Luminescent glass ceramic light converter for LED applications

Juliane Steinbrück*, A. Charlotte Rimbach*, Peter W. Nolte**, Franziska Steudel**, and Stefan Schweizer*,**

*Faculty of Electrical Engineering, South Westphalia University of Applied Sciences, Lübecker Ring 2, 59494 Soest, Germany

**Fraunhofer Application Center for Inorganic Phosphors, Branch Lab of Fraunhofer Institute for Microstructure of Materials and Systems IMWS, Lübecker Ring 2, 59494 Soest, Germany

mailto: Steinbrueck.Juliane@fh-swf.de

Lanthanide-doped lithium-aluminoborate glasses are investigated for their potential as light converter for LED applications. Processing the glass to a glass ceramic results in a significant increase in luminescence yield. The luminous intensity distribution and the spectral characteristics of the glass are compared to those of the glass ceramic.

1 Introduction

The constant improvement of LEDs with respect to power density and size as well as the growing use of laser diodes for lighting applications lead to increased requirements for the light-converting phosphors. Here, lanthanide-doped borate glasses and glass ceramics represent an interesting alternative due to their high thermal and chemical stability. However, the low absorption coefficients of the lanthanide ions result in low luminescence intensities despite their good quantum efficiency values. Eu^{3+}-doped lithium-aluminoborate glass is used as a model system to study the increase in luminescence yield by transforming the glass into a glass ceramic.

2 Experimental Details

Glasses are made from 59.40 mol% boron oxide (B_2O_3) as network former, 33.00 mol% lithium oxide (Li_2O) as network modifier, and 6.60 mol% aluminium oxide (Al_2O_3) as property modifier to prevent devitrification of the glass. Europium oxide (1 mol%) is added for optical activation. The materials are mixed and melted in a Pt/Au (95/5) crucible at 1000 °C over a period of 3 hours. The melt is cast onto a 450 °C preheated brass plate and held at that temperature before it is slowly cooled down to room temperature. Glass samples are prepared in dimensions of 10 mm × 10 mm × 1.8 mm and polished to optical quality. The glasses are processed to glass ceramics in a subsequent heat treatment step at 487 °C for 800 minutes. The selected temperature is at the end of the glass transition range as determined by differential scanning calorimetry [1].

Fig. 1 shows the glass and the glass ceramic sample on top of a 391-nm LED (OSRAM OSLON®). This setup is used for the far-field measurements performed with a robot goniophotometer system ("robogonio") from opsira GmbH. The LED has a Lambertian luminous intensity distribution with a luminous flux of 0.35 lm at a current of 200 mA and a forward voltage of 3.3 V.

Absolute photoluminescence quantum yield (Hamamatsu C9920-02G) as well as total and diffuse transmittance measurements (Agilent Technologies Cary 5000 UV-Vis-NIR spectrophotometer) are performed to analyse the scattering and luminescence properties of the samples.

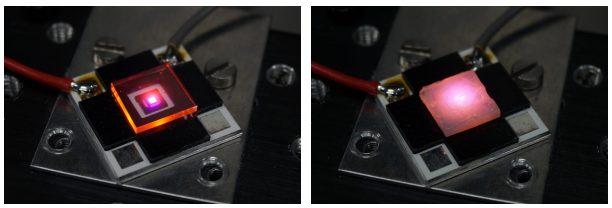

Fig. 1 *Experimental setup for far-field measurements: glass (left) and glass ceramic (right) on top of a 391-nm LED.*

3 Experimental Results

Fig. 2 shows the transmittance of the glass and the glass ceramic. The solid curves show the total transmittance, while the dashed curves indicate the scattered part of the total transmittance. The latter one is close to zero for the glass, i.e., all light light is transmitted directly. For the glass ceramic, however, the situation is reversed: Here, the curves for total and scattered transmittance are almost identical, i.e., the directly transmitted part is almost zero and the transmitted light is completely scattered. Both the glass and the glass ceramic show absorption bands due to the Eu^{3+} doping, in particular at 394 nm and 465 nm corresponding to transitions from the ground state $^7F_0$ to the excited states $^5L_6$ and $^5D_2$, respectively [2]. The short-wavelength transition is in good agreement to the emission wavelength of the used 391-nm LED.

Far-field measurements are made for the LED/glass

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and the LED/glass ceramic combination (Fig. 3). The luminous intensity distribution comprises to a large amount the Eu^{3+}-related luminescence light only, since the 391-nm emission from the LED is mainly blocked by the $V(\lambda)$ filter. The shape of the luminous intensity distribution of the glass is given by the sample's geometry, while the glass ceramic shows a Lambertian intensity distribution and is thus an almost perfect scatterer. Most importantly, the luminous flux has increased from 2.74 lm (glass) to 4.90 lm (glass ceramic).

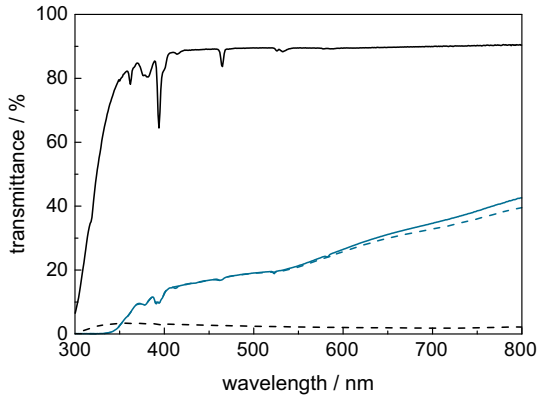

Fig. 2 *Total transmittance (solid) and scattered portion of the transmittance (dashed) for the glass (black curve) and the glass ceramic (blue curve).*

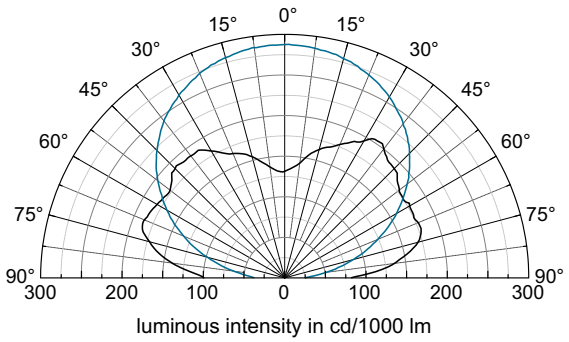

Fig. 3 *Luminous intensity distributions of the LED/glass (black curve) and the LED/glass ceramic (blue curve) combination.*

To further analyse the spectral characteristics of the luminous intensity distribution, angular-dependent emission spectra are recorded. The LED/glass combination shows significant changes in the LED-to-Eu^{3+} intensity ratio over the angle, while for the LED/glass ceramic combination the LED-to-Eu^{3+} intensity ratio remains unchanged. Figure 4 shows the emission spectra of the LED/glass and the LED/glass ceramic combination, averaged over all angle steps (1°) from 0° to 90°. Both averaged spectra are dominated by the LED emission at 391 nm. Note that the spectral range from 500 nm to 800 nm is scaled by a factor of 20. The integrated Eu^{3+}-related luminescence intensity of the glass ceramic is approximately 2.5 times that of the glass. In addition, the emission spectrum of Eu^{3+} changes due to its crystalline environment in the glass ceramic [3]. For the glass, the Eu^{3+} emission spectrum is dominated by the $^5D_0$ to $^7F_2$ transition, while the $^5D_0$ to $^7F_0$ transition dominates the glass-ceramic spectrum.

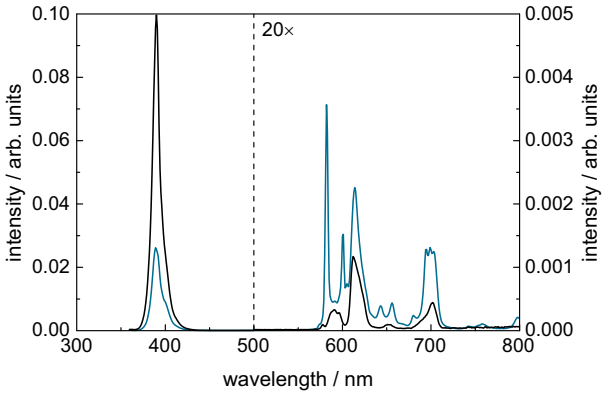

Fig. 4 *Emission spectra for the LED/glass (black curve) and the LED/glass ceramic (blue curve) combination, averaged over an angular range from 0° to 90°.*

4 Conclusion

Luminescent borate glass is successfully processed to a luminescent glass ceramic. For the glass, only a small fraction of the excitation light is absorbed by Eu^{3+}, while for the glass ceramic, the excitation light is scattered at the grown crystallites. This results in a longer optical pathway, i.e., a larger portion of the excitation light is absorbed, and thus in an enhanced light yield for the glass ceramic. The transition from glass to glass ceramic is also noticeable in the Eu^{3+} emission spectrum.

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