with the composition of $60Li_2O$:$10Gd_2O_3$:(30-x)B_2O_3:xSm_2O_3 where x = 0.05, 0.10, 0.50, 1.00 and 1.50 mol% each of about 20 g.

Another work used the ZBaB: Sm^{3+} glasses of chemical composition of (60-x)B_2O_3: 30BaO: 10ZnO: xSm_2O_3 where x = 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 mol%. The glasses were melted at high temperature for 3 hrs. They were annealed at lower temperature for hours and cooled down to the room temperature. For further reproduction by other investigators, please add both temperatures and times for melting and annealing processes. Densities of the glasses were measured using a digital balance (4-digit sensitive microbalance A&D, HR-200) and then molar volumes were calculated. UV-VIS-NIR spectro-photometer (UV-3600 Shimadzu) was used to measure the absorption spectra from 350 to 1700 nm. Emission and excitation spectra were measured using Cary Eclipse Fluorescence Spectrophotometer with 404 nm excited radiation from a Xenon compact arc lamps.

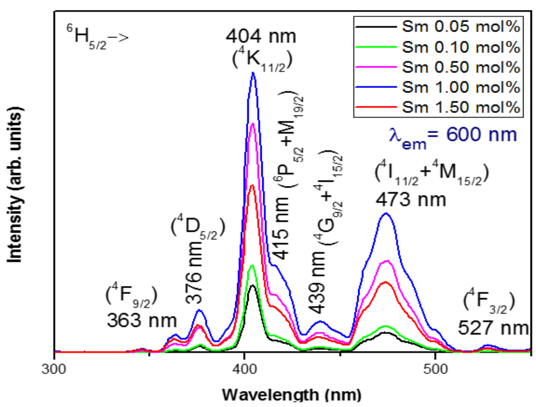

Figure 5. The excitation spectra for LGBO glasses doped with different mol% of Sm^{3+}.

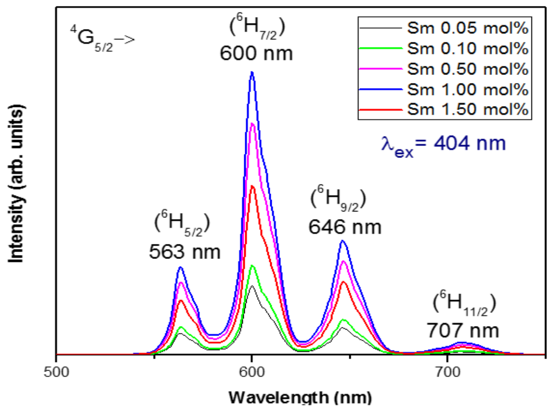

Figure 7. The emission spectra for LGBO glasses doped with different mol% of Sm^{3+}.

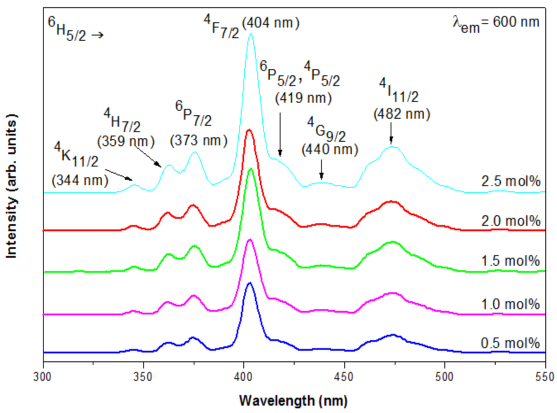

Figure 6. The excitation spectra for ZBaB glasses doped with different mol% of Sm^{3+}.

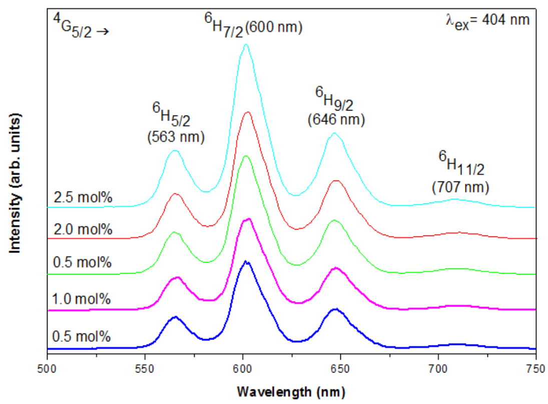

Figure 8. The emission spectra for ZBaB glasses doped with different mol% of Sm^{3+}.

3. Results and discussion

Fig. 1 shows density and molar volumes of LGBO glasses. The density dropped until 0.10 mol% and tends to increase after that point, while molar volume of the glasses tends to increase with concentration of Sm_2O_3. This is similar to those of ZBaB glasses where both properties tend to increase from zero concentration of Sm^{3+}. The decrease of density indicates that non-bridging oxygen (NBOs) increase while the increase of density shows the increase in oxygen packing density and hence the structure becomes more compact [7]. The increase of molar volume connected with the increase in inter-atomic spacing. Sm_2O_3 ions act as network modifiers which also made up the NBOs in glass structure [5].

The absorption bands for LGBO glasses indicate the transitions from the ground state $^6H_{5/2}$ to different higher-level states. As shown in Fig.3, The various spectroscopic transitions observed are as follows: $^4K_{11/2}$ (403 nm) and $^4F_{5/2}$ + $^4I_{13/2}$ (470 nm) for the UV-VIS range, and $^6F_{9/2}$ (1076 nm), $^6F_{7/2}$ (1225 nm), $^6F_{5/2}$ (1370 nm), $^6F_{3/2}$ (1472 nm), $^6H_{15/2}$ (1524 nm), and $^6F_{1/2}$ (1586 nm) for NIR range indicating the Sm^{3+} in glass matrices. For ZBaB glasses in Fig.4, the spectra show the transitions from the same ground state to similar states. The transitions observed are as follows: $^6P_{3/2}$ (402 nm) and $^4F_{5/2}$ + $^4I_{13/2}$ (470 nm) for the UV-VIS range, and $^6F_{11/2}$ (946 nm), $^6F_{9/2}$ (1079 nm), $^6F_{7/2}$ (1226 nm), $^6F_{5/2}$ (1370 nm), $^6F_{3/2}$ (1472 nm), $^6H_{15/2}$ (1524 nm), and $^6F_{1/2}$ (1586 nm) for NIR range.

The first study found 7 obvious peaks in excitation spectra (Fig. 5) indicating the energy transition from the ground state $^6H_{5/2}$ to the excited states : $^4F_{9/2}$ (363 nm), $^4D_{5/2}$ (376 nm), $^4K_{11/2}$ (344 nm), $^6P_{5/2}$ + $^4M_{19/2}$ (415 nm), $^4G_{9/2}$ + $^4I_{15/2}$ (439 nm), $^4I_{11/2}$ + $^4M_{15/2}$ (473 nm), and $^4F_{3/2}$ (527 nm) of Sm^{3+}. While the latter one found the similar positions of peaks for the transitions to the states: $^4K_{11/2}$ (344 nm), $^4H_{7/2}$ (359 nm), $^6P_{7/2}$ (373 nm), $^4F_{7/2}$ (404 nm), $^6P_{5/2}$ + $^4P_{5/2}$ (419 nm), $^4G_{9/2}$ (440 nm), and

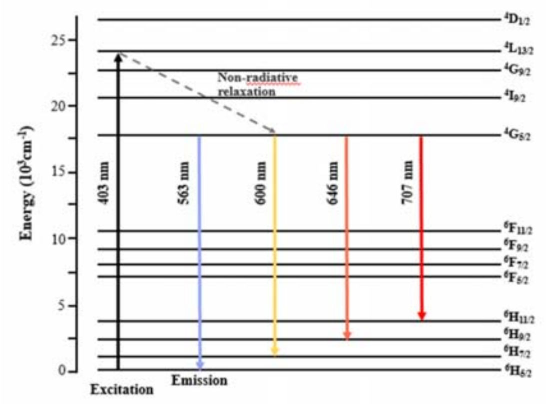

Figure 9. The energy level diagrams of Sm^{3+}

$^4I_{11/2}$ (482 nm) of Sm^{3+}, as shown in Fig.6. Although both studies had identified the similar peaks but the states were reported differently. The radiative emissions in both LGBO and ZBaB glass structures occurred by the transition from $^4G_{5/2}$ level to the lower level: $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, and $^6H_{11/2}$ corresponding to the emission spectra shown in Fig 7-8. For LGBO glasses, the concentration quenching effect (CQE) was found at 1.0 mol% of Sm_2O_3, due to not observed for ZBaB glass. When Sm^{3+} ions are excited to any energy level above $^4G_{5/2}$ level, the non-radiative decay will occurred. There are fast non-radiative multiphonon relaxation to $^4G_{5/2}$ level [8], as shown in the energy level diagram in Fig. 9 [9, 10].

4. Conclusions

In this study, The result comparisons were conducted on the samarium-doped lithium-gadolinium-borate glasses [$60Li_2O$: $10Gd_2O_3$: $(30\text{-}x)B_2O_3$:xSm_2O_3] (LGBO: Sm^{3+}) (x = 0.05, 0.10, 0.50, 1.00, and 1.50 mol%) and zinc-barium-borate glasses [$(60\text{-}x)B_2O_3$:30BaO:10ZnO: xSm_2O_3] (ZBaB: Sm^{3+}) (x= 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 mol%) The density of LGBO: Sm^{3+} glasses dropped until 0.10 mol% and tends to increase after that point, while molar volume of the glasses tends to increase with concentration of Sm_2O_3. While those properties for ZBaB: Sm^{3+} tends to increase with the concentration of Sm_2O_3. The intensity of absorption spectra also increases with concentration of sm^{3+} for both glass systems. The spectra are similar in transitions from the ground state $^6H_{5/2}$ to the excited states with minor different. Both glass system gave the emission spectra with intensity peaks at 562, 600, 646, 707 nm arise from the transition $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, and $^6H_{11/2}$ respectively, under 404 nm light. The concentration quenching effect (CQE) was found at 1.0 mol% of the dopant for LGBO: Sm^{3+}, but not for ZBaB: Sm^{3+}.

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