Luminescence Properties of Tb, SmCo-doped in Alkali Aluminoborate Glasses

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Abstract: Spectroscopic properties of Tb$^{3+}$ and Sm$^{3+}$ ions co-doped in alkali aluminoborate glasses (70-x-y)B$_2$O$_3$.28Li$_2$O.2Al$_2$O$_3$.xSm$_2$O$_3$.yTb$_2$O$_3$ (ABL:Tb, Sm) fabricated by melting method have been studied. The emission intensity of Tb$^{3+}$ or Sm$^{3+}$ in ABL:Tb or ABL:Sm glasses is influenced by the Tb$^{3+}$ or Sm$^{3+}$doping concerning with the 0.75 mol% and 1.0 mol% optimum concentrations, respectively. The concentration quenching effect of Tb$^{3+}$ or Sm$^{3+}$ in ABL:Tb, Sm glasses is observed. The mechanism of this phenomenon is attributed to the f-f interaction for either Tb$^{3+}$/Sm$^{3+}$. The ABL:Tb, Sm glasses can produce color emission from green to red by properly tuning the relative ratio between Tb$^{3+}$ and Sm$^{3+}$. The emission intensity of Tb$^{3+}$/Sm$^{3+}$ in ABL:Tb, Sm glasses can be enhanced by the energy transfer from Tb$^{3+}$/Tb$^{3+}$ and Sm$^{3+}$/Sm$^{3+}$. The results indicate that ABL:Tb, Sm may be a promising double emission for white light emitting diodes.

Keywords: Sm$^{3+}$ and Tb$^{3+}$ ions; alkali aluminoborate glass, the concentration quenching mechanism.

1. Introduction

White light-emitting diodes (LEDs) offer many advantages such as long service lifetime, thermal resistance, and high efficiency [1-3]. Therefore, white LEDs are expected to be a new light source in the illumination field. Besides that, due to the unique structural and physicochemical properties, alkali aluminoborate glasses doped with RE ions with the ingredients focus on the advantages: mechanical stability, chemical, thermal, low melting point, the solubility of rare earth ions good and high
transparency[4-5]. The presence of structurally different borate units in alkali metal borate glasses is favorable for spectroscopic investigations of RE ions. These structural differences are usually correlated to chemical composition, type of modifiers and conditions during glass preparation. Broadband emitters are usually used to sensitize the luminescence of rare earth and transition metal ions. Particularly, the Tb³⁺ and Sm³⁺ ions show an efficient narrowband emission due to its f–f electric dipole allowed transitions. In most of cases, this kind of energy transfer belongs to resonance type. In recent years, the resonance energy transfer between impurity ions in a solid material has been the subject of intense research, mainly because of its importance in the development of efficient phosphor materials for solid-state lighting. Among the rare-earth ions, Tb³⁺ and Sm³⁺ ions are two of the important luminescent centers. Therefore, in the present paper, the luminescent characteristics Tb³⁺ and Sm³⁺ ions co-doped in ABL glasses are investigated. The glasses can create color emission from green to red. They can be effectively excited by near-UV, and are suitable for serving as white LEDs.

2. Experiments

Alkali aluminoborate glass doped with Sm³⁺ or/and Tb³⁺ were prepared by conventional melt quenching technique. The stoichiometric ratio of ABL glasses is (70-x-y)B₂O₃-2Al₂O₃-28Li₂O-xSm₂O₃-yTb₂O₃. The metal oxides were weighed accurately in an electronic balance mixed thoroughly and ground to a fine powder. The batches were then placed in quartz cup and melted in an electrical furnace in the air at 1323 K for 1.5 hours. The melt was quenched to room temperature in air. The glasses were then annealed at 630 K for 2 hours. The glasses thus obtained were throughout, evenly, no bubble. The samples were cut, ground, polished to form cylinder block shape with product size: thickness d = 0.1 mm, radius r = 6.0 mm (used for the measurement of refractive index n, density, absorption, and fluorescence); crushing and sorting grab particles range in size from 76 to 150 micron powder products (used for X-ray diffraction). The glass formation was confirmed by powder X-ray diffraction.

The measurement of the refractive index n is performed on the system Abbe refractometer at a wavelength of Na lamp, 589 nm with C₁₀H₂Br (1 - bromonaphthalin ) used as the liquid in contact. The measurement of density made by Archimede method, using xylene as immersion liquid form. Optical absorption spectra were recorded in the wavelength regions 200 nm – 2500 nm using Varian spectrometer system Cary 5E UV-VIS-NIR, with a resolution of 1 nm. Fluorescence spectra were obtained at room temperature using Fluorolog - 3 Model FL3 - 22, resolution of 0.3 nm, excitation light xenon (Vehicle).

3. Results and discussion

3.1. Spectral properties of ABL:Tb³⁺ glasses

Figure 1 depicts the excitation and emission spectra of ABL:Tb³⁺ glasses. The excitation spectrum exhibits a series of sharp peaks between 250 nm and 400 nm. The sharp bands between 280 nm and 400 nm are assigned transitions within 4f⁶ from ⁷F₅, ⁷F₆ ground level to ⁵F₅, ⁵H₇, ⁵D₁₀, ⁵L₁₀, ⁵G₆, ⁵D₂, and ⁵D₂-⁴ excitation levels [1]. The emission spectrum of ABL:Tb³⁺ glasses excited by 365 nm presents four peaks at around 487 nm, 541 nm, 584 nm, and 621 nm which originate to the transitions between the excited ⁵D₁ level and ⁷F₇ (J=6,5,4,3) level of Tb³⁺ ion, respectively [6]. The strongest emission peak is located at 541 nm, corresponding to the typical transition ⁵D₄→⁷F₅ of Tb³⁺ ion.
For ABL:Tb\textsuperscript{3+} glasses, the values of Tb\textsuperscript{3+} optimum doping content are discussed (the results are shown in Fig 2), the emission intensity first increases with the increasing of Tb\textsuperscript{3+} doping content, and reaches a maximum at 0.75 mol\% Tb\textsuperscript{3+}, then decreases. The phenomenon of decrease in emission intensity after a certain concentration is called concentration quenching, the concentration quenching mechanism due to concentration may be due to energy emitted from the excitatory state being lost along the cross-relaxation. This is a restoration mechanism that occurs by transmitting the resonance energy between two adjacent ions due to the unique energy level structure of these rare earth ions (in Fig 3) or the non-radiative energy transfer from one Tb\textsuperscript{3+} to another Tb\textsuperscript{3+} ion may occur by exchange interaction, radiation reabsorption or multiple-multiple interaction [7]. The transition of Tb\textsuperscript{3+} is allowed while exchange interaction is responsible for the energy for forbidden transitions. It means that the mechanism of exchange interaction plays main role in the energy transfer between Tb\textsuperscript{3+} ions in ABL:Tb\textsuperscript{3+} glasses [7].
3.2. Spectral properties of ABL: Sm$^{3+}$ glasses

Figure 4 depicts the excitation and emission spectra of ABL: Sm$^{3+}$ glasses. The excitation spectrum exhibits a series of sharp peaks between 270 nm and 500 nm. The sharp bands between 300 nm and 500 nm are assigned to transitions between the $^6H_{5/2}$ and $^4I_{11/2}$, $^6P_{3/2}$, and $^4D_{3,5,7/2}$ levels [8]. The emission spectrum of BLN: Sm$^{3+}$ glasses excited by 400 nm presents four peaks at around 562 nm, 600 nm, 646 nm, and 707 nm, which are originated from the transitions between the excited $^4G_{5/2}$ level and $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, and $^6H_{11/2}$ levels of Sm$^{3+}$ ion, respectively [8, 9].

The data analyzed from the emission spectra has shown that three bands having strong intensity and narrow width appear at 562 nm, 600 nm, and 646 nm. While the wide range with weak strength is revealed at 700 nm. On the other hand, the fluorescence spectra have seen that all 4 bands are overlapping each other a maximum of two (types are the same), as explained by the authors in [3, 4, 9], it is the splitting of the flow allowed by the electric dipole (which is allowed by the electric dipole).

![Fig 4. Emission and excitation spectra of Sm$^{3+}$ doped ABL: Sm glasses](image1)

For ABL: Sm$^{3+}$ glasses, the values of Sm$^{3+}$ optimum doping content were discussed (as shown in Fig. 5). Firstly, The emission intensity increases with the increasing of Sm$^{3+}$ doping content, and reaches a maximum at 1.0 mol% Sm$^{3+}$ before decreasing. The decrease of luminescence intensity after a certain concentration is called concentration quenching or self-quenching (SQC). The SQC phenomenon is attributed to the nonradiative transfer processes, which consists of multiphonon relaxation and energy transfer between the pairs of Sm$^{3+}$ ions [9]. In the case of Sm$^{3+}$ ions, the energy gap between fluorescent level $^4G_{5/2}$ and next lower level $^4F_{11/2}$ is around 7300 cm$^{-1}$. This energy gap is 5-6 times higher than the highest phonon energy in borate glass. Thus multiphonon relaxation rate is negligible and concentration quenching may be mainly due to energy transfer. The main interaction mechanism between the ions is usually dipole-dipole (DD), when the selected rule is not satisfied, it can happen by the interaction of higher order: dipole-quadrupole (DQ), quadrupole-quadrupole (QQ). The Inokuti and Hirayama model allow us to find the dominant interaction mechanism between the ions.
Fig. 6 presents the experimental decay curves obtained for different Sm$^{3+}$ ion concentrations. By using the Inokuti-Hirayama model: when the migration process is negligible, decay curves can be expressed as:

$$ I = I_0 \exp \left\{ -\frac{t}{\tau_0} - Q \left( \frac{t}{\tau_0} \right)^{3S} \right\} $$

where $t$ is the time after excitation, $\tau_0$ is the intrinsic decay time of donor in absence of acceptor. The value of $S$ (=6, 8, 10) depends on whether the dominant mechanism of interaction is dipole-dipole, dipole–quadrupole or quadrupole–quadrupole, respectively. The energy transfer parameter ($Q$) is found in the fitting process and is calculated by:

$$ Q = \frac{4\pi}{3} \Gamma \left( 1 - \frac{3}{S} \right) N R_0^3 $$

$\Gamma(x)$ is the gamma function, its value is equal to 1.77 for dipole-dipole (DD), 1.43 for dipole–quadrupole (DQ) and 1.30 for quadrupole–quadrupole (QQ), respectively. $N$ is the concentration of Sm$^{3+}$ ions, $R_0$ is the critical distance defined as donor-acceptor separation for which the rate of energy transfer to the acceptors is equal to the rate of intrinsic decay of the donor. The fluorescence decay curve of ABL:Sm$^{3+}$ with 0.25 and 0.5 mol% of Sm$^{3+}$ ions to have the best fitting with $S = 6$, where we used $\tau_0$ value (~2.62 ms) obtained for the ABL doped with 0.5 mol% of Sm$^{3+}$ ions. The value of $S = 6$ indicated that the dominant interaction for energy transfer through cross-relaxation is of dipole-dipole type. The parameter ($S$) is good as an agreement with other reports [8]. Energy transfer parameters $Q$, CDA and critical distance ($R_0$) are calculated and were shown in table 1.

![Fig. 6. Decay curves of Sm$^{3+}$ ions in ABL glasses.](image)

Table 1. Variation of lifetime ($\tau$, ms), quantum efficiency ($\eta$, %), cross-relaxation rate ($W_{DA}$ s$^{-1}$), energy transfer parameter ($Q$), critical distance ($R_0$, Å) and donor-acceptor interaction parameter ($C_{DA}$,×10$^{-40}$ cm$^6$/s) with respect to concentration (mol%) of Sm$^{3+}$ ions in BLN glasses.

<table>
<thead>
<tr>
<th>Concentrations (% mol)</th>
<th>$\tau$ (ms)</th>
<th>$\eta$ (%)</th>
<th>$W_{DA}$ s$^{-1}$</th>
<th>$Q$</th>
<th>$R_0$(Å)</th>
<th>$R$ (Å)</th>
<th>$C_{DA}$,×10$^{-40}$ cm$^6$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>2.95</td>
<td>89.3</td>
<td>-</td>
<td>-</td>
<td>6.84</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>2.62</td>
<td>73.7</td>
<td>35.5</td>
<td>0.54</td>
<td>6.84</td>
<td>9.56</td>
<td>0.39</td>
</tr>
</tbody>
</table>
From the emission spectra of ABL:Sm$^{3+}$ glasses, the energy level diagram of Sm$^{3+}$ ion is shown in Fig. 7. When Sm$^{3+}$ ions are excited to the excited levels above the $^4G_{5/2}$, there is a fast non-radiative relaxation to the $^4G_{5/2}$ lowest excited level and emission takes place from $^4G_{5/2}$ level to its lower levels. The energy transfer process through cross – relaxation (CR) between the pair of Sm$^{3+}$ ions (as shown in Fig. 7) leads luminescence quenching. The cross – relaxation channels in ABL glasses may be estimated to be ($^4G_{5/2} \rightarrow ^6F_{5/2}$) → ($^6H_{5/2} \rightarrow ^6F_{11/2}$) and ($^4G_{5/2} \rightarrow ^6F_{11/2}$) → ($^6H_{5/2} \rightarrow ^6F_{5/2}$) as the energy difference between these transitions are negligible. The cross – relaxation is due to the energy transfer from the Sm$^{3+}$ ion in an excited $^4G_{5/2}$ state to a near Sm$^{3+}$ ion in the ground state $^6H_{5/2}$ state. This transfer leads the first ion into the intermediate level of $^6F_{5/2}$ (or $^6F_{11/2}$) at around 1373 nm (or 946 nm) and the second one in $^6F_{11/2}$ (or $^6F_{5/2}$) at around 946 nm (or 1373 nm), which occur in resonance with the $^4G_{5/2} \rightarrow ^6F_{5/2}$ (or $^4G_{5/2} \rightarrow ^6F_{11/2}$) transition. Then, from these states, the Sm$^{3+}$ ions will relax to ground state by nonradiative relaxation. Thus, emission will be quenched [8, 9].

Fig 7. Energy level diagram and cross-relaxation channels for Sm$^{3+}$ ions in ABL glasses.

### 3.3. Spectral properties of ABL:Sm$^{3+}$,Tb$^{3+}$ glasses

Figure 8 exhibits the emission spectra of ABL:1.0Sm$^{3+}$,xTb$^{3+}$. With the increase of Tb$^{3+}$ concentration, the phosphors can create color emission from blue to yellowish – green. Moreover, while the emission intensity of Sm$^{3+}$ almost unchanged, the emission intensity of Tb$^{3+}$ increases and has a maximum intensity at $x = 0.75$. The forbidden 4f – 4f electronic transitions within the 4f$^n$ configuration of Tb$^{3+}$ increases. Therefore, there is no effective energy transfer from the Sm$^{3+}$ to the Tb$^{3+}$ to enhance the emission of Tb$^{3+}$[10-13].

The same results can also be seen from Fig 9 which exhibits the emission spectra of ABL:0.75Tb$^{3+}$,xSm$^{3+}$. It has shown that the color emission from blue to red can be observed with the increase of Sm$^{3+}$ concentration. The emission intensity of Sm$^{3+}$ increases until reaching maximum intensity at $x = 1.0$%mol.
Fig. 8. Emission spectra of ABL: xTb$^{3+}$,1.0Sm$^{3+}$ with several different values of Sm$^{3+}$ content.  

Fig. 9. Emission spectra of ABL: 0.75Tb$^{3+}$,xSm$^{3+}$ with several different values of Sm$^{3+}$ content.

As such, Tb$^{3+}$ and Sm$^{3+}$ ions are isolated emission center. This can be explained by the fact that the structure of energy levels of these ions does not allow for the coherent energy transfer from Sm$^{3+}$ ion to Tb$^{3+}$ ion.

4. Conclusion

Spectroscopic properties of Tb$^{3+}$ and Sm$^{3+}$ ions co-doped in alkali aluminoborate glasses (70-x-y)B$_2$O$_3$.28Li$_2$O.2Al$_2$O$_3$.xSm$_2$O$_3$.yTb$_2$O$_3$ have been studied. The emission intensity of Sm$^{3+}$ or Tb$^{3+}$ in ABL:Sm or ABL:Tb glasses is influenced by the Sm$^{3+}$ or Tb$^{3+}$ doping content, concerning with the 1.0 mol and 0.75 mol optimum concentrations, respectively. The concentration quenching effect of Tb$^{3+}$ or Sm$^{3+}$ in ABL:Tb$^{3+}$, Sm$^{3+}$ glasses was obtained which is attributed to the f-f interaction for either Tb$^{3+}$ and Sm$^{3+}$. The ABL:Tb$^{3+}$,Sm$^{3+}$ glasses can produce color emission from green to red by properly tuning the relative ratio between Tb$^{3+}$ and Sm$^{3+}$. The results indicate that ABL:Tb$^{3+}$,Sm$^{3+}$ may be a promising double emission for W-LED.

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