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Effect of induced crystallization in rare-earth doped lithium borate glass

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HIGHLIGHTS

- Thermally-induced formation of nanocrystals in rare-earth doped Li borate glass.
- Higher crystallization tendency in undoped compared to the rare-earth doped glass.
- Increase of glass transition and crystallization temperatures with Eu^{3+} doping.
- Decrease of transmittance and luminescence quantum efficiency with crystallization.

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ABSTRACT

Rare-earth doped borate glasses and glass ceramics are investigated for their potential as photon converters. Thermal processing of the as-made glass results in the formation of nanocrystals therein. For optical activation, the glasses are doped with Eu^{3+} and Tb^{3+}, both enabling an intense emission under ultraviolet excitation. Differential scanning calorimetry and X-ray diffraction are applied to analyze the crystallization behavior. Compared to the undoped glass, the glass transition temperature as well as the crystallization temperature are increased with Eu^{3+} doping. Upon thermal processing of the as-made glasses, the transmittance is significantly reduced. Preliminary photoluminescence quantum efficiency measurements yield lower values for the glass ceramics.

1. Introduction

Borate glass has been widely studied due to its interesting structural and optical properties (Babu and Jayasankar, 2000; El-Fayoumi and Farouk, 2009; Ferreira et al., 2011; Dongare and Lad, 2015), i.e., high optical transparency as well as mechanical, chemical and thermal stability (Lin et al., 2005; Soga et al., 1988). Due to its good rare-earth ion solubility (Anjaiah et al., 2014), luminescent borate glasses gain increasing importance in optical devices, such as laser amplification (Vázquez et al., 2015), display devices (Umamaheswari et al., 2012) or solid-state lighting (Swapna et al., 2013). Since its effective atomic number ($Z_{eff} = 7.42$) is close to that of human tissue (Prokic, 2001; Ayta et al., 2010), borate glass is often investigated for medical applications such as bioactive micro-fibers (Yang et al., 2015; Rahaman et al., 2011) or thermoluminescence dosimetry (Prokic, 2001; Ayta et al., 2010; Driscoll et al., 1983; Ogorodnikov and Poryvai, 2012). Furthermore, rare-earth doped lithium borate single crystals are promising as neutron scintillator due to the large cross-section for thermal neutrons of ^{6}Li and ^{10}B of $\sigma_a = 940$ b and 3835 b, respectively (Singh et al., 2015; Fawad et al., 2015; Sears, 1992). The charged particles generated in ^{6}Li and ^{10}B excite the rare-earth ions resulting in a visible emission (Singh et al., 2015). However, the growth of borate crystals is difficult due to their high viscous nature of melt, slow growth rate and complex crystal structure (Fawad et al., 2015). Challenges in their manufacture are the supercooling of the melt, cleavage crack and the inversion of

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the solid–liquid interface (Pan et al., 2014). In contrast to single crystals, glasses and glass ceramics are easy to prepare, cost-effective and have similar properties. In this work, luminescent lithium borate glasses and glass ceramics are prepared and their optical and structural properties are compared.

2. Experimental details

Borate glasses, using lithium oxide (Li_2O) and aluminium oxide (Al_2O_3) as network modifier, were prepared. A ratio of three moles of boron oxide (B_2O_3) and two moles of network modifier was used. The glasses were additionally doped either with europium oxide (Eu_2O_3) or terbium oxide (Tb_4O_7). The nominal composition of the samples is as listed in Table 1. The chemicals were weighed in a platinum gold crucible (Pt/Au 95/5) and melted at 1000 °C for approximately 3 h. The melt was then poured onto a brass block at 400 °C, which is below the glass transition temperature of undoped lithium borate glasses of $T_g = 459$ °C (see Section 3.1). The glass was kept at this temperature for 3 h to eliminate residual mechanical and thermal stresses before allowing it to slowly cool to room temperature. The glass samples were then cut into squares of 15 mm × 15 mm with a thickness of 1.5 mm and polished to optical quality (Fig. 1, upright samples). To initiate crystallization, the samples were annealed at a temperature of 530 °C for 10 min. This is in analogy to the procedure reported by Appleby et al. (Appleby et al., 2006). At this temperature and time all three samples are fully ceramic. The glass ceramics are shown in Fig. 1, lying samples.

Transmittance, photoluminescence (PL) and absolute PL 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 quantum efficiency describes the ratio between the number of emitted photons and the number of absorbed photons. The number of absorbed photons was determined from absorption spectra, while the number of emitted photons was determined from emission spectra in the spectral range from 500 to 900 nm and from 470 to 900 nm for Eu^{3+} and Tb^{3+}, respectively. Differential scanning calorimetry (DSC) was performed with a commercial system suited for temperatures up to 1700 °C (Netzsch DSC 404 F1 Pegasus). The samples were cut into small pieces of about 25 mg, ground in a mortar to a fine powder, and then filled in a platinum rhodium crucible (Pt/Rh 80/20). An empty crucible was used as a reference. The temperature was increased with a heating rate of 10 K · min^{-1}. A nitrogen flow of 20 ml· min^{-1} was used during the measurements. All characteristic temperatures are determined from the DSC data by the onset method, only $T_{g'}$ is evaluated with the inclination method. X-ray diffraction (XRD) measurements were performed on bulk samples at 40 kV/40 mA in Bragg-Brentano geometry using copper K_α radiation and a detection range of 2θ from 20° to 100° in steps of 0.005° (Bruker AXS D8 ADVANCE).

Table 1
Nominal composition of the investigated samples.

Dopant	Composition/mol%					RE content/at.%
	B_2O_3	Li_2O	Al_2O_3	Eu_2O_3	Tb_4O_7	
–	60.0	33.3	6.7	–	–	–
Eu^{3+}	59.3	33.1	6.6	1.0	–	0.5
Tb^{3+}	59.7	33.2	6.6	–	0.5	0.5

Fig. 1. REdoped borate glasses (upright) and glass ceramics (lying): undoped (left), Eu^{3+} doped (middle), and Tb^{3+} doped (right) under ultraviolet irradiation. The undoped reference glass does not show any luminescence.

3. Results and discussion

3.1. Thermal and structural properties

The DSC curves of the glass samples are as shown in Fig. 2. The obtained values of the onset and inclination glass transition temperature (T_g and $T_{g'}$), the onset glass crystallization temperature (T_x), the glass crystallization peak temperature (T_p), and the melting temperatures (T_m) are summarized in Table 2. The undoped glass sample shows an increasing heat flow at approximately 460 °C, which represents the glass transition temperature T_g. At a temperature of $T_x = 587$ °C, the onset of an exothermic peak is observed with its maximum at $T_p = 608$ °C. This peak is due to glass crystallization. Between 700 °C and 800 °C, three endothermic peaks occur, originated from the glass melting process.

Upon Eu^{3+} doping, the glass transition temperature (T_g) increases for approximately 10 °C whereas for Tb^{3+} doping it does not change. The onset crystallization temperature T_x increases by 8 °C to 595 °C for the Tb^{3+} doped glass and even higher to 615 °C for Eu^{3+} doped glass. The peak crystallization temperature is found to be the same for the undoped glass and the Tb^{3+} doped glass at

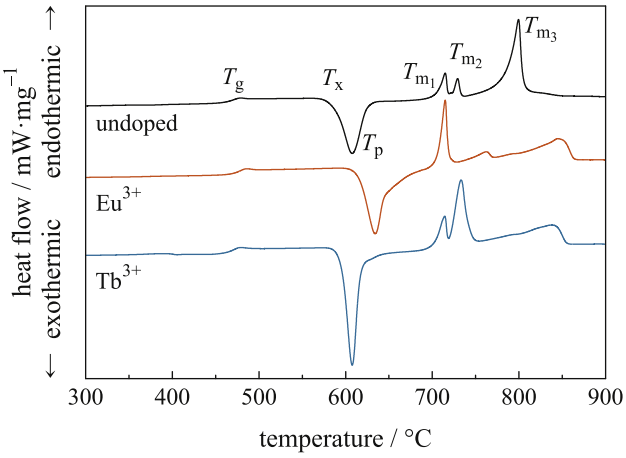

Fig. 2. DSC data of the undoped reference glass (black), the Eu^{3+} (orange) and the Tb^{3+} doped borate glass (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)