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# Quantum efficiency and energy transfer processes in rare-earth doped borate glass for solid-state lighting



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## ABSTRACT

$\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  doped borate glass is investigated for its potential as light converting phosphor for solid-state lighting applications. Concentration-dependent luminescence, quantum efficiency and radiative lifetimes are analysed. The luminescence quantum efficiency exceeds values of more than 80%. Cross-relaxation processes in the single-doped glasses result in luminescence quenching for  $\text{Sm}^{3+}$  with increasing doping level, whereas for  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  an increase is observed. In  $\text{Sm}^{3+}/\text{Eu}^{3+}$  and  $\text{Tb}^{3+}/\text{Eu}^{3+}$  double-doped glass the energy transfer processes between the rare-earth ions are investigated in detail. The colour coordinate of the  $\text{Tb}^{3+}/\text{Eu}^{3+}$  double-doped glass can be shifted from the green to the red spectral range by changing the  $\text{Tb}^{3+}$ -to- $\text{Eu}^{3+}$  ratio in favour of  $\text{Eu}^{3+}$ . In addition, double doping allows for a change in colour coordinate by using different excitation wavelengths.

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## 1. Introduction

Glass is very versatile and a good host for rare-earth (RE) ions; it provides high optical transparency, good RE ion solubility, and it can be cast in almost any shape or size. Luminescent glasses have attracted much attention in the last decades, in particular for lasers, optical fibres, and optical amplifiers [1]. Borate glass is a suitable optical material with high mechanical, chemical and thermal stability [1,2]. A widespread interest in borate glass is recorded by multiple publications on spectroscopy of RE ions in borate glasses in 2014 [3–8].

For many applications, in particular for high-efficiency devices, the knowledge of the radiative quantum efficiency and the radiative lifetime of the luminescent material is of decisive importance. For solid-state lighting applications, e.g. white light-emitting diodes (LEDs), the colour impression is of great significance and appropriate doping with multiple rare-earth ions becomes important. In particular, the rare-earth ions  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  gained a great technological relevance. Their red and green luminescence is used in cathode ray tubes, fluorescent lamps, and plasma displays and have therefore been intensively studied. In addition,  $\text{Tb}^{3+}$  was found to be a good sensitizer to enhance luminescence efficiency of  $\text{Eu}^{3+}$  via energy transfer [9].

In the last years,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  owned increased interest as a phosphor for white light-emitting diodes. White LEDs are replacing conventional light sources due to their high efficiency, compactness, long operational lifetime, and resultant energy saving. Traditional white LEDs combine a blue LED chip and a yellow  $\text{YAG}:\text{Ce}^{3+}$  phosphor [10]. However, this method has a low colour-rendering index (CRI) and high colour temperature due to a lack of red emission. For higher CRI conventional phosphors can be double-doped with a red emitter, i.e.  $\text{Sm}^{3+}$  or  $\text{Eu}^{3+}$  or both. Another possibility for white light generation is the combination of a blue LED chip with a  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  doped phosphor.

In this work, the optical properties of  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Tb}^{3+}$  single-doped barium borate glasses are analysed and cross-relaxation processes between the ions are investigated. Furthermore, the influence of  $\text{Sm}^{3+}/\text{Eu}^{3+}$  and  $\text{Tb}^{3+}/\text{Eu}^{3+}$  double-doping and the energy transfer processes between the two different rare-earth ions are analysed. Both effects play an essential role in optimization of the luminescent glasses for their implementation in phosphor-converted LEDs (pc-LEDs).

## 2. Experimental details

### 2.1. Sample preparation

Borate glasses using barium oxide as network modifier were prepared. A ratio of two moles of boron oxide ( $\text{B}_2\text{O}_3$ ) and one mole of barium oxide (BaO) was used. In this ratio the glass network

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**Table 1**  
Nominal composition of the double-doped samples under study.

Dopant	Composition (mol%)					RE-content (at%)
	B <sub>2</sub> O <sub>3</sub>	BaO	Sm <sub>2</sub> O <sub>3</sub>	Eu <sub>2</sub> O <sub>3</sub>	Tb <sub>2</sub> O <sub>3</sub>	
Sm <sup>3+</sup> /Eu <sup>3+</sup>	65.67	32.83	1.0	0.5	–	0.50/0.25 / –
	65.33	32.67	1.0	1.0	–	0.50/0.50 / –
	64.67	32.33	1.0	2.0	–	0.50/1.00 / –
Tb <sup>3+</sup> /Eu <sup>3+</sup>	65.93	32.97	–	0.1	1.0	–/0.05/0.50
	65.67	32.83	–	0.5	1.0	–/0.25/0.50
	65.33	32.67	–	1.0	1.0	–/0.50/0.50

consists of the highest possible amount of four-coordinated boron [11]. The glasses were additionally doped with different doping levels of samarium oxide (Sm<sub>2</sub>O<sub>3</sub>), europium oxide (Eu<sub>2</sub>O<sub>3</sub>), or terbium oxide (Tb<sub>2</sub>O<sub>3</sub>). The single-doped glasses are comprised of (66.67–0.67*x*)B<sub>2</sub>O<sub>3</sub> · (33.33–0.33*x*)BaO · *x*RE<sub>2</sub>O<sub>3</sub> with *x*=0.1, 0.3, 0.5, 1.0, 2.0, 3.0 and 5.0 mol% which equals 0.05–2.5 at%. Table 1 summarizes the nominal chemical composition of the double-doped glasses.

The chemicals were weighed in a platinum gold crucible (Pt/Au 95/5) and melted at 1100 °C for approximately 3 h. The melt was then poured onto a brass block at 500 °C, which is below the glass transition temperature of *T*<sub>g</sub>=605 °C for barium borate glass [12]. The glass was kept at this temperature for 3 h to eliminate residual mechanical and thermal stresses before being slowly cooled to room temperature. The glass was then cut into squares of 20 mm × 20 mm with a thickness of 3.2 mm and polished to optical quality.

## 2.2. Experimental set-up

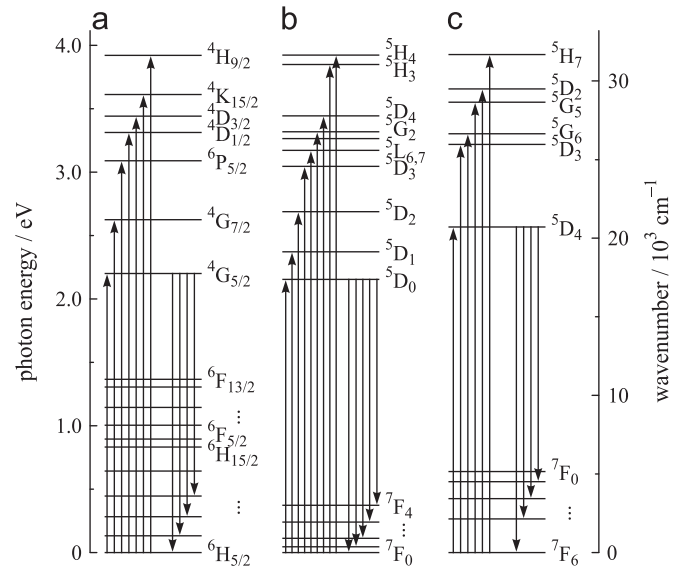
Absolute photoluminescence quantum efficiency (QE) measurements were performed with a commercial quantum yields measurement system (Hamamatsu C9920-02G) coupled to a 3.3 inch integrating sphere with a xenon lamp (150 W) as excitation source and a photonic multichannel analyser (PMA 12) as detector. The setup has a measurement accuracy of approx. 3%. The quantum efficiency was determined from emission spectra in the spectral range from 450 to 900 nm. Radiative lifetime measurements were performed under excitation with a temperature-stabilized 405-nm laser-diode (Sanyo DL-3146-151) in case of Sm<sup>3+</sup> single- and Sm<sup>3+</sup>/Eu<sup>3+</sup> double-doped glasses and a 370-nm ultraviolet (UV) LED (Winger WEEUV00-CS) in case of Eu<sup>3+</sup> and Tb<sup>3+</sup> single- and double-doped glasses. A peltier-cooled photomultiplier (EMI 9863/492) coupled to a 300 mm focal length monochromator (Princeton Instruments Acton 2300) was used for detection.

## 3. Results and discussion

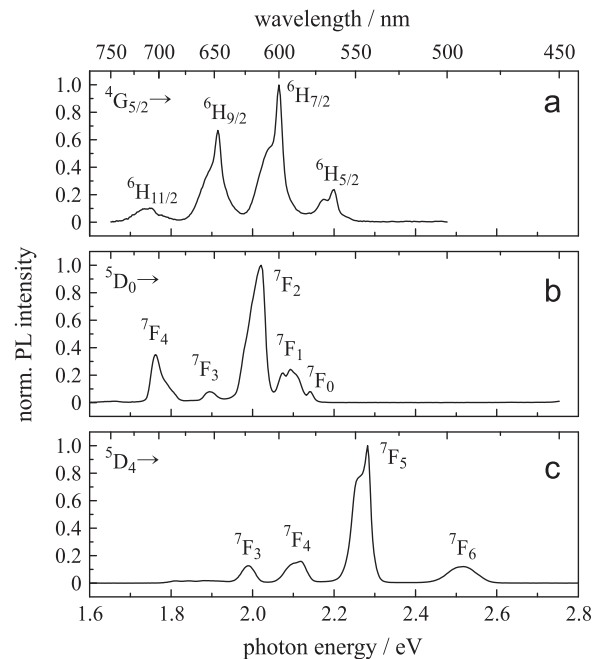
### 3.1. Single-doped glasses

#### 3.1.1. Photoluminescence

Fig. 1 shows the energy level diagrams of (a) Sm<sup>3+</sup>, (b) Eu<sup>3+</sup>, and (c) Tb<sup>3+</sup> [13,14]. Possible excitation (arrows from bottom to top) and emission routes (arrows from top to bottom) are indicated. For all three RE ions, emissions in the blue spectral range (from higher energy levels) are quenched due to the high maximum phonon frequency of 1400 cm<sup>-1</sup> in borate glass [15]. Though the spectral positions of rare-earth ion emission are well known, the transition intensity ratios vary due to differences in crystallinity and phonon frequencies of the host material.



**Fig. 1.** Energy level diagram of (a) Sm<sup>3+</sup>, (b) Eu<sup>3+</sup>, and (c) Tb<sup>3+</sup>. Possible excitation (arrows from bottom to top) and emission routes (arrows from top to bottom) are indicated [14].



**Fig. 2.** Normalized emission spectra of borate glass doped with (a) Sm<sup>3+</sup>, (b) Eu<sup>3+</sup> and (c) Tb<sup>3+</sup>. The excitation was carried out at 402 nm (Sm<sup>3+</sup>), 393 nm (Eu<sup>3+</sup>), and 370 nm (Tb<sup>3+</sup>). The emission transitions are indicated.

The emission spectra of Sm<sup>3+</sup>, Eu<sup>3+</sup> and Tb<sup>3+</sup> single-doped borate glasses are shown in Fig. 2. For Sm<sup>3+</sup> doping (Fig. 2a), the emission spectra show transitions from the excited state <sup>4</sup>G<sub>5/2</sub> to the ground state levels <sup>6</sup>H<sub>5/2</sub>, <sup>6</sup>H<sub>7/2</sub>, <sup>6</sup>H<sub>9/2</sub>, and <sup>6</sup>H<sub>11/2</sub> (550–700 nm); the emission is excited at 402 nm. Upon excitation at 393 nm, the Eu<sup>3+</sup>-doped glass (Fig. 2b) shows the typical Eu<sup>3+</sup> emissions in the red spectral range, which are caused by transitions from the excited state <sup>5</sup>D<sub>0</sub> to the ground state levels <sup>7</sup>F<sub>0</sub> (580 nm), <sup>7</sup>F<sub>1</sub> (592 nm), <sup>7</sup>F<sub>2</sub> (613 nm), <sup>7</sup>F<sub>3</sub> (652 nm), and <sup>7</sup>F<sub>4</sub> (700 nm). The electric-dipole transition <sup>5</sup>D<sub>0</sub> to <sup>7</sup>F<sub>2</sub> is hypersensitive to variations in crystal symmetry [16]. The high intensity of this transition in borate glass indicates the amorphous nature of the matrix material with low inversion symmetry for the Eu<sup>3+</sup> ion. In Fig. 2c, the typical Tb<sup>3+</sup>-related emissions at 490 nm, 543 nm,

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