



## Spectroscopy and energy transfer in Tb<sup>3+</sup>/Sm<sup>3+</sup> co-doped lead borate glasses

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### ABSTRACT

In this work, luminescence properties of Tb<sup>3+</sup>/Sm<sup>3+</sup> co-doped lead borate glasses are examined in details. Luminescence spectra of rare earths were measured under different excitation wavelengths. Characteristic luminescence bands corresponding to electronic transitions of terbium and samarium ions were detected under direct excitation of Tb<sup>3+</sup>. The energy transfer from Tb<sup>3+</sup> to Sm<sup>3+</sup> ions in lead borate glass occurs through a nonradiative process with an efficiency from 0.6% to 16%, depending on samarium concentration. Luminescence decay curves for the <sup>4</sup>G<sub>5/2</sub> state of Sm<sup>3+</sup> ions in lead borate glasses were fitted using the Inokuti-Hirayama model. The concentration-dependent luminescence quenching was explained by the non-radiative energy transfer process between the Sm<sup>3+</sup> ions through the cross-relaxation mechanism. The CIE chromaticity coordinates and correlated color temperatures for Tb<sup>3+</sup>/Sm<sup>3+</sup> co-doped lead borate glasses are also presented and discussed.

### 1. Introduction

In the last years, numerous published works are devoted to down- and up-conversion luminescence processes of rare earth ions in inorganic glasses [1–7] and glass-ceramics [8–10] related to their potential applications in solid-state lasers, up-conversion sensor thermometry, solar cell technology, and white light emitting diodes (W-LEDs). The latter ones, i.e. white light emitting glasses are considered to be promising materials for W-LEDs technology due to their homogeneous light emission, simpler manufacture procedure, lower production cost, free of halo effect, and better thermal stability [6,7]. Glasses pumped by UV LEDs could be appropriate for solid-state-lighting (SSL) technology and white light generating sources. In particular, many efforts have been made to develop glass materials doubly [6] or triply [7] doped with rare earth ions suitable for white LEDs and their energy transfer processes.

Among rare earths, samarium ions belonging to 4f<sup>5</sup> electronic configuration are important optical activators widely used in various glass host systems, especially borate, fluoroborate and lead borate based glasses [11–22]. The trivalent Sm<sup>3+</sup> ions exhibit strong reddish-orange luminescence related to <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>9/2</sub> transition. On the other hand, the trivalent Tb<sup>3+</sup> ions in borate based glasses are known as green emitters due to main <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition [23–32]. However, terbium ions as the optically active ions play dual role, when second rare earth ion is introduced to the glass host. Tb<sup>3+</sup> can be also efficient sensitizer

for Sm<sup>3+</sup>, giving important contribution to reddish-orange luminescence. In Tb<sup>3+</sup>/Sm<sup>3+</sup> co-doped system, terbium plays the role as sensitizer/donor, whereas samarium is an activator/acceptor. The sensitizer/donor transfers nonradiatively its excitation energy to activator/acceptor by quenching (Tb<sup>3+</sup>) and enhancing (Sm<sup>3+</sup>) luminescence. Energy transfer process occurs between a sensitizer/donor and an activator/acceptor, if the energy difference between the excited state of sensitizer (Tb<sup>3+</sup>) and ground state activator (Sm<sup>3+</sup>) are in resonance. The spectroscopic investigations indicates that Tb<sup>3+</sup>/Sm<sup>3+</sup> co-doped systems are promising for energy transfer processes. Since luminescence properties of borate based glasses singly doped with Sm<sup>3+</sup> and Tb<sup>3+</sup> [11–32] are well documented in literature, only a few published works is devoted to Tb<sup>3+</sup>/Sm<sup>3+</sup> co-doped glass host matrices. In particular, emission properties of Tb<sup>3+</sup>/Sm<sup>3+</sup> and their energy transfer mechanisms in aluminosilicate [33–35], lead fluorotellurite [36], zinc phosphate [37,38], potassium-fluoro-phosphate [39], multicomponent Na<sub>2</sub>O-CaO-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> glasses [40] and other inorganic phosphors [41,42] are well reported. The previous scientific works suggest that glasses co-doped with Tb<sup>3+</sup>/Sm<sup>3+</sup> exhibiting strong luminescence in the blue/green (Tb<sup>3+</sup>) and reddish/orange (Sm<sup>3+</sup>) spectral region are useful in high density optical storage, color displays and solid-state lasers. Furthermore, they are also promising materials for white light emitting diodes [43].

It is generally accepted that glasses containing PbO and/or PbF<sub>2</sub> are classified as toxic raw materials and consequently they are being often

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eliminated from various practical applications due to their hazardous effect on health and environment. On the other hand these components were established to play important role in glass formation and further strengthening of glass host network [44,45]. Previous investigations indicate that lead oxide is an important glass modifier not only for affecting the chemical and mechanical stabilities of glasses, but also for improving their thermal and optical properties [46]. Germanate glass containing lead exhibits broad potential applications in photonics and catalysis [47]. For that reason, numerous results published lastly were focused on studies done for the luminescence properties of rare earth ions in oxide glasses containing lead [48–51]. Also, mixed oxyfluoride glasses and transparent glass-ceramics containing  $\text{PbF}_2$  were investigated [52–54]. Currently, a special attention has been paid to lead alumino borate glasses singly doped with rare earth ions, which are excellent amorphous materials for visible luminescent device applications [55–57].

The intention of our work is to study the energy transfer processes between  $\text{Tb}^{3+}$  and  $\text{Sm}^{3+}$  ions in lead borate glasses. We believe that the received experimental results give important contribution to the knowledge of spectroscopy and luminescence characteristics of rare earth co-doped glass systems containing lead and their energy transfer processes. The energy transfer in  $\text{Tb}^{3+}/\text{Sm}^{3+}$  co-doped lead borate glass was not earlier presented and discussed. Recently, the energy transfer processes and their mechanisms in  $\text{Pr}^{3+}/\text{Yb}^{3+}$  [58],  $\text{Ce}^{3+}/\text{Sm}^{3+}$  [59],  $\text{Dy}^{3+}/\text{Tb}^{3+}$  and  $\text{Tb}^{3+}/\text{Eu}^{3+}$  [60,61] co-doped lead borate glasses were examined in details.

## 2. Experimental

Series of lead borate glass samples singly and doubly doped with  $\text{Tb}^{3+}$  and  $\text{Sm}^{3+}$  ions were prepared by mixing and melting appropriate amounts of metal anhydrous oxides of high purity (99.99%, Aldrich Chemical Co.) as starting materials. In order to prepare the samples, appropriate amounts of all components were mixed homogeneously together and heated at the atmosphere of dry argon. Then, they were melted at 850 °C for 1 h. The fully amorphous and transparent glass samples were obtained, which was confirmed by X-ray diffraction analysis using INEL diffractometer. The characteristic temperatures of the glass samples were determined based on the measurement taken with a SETARAM Labsys thermal analyzer. DSC curves were measured under standard heating rate of 10 °C/min. Characteristic temperatures and thermal stability parameters were determined with accuracy of 0.5 °C.

The optical absorption spectra were recorded using a Varian 5000 UV–VIS–NIR spectrophotometer. The excitation and emission spectra as well as decay measurements were performed on a PTI QuantaMaster QM40 coupled with tunable pulsed optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser (Opotek Opolette 355 LD). The luminescence was dispersed by double 200 mm monochromators. The luminescence spectra were recorded using a multi-mode UVVIS PMT (R928) detector controlled by a computer. The spectral measurements were carried out with a resolution of 0.1 nm. Luminescence lifetimes were determined with accuracy of 1  $\mu\text{s}$ . All measurements were carried out at room temperature.

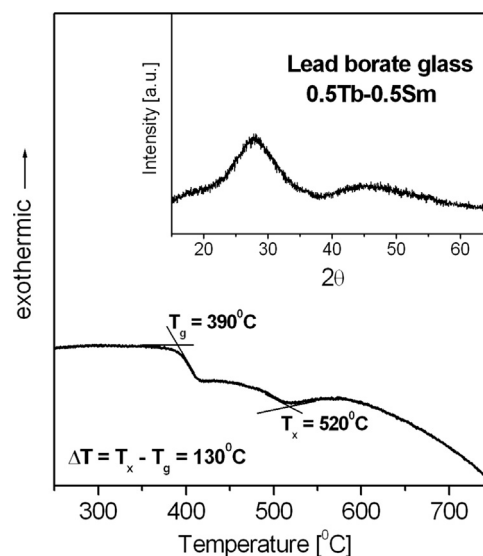
## 3. Results and discussion

$\text{Tb}^{3+}/\text{Sm}^{3+}$  co-doped lead borate glasses were synthesized. The obtained samples were transparent and free from crystalline inclusions. The chemical compositions of glass samples are given in Table 1. Next, lead borate glasses co-doped with rare earths were characterized by DSC and XRD measurements. Fig. 1 shows typical DSC curve measured for lead borate glass. From DSC curve glass transition temperature  $T_g$  and crystallization onset  $T_x$  were evaluated. The values of  $T_g$  and  $T_x$  are close to 390 °C and 520 °C, respectively, and they are nearly independent on rare earth ions ( $\text{Tb}^{3+}/\text{Sm}^{3+}$ ) concentrations. Based on

**Table 1**

Chemical composition of rare earth - doped lead borate glasses.

Glass sample	Chemical composition [in wt%]
0.5Sm	72PbO - 18B <sub>2</sub> O <sub>3</sub> - 6.5Al <sub>2</sub> O <sub>3</sub> - 3WO <sub>3</sub> - 0.5Sm <sub>2</sub> O <sub>3</sub>
0.5Tb	72PbO - 18B <sub>2</sub> O <sub>3</sub> - 6.5Al <sub>2</sub> O <sub>3</sub> - 3WO <sub>3</sub> - 0.5Tb <sub>2</sub> O <sub>3</sub>
0.5Tb-0.1Sm	72PbO - 18B <sub>2</sub> O <sub>3</sub> - 6.4Al <sub>2</sub> O <sub>3</sub> - 3WO <sub>3</sub> - 0.5Tb <sub>2</sub> O <sub>3</sub> - 0.1Sm <sub>2</sub> O <sub>3</sub>
0.5Tb-0.25Sm	72PbO - 18B <sub>2</sub> O <sub>3</sub> - 6.25Al <sub>2</sub> O <sub>3</sub> - 3WO <sub>3</sub> - 0.5Tb <sub>2</sub> O <sub>3</sub> - 0.25Sm <sub>2</sub> O <sub>3</sub>
0.5Tb-0.5Sm	72PbO - 18B <sub>2</sub> O <sub>3</sub> - 6Al <sub>2</sub> O <sub>3</sub> - 3WO <sub>3</sub> - 0.5Tb <sub>2</sub> O <sub>3</sub> - 0.5Sm <sub>2</sub> O <sub>3</sub>
0.5Tb-0.75Sm	72PbO - 18B <sub>2</sub> O <sub>3</sub> - 5.75Al <sub>2</sub> O <sub>3</sub> - 3WO <sub>3</sub> - 0.5Tb <sub>2</sub> O <sub>3</sub> - 0.75Sm <sub>2</sub> O <sub>3</sub>
0.5Tb-1.0Sm	72PbO - 18B <sub>2</sub> O <sub>3</sub> - 5.5Al <sub>2</sub> O <sub>3</sub> - 3WO <sub>3</sub> - 0.5Tb <sub>2</sub> O <sub>3</sub> - 1Sm <sub>2</sub> O <sub>3</sub>
0.5Tb-1.5Sm	72PbO - 18B <sub>2</sub> O <sub>3</sub> - 5Al <sub>2</sub> O <sub>3</sub> - 3WO <sub>3</sub> - 0.5Tb <sub>2</sub> O <sub>3</sub> - 1.5Sm <sub>2</sub> O <sub>3</sub>
0.5Tb-3.0Sm	72PbO - 18B <sub>2</sub> O <sub>3</sub> - 3.5Al <sub>2</sub> O <sub>3</sub> - 3WO <sub>3</sub> - 0.5Tb <sub>2</sub> O <sub>3</sub> - 3.0Sm <sub>2</sub> O <sub>3</sub>



**Fig. 1.** Typical DSC curve for lead borate glass. Inset shows X-ray diffraction pattern.

characteristic temperatures  $T_g$  and  $T_x$ , the thermal stability parameter  $\Delta T$  was also calculated. The difference between the crystallization onset and the glass transition temperature ( $\Delta T = T_x - T_g$ ) is usually chosen as an approximate measure of glass formation ability. If  $\Delta T$  is higher than 100 °C, glass can be considered as a glass with relatively good thermal stability. This situation is observed for SrO–ZnO–P<sub>2</sub>O<sub>5</sub> based glasses, where thermal stability parameter  $\Delta T$  increases from 87 °C to 121 °C with increasing P<sub>2</sub>O<sub>5</sub> concentration and P/O molar ratios in chemical composition [7]. In our case, the value of  $\Delta T$  is close to 130 °C, which suggests that the studied glass samples exhibit good thermal stability against devitrification. Further structural investigations indicate that the received samples are fully amorphous. To confirm their amorphous character the X-ray diffraction measurements were used. The XRD patterns for all studied samples revealed only two broad bands, characteristic for an amorphous state. Typical X-ray diffraction pattern for lead borate glass is shown in the inset of Fig. 1.

Fig. 2 presents optical absorption spectrum measured for lead borate glass singly doped with  $\text{Sm}^{3+}$ . The UV–VIS cut-off wavelength defined as the intersection between the zero base line and the extrapolation of the absorption edge is located near 400 nm. Its value is similar to that one obtained earlier for lead borate glass singly doped with  $\text{Dy}^{3+}$  [62]. The absorption bands located at 400–525 nm spectral ranges correspond to transitions originating from the  ${}^6\text{H}_{5/2}$  ground state to the excited states of  $\text{Sm}^{3+}$ . However, several absorption bands are also located in the near-infrared (NIR) region, which are assigned to transitions from the  ${}^6\text{H}_{5/2}$  state to the  ${}^6\text{F}_{11/2}$ ,  ${}^6\text{F}_{9/2}$ ,  ${}^6\text{F}_{7/2}$ ,  ${}^6\text{F}_{5/2}$ ,  ${}^6\text{F}_{3/2}$ ,  ${}^6\text{H}_{15/2}$ ,  ${}^6\text{F}_{1/2}$  and  ${}^6\text{H}_{13/2}$  excited states, respectively (Fig. 3). The NIR band intensities are often quite strong, whereas some absorption transitions in UV–vis spectral region are overlapped due to presence of various energy levels, which are very close to each other [20]. This

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