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Tb^{3+}, Eu^{3+}, and Dy^{3+} doped lithium borate and lithium aluminoborate glass: Glass properties and photoluminescence quantum efficiency

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ABSTRACT

The glass properties as well as the photoluminescence quantum efficiency of Li_2O-B_2O_3 and Li_2O-Al_2O_3-B_2O_3 glasses are investigated; both glass systems are optically-activated by the addition of the lanthanide ions Tb^{3+}, Eu^{3+}, and Dy^{3+}. Glass transition, glass crystallization, and glass melting temperatures as well as glass forming temperature ranges are determined upon varying the modifier-to-former (Li_2O-to-B_2O_3) ratio in the range between 1:6 to 1:2. For lithium borate glass, the risk of spontaneous crystallization decreases upon decreasing the lithium concentration. The photoluminescence quantum efficiency increases slightly upon decreasing the lithium concentration with the value of a Al_2O_3-containing sample always lower than that of the Al_2O_3-free correspondent.

1. Introduction

The optical activation of lithium borate glass with luminescent lanthanide ions seems to be a promising route towards the development of optical materials for light-emitting diode (LED) [1, 2] or laser [3–5] applications. For a potential application of these luminescent glasses, an intense and efficient light conversion is crucial and is described by the absolute photoluminescence quantum efficiency, which is given by the ratio between the number of emitted photons to the number of absorbed photons. Apart from optical applications, lithium borate glass is also an interesting material as solid electrolyte for Li ion batteries [6] and for thermoluminescence dosimetry [5, 7, 8].

In general, borate glasses impress with high transparency, a wide glass forming range, and thermal stability [4, 9, 10]. Compared to other oxide-based glasses, they have a lower melting point than silicate glasses, but a higher one than phosphate glasses [11]. The relatively low melting point of phosphate glasses is disadvantageous for high temperature applications. The borate glass structure is versatile, since it comprises different boron oxide structure units, such as diborates, methaborates, and boroxol rings. The structure changes upon varying the network former (boron oxide) to network modifier (metal oxide) ratio [12, 13] and causes non-linear changes in glass transition temperature [14] and viscosity [15]. The network modifier Li_2O disrupts the glass network, opens the network structure, weakens the bond strength, and lowers the viscosity of the glass [16]. Lithium borate glass is one of the most versatile glass systems in the borate glass family. The addition of Al_2O_3 as property modifier to the lithium borate glass system improves the chemical stability of the glass [10, 17].

Borate glass offers a good solubility for lanthanide ions and is thus a promising candidate as host for optical activators. In particular, the lanthanide ions Tb^{3+}, Eu^{3+} and Dy^{3+} are of great interest due to their emission in the visible spectral range. Tb^{3+} and Eu^{3+} doped glasses show an intense green and red emission, respectively, which makes these systems interesting as light converter for LED applications [17–20]. For lithium aluminoborate glass, the absolute photoluminescence quantum efficiency (QE) of Tb^{3+} and Eu^{3+} amounts to 32 % ($^7F_6$ to $^5D_4$ transition at 486 nm) and 81 % ($^7F_0$ to $^5L_6$ transition at 394 nm), respectively [18]. For lithium borate glass, the main emission bands for Dy^{3+} are at 485 nm and 585 nm leading to a yellow colour impression [2, 21, 22]. The QE at 452 nm ($^4H_{15/2}$ to $^4I_{15/2}$ transition) amounts between 18 % and 27 % depending on the modifier-to-former ratio [23].

In this work, the influence of the modifier-to-former ratio on the absolute photoluminescence quantum efficiency is investigated for Tb^{3+}, Eu^{3+}, and Dy^{3+} activated lithium borate and lithium aluminoborate glass.

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Table 1
Nominal composition and mass density of the investigated lithium borate and lithium aluminoborate glass samples.

Luminescent	Glass series	Li-to-(B + Al)	Composition / mol%				Density / g ·cm^{-3}
modifier		ratio	Li_2O	B_2O_3	Al_2O_3	Ln_xO_y	
Tb_4O_7	w/o Al_2O_3	1:6	14.21	85.29	–	0.5	2.22
		1:5	16.58	82.92	–	0.5	2.21
		1:4	19.90	79.60	–	0.5	2.26
		1:3	24.88	74.63	–	0.5	2.31
		1:2	33.17	66.33	–	0.5	2.48
	w Al_2O_3	1:6	14.21	76.76	8.53	0.5	2.20
		1:5	16.58	74.63	8.29	0.5	2.23
		1:4	19.90	71.64	7.96	0.5	2.25
		1:3	24.88	67.16	7.46	0.5	2.31
		1:2	33.17	59.70	6.63	0.5	2.38
Eu_2O_3	w/o Al_2O_3	1:6	14.14	84.86	–	1.0	2.21
		1:5	16.50	82.50	–	1.0	2.25
		1:4	19.80	86.20	–	1.0	2.29
		1:3	24.75	74.25	–	1.0	2.38
		1:2	33.00	66.00	–	1.0	2.44
	w Al_2O_3	1:6	14.14	76.37	8.49	1.0	2.23
		1:5	16.50	74.25	8.25	1.0	2.26
		1:4	19.80	71.28	7.92	1.0	2.30
		1:3	24.75	66.83	7.43	1.0	2.35
		1:2	33.00	59.40	6.60	1.0	2.40
Dy_2O_3	w/o Al_2O_3	1:6	14.21	85.29	–	0.5	2.12
		1:5	16.58	82.92	–	0.5	2.18
		1:4	19.90	79.60	–	0.5	2.23
		1:3	24.88	74.63	–	0.5	2.28
		1:2	33.17	66.33	–	0.5	2.40
	w Al_2O_3	1:6	14.21	76.76	8.53	0.5	2.17
		1:5	16.58	74.63	8.29	0.5	2.20
		1:4	19.90	71.64	7.96	0.5	2.23
		1:3	24.88	67.16	7.46	0.5	2.28
		1:2	33.17	59.70	6.63	0.5	2.34

2. Experimental details

2.1. Samples

Borate glass samples are prepared using boron oxide (B_2O_3, Alfa Aesar, 99.98 % purity) as network former and lithium oxide (Li_2O, Alfa Aesar, 99.5 % purity) as network modifier. The network modifier-to-network former ratio varies from 1:2 to 1:6. Two glass series are prepared, one without aluminium oxide (Al_2O_3, Alfa Aesar, 99.9 % purity) and a second series replacing 10 % of the boron oxide by Al_2O_3 to reduce hygroscopic effects and to investigate the effect of aluminium ions on the luminescence properties [10]. Both sample series are additionally single doped with the luminescent modifiers Tb^{3+} (Tb_4O_7, Alfa Aesar, 99.9 % purity), Eu^{3+} (Eu_2O_3, Alfa Aesar, 99.99 % purity), and Dy^{3+} (Dy_2O_3, Alfa Aesar, 99.99 % purity). The nominal compositions are listed in Table 1. The chemicals are weighed and melted in a platinum gold crucible (Pt/Au 95/5) at 1000 °C for approximately 3 h. The melt is then poured onto a brass mould pre-heated at 400 °C (the glass transition temperature is at approximately 480 °C). The glass is kept at this temperature for 3 h to remove the residual mechanical and thermal stress and then it is slowly cooled down to room temperature. The glasses with a modifier-to-former ratio of 1:2 and without additional Al_2O_3 show a spontaneous crystallization during the melt-quenching process. The samples are sized into 20.0 mm × 20.0 mm × 3.2 mm and polished to optical quality. Fig. 1 shows the various sample sets under ultraviolet excitation. The Tb^{3+}, Eu^{3+}, and Dy^{3+} doped glasses show a bright green, red, and yellowish luminescence, respectively. The modifier-to-former ratio changes from 1:6 (top row) to 1:2 (bottom row). For each lanthanide, two samples sets are prepared: one with the property modifier Al_2O_3 (left column) and one without additional property modifier (right column).

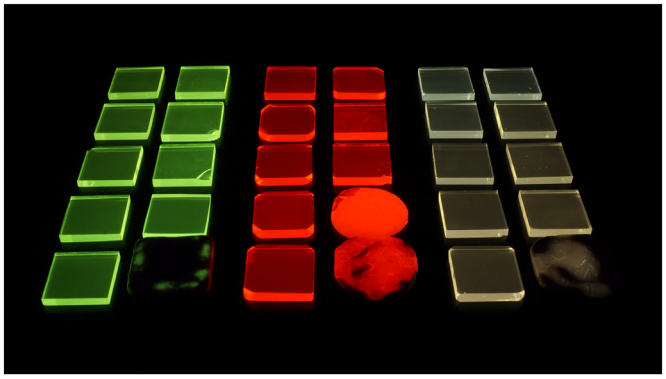

Fig. 1. Samples: the lanthanide-doped lithium borate glasses show a bright luminescence under 365-nm excitation: Tb^{3+} (green), Eu^{3+} (red), and Dy^{3+} (yellowish). The ratio between the network modifier (Li_2O) and the network former (B_2O_3) changes from 1:2 (bottom row) to 1:6 (top row). For each lanthanide, two samples series are prepared: one with the property modifier aluminium oxide (left column) and one without additional property modifier (right column). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Methods

The mass density, ρ, of the different glasses is measured by a density determination kit of an analytical balance (Mettler-Toledo XS105DU) based on the Archimedes' principle. The density values listed in Table 1 represent the arithmetic mean of ten measurements; the experimental error amounts to $\Delta\rho = \pm 0.02$ g/cm^3.

X-ray diffraction studies are performed with an X-ray diffractometer (PANalytical Empyrean 2) using a Cu anode operating at 40 kV and