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XANES studies on Eu-doped fluorozirconate based glass ceramics

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Abstract

The influence of adding InF₃ as a reducing agent on the oxidation state of Eu in fluorochloro- (FCZ) and fluorobromozirconate (FBZ) glass ceramics was investigated using x-ray absorption near edge (XANES) and photoluminescence (PL) spectroscopy. For both materials, it was found that InF₃ decreases the Eu²⁺-to-Eu³⁺ ratio significantly. PL spectroscopy proved that an annealing step leads to the formation of Eu-doped BaCl₂ and BaBr₂ nanocrystals in the FCZ and FBZ glasses, respectively. In the case of FCZ glass ceramics the hexagonal phase of BaCl₂ could be detected in indium-free and InF₃-doped ceramics, but only for InF₃ containing FCZ glass ceramics a phase transition of the nanoparticles from hexagonal to orthorhombic structure is observed. For the FBZ glass ceramics, the hexagonal phase of BaBr₂ can be formed with and without indium doping, but only in the indium-free case a phase transition to orthorhombic BaBr₂ could be found.

INTRODUCTION

A class of fluorochloro- (FCZ) and fluorobromozirconate (FBZ) glass ceramics has been developed for ionizing radiation detection. The composition of these materials is derived from a standard ZBLAN glass, i.e. a fluoride glass, made from Zr, Ba, La, Al, and Na fluorides. Several synthesis routes have been derived to maintain Zr in the 4+ state where the addition of a small amount of InF₃ plays a key role in the glass production process. The glasses under investigation were additionally doped with Cl or Br ions by partial substitution of the fluorides BaF₂ and NaF for BaX₂ and NaX (X = Cl, Br), respectively. This enabled precipitation of BaX₂ nanocrystals within the glass upon appropriate annealing.

For ionizing radiation detection, Eu is added to the glass for optical activation. Depending on the structural phase of the BaX₂, the glass-ceramic material can act either as a scintillator

(able to convert ionizing radiation to visible light), or as a storage phosphor (able to convert the radiation into stable electron-hole pairs, which can be released at a later time with a scanning laser beam).

To obtain luminescence from these materials, the critical component is the Eu^{2+} , in particular the Eu^{2+} present in the BaX_2 nanocrystals. However, there is always a significant amount of Eu^{3+} in the glass which reduces the performance of these materials as both scintillators and storage phosphors. X-ray absorption near edge spectroscopy (XANES) measurements showed that one source was found to be in the as-received EuF_2 , in which Eu^{2+} is oxidized to Eu^{3+} before and/or during glass melting [1]. In such a complex system, the addition of each new chemical and each change in processing affects the material properties. In an earlier work on Eu-doped FCZ glass ceramics, the influence of InF_3 and remelting on the Eu^{2+} -to- Eu^{3+} ratio was investigated [2]. It was shown that the addition of InF_3 decreases the Eu^{2+} -to- Eu^{3+} ratio whereas remelting increases the Eu^{2+} -to- Eu^{3+} ratio.

This work is a step on the road to identify the role of each chemical component and to improve the material for luminescence applications such as ionizing radiation detection. In particular, we investigate the influence of adding InF_3 on the Eu^{2+} -to- Eu^{3+} ratio in FBZ glass ceramics and compare the results with those from FCZ glass ceramics.

EXPERIMENT

XANES

Fig. 1 shows the normalized Eu L_3 XANES spectrum of the as-made Eu-doped FBZ glass without InF_3 doping. The two resonances at about 6976 eV and 6986 eV are the characteristic white lines (WLs) of Eu^{2+} and Eu^{3+} [3] and are associated with a dipole-allowed transition from a $2p_{3/2}$ core level into an empty $5d$ state. The Eu^{2+} -to- Eu^{3+} ratio can be determined by building the relative intensity of the two WLs [4, 5]. A pseudo-Voigt function and an arctan function were used to fit each WL and the absorption edge, respectively. The corresponding fitted curve (solid curve) and the individual fitted components (dashed and dotted curves) are shown in the inset of Fig. 1. The mole ratio M_{Eu} of Eu^{2+} to Eu^{3+} can be determined from the area ratio A_{Eu} of the WLs $M_{\text{Eu}} = RA_{\text{Eu}}$, where R is a constant that is related to the $2p \rightarrow 5d$ transition probabilities of Eu^{2+} and Eu^{3+} [5]. Due to the low Eu-doping level of 3 mol%, the R value is set to 1.5, which was determined for dilute systems from an “in situ” XANES analysis of electrochemical conversion between Eu^{2+} and Eu^{3+} in a EuCl_3 solution [5]. For the Eu-doped FCZ glasses the curve fitting results and the calculated mole fractions are listed in [2].

Fig. 2 shows the normalized Eu L_3 XANES spectra of as-made FBZ glass ceramics without (solid curve) and with 1.5 mol% (dashed curve) InF_3 doping. While there is no significant shift in the energy of the XANES WLs in any of the spectra, the WL intensity and thus the Eu^{2+} -to- Eu^{3+} mole ratio changes significantly upon increasing the InF_3 doping level. In Fig. 3 the effect of thermal annealing on the Eu^{2+} -to- Eu^{3+} ratio of the Eu-doped FCZ and FBZ glass ceramics is presented. Obviously, thermal annealing has no significant influence on the Eu^{2+} -to- Eu^{3+} ratio. The InF_3 doping, however, changes the Eu^{2+} -to- Eu^{3+} ratio significantly. Thus, the InF_3 doping leads generally to a decrease in the Eu^{2+} -to- Eu^{3+} ratio from 2.2 (0

mol% InF_3) to 1.2 (1.5 mol% InF_3) and from 1.8 (0 mol% InF_3) to 0.85 (0.5 mol% InF_3) for the FBZ and FCZ glasses, respectively.

Photoluminescence (PL)

PL spectra of differently annealed Eu-doped FCZ and FBZ samples (with and without InF_3) are plotted in Fig. 4. The indium-free FCZ sample annealed at 270 °C (top left, dotted curve) shows the typical PL spectrum for a glass ceramic containing predominantly hexagonal phase BaCl_2 particles [6]. The peak at 406 nm is attributed to the $5d-4f$ transition of Eu^{2+} in hexagonal BaCl_2 ; the origin of the less intense but broader emission at 485 nm is unknown. When annealing up to 290 °C (solid curve), the intensity of the 485 nm band lessens but there is no phase transformation from hexagonal to orthorhombic phase BaCl_2 , as was reported in [6]. The InF_3 doped FCZ sample (top right) also shows the hexagonal phase after annealing at 270 °C, but annealing at 290 °C leads to the formation of orthorhombic phase BaCl_2 : The 406 nm band is shifted to 401 nm while the 485 nm band is almost gone.

In contrast to the FCZ samples, the Eu-doped FBZ samples without indium (bottom left) show a phase transformation to orthorhombic BaBr_2 upon increasing the annealing temperature from 280 to 300 °C. Here, the $5d-4f$ transition of Eu^{2+} in hexagonal BaBr_2 peaks at 407 nm and is shifted to 402 nm for orthorhombic BaBr_2 [7]. In analogy to the FCZ samples, the 485 nm band is only observed in glass ceramics containing hexagonal phase BaBr_2 nanoparticles [7]. Interestingly, the FBZ samples doped with InF_3 (bottom right) do not show a phase transition, but only hexagonal phase BaBr_2 particles.

DISCUSSION

The results show that the Eu^{2+} -to- Eu^{3+} ratio in Eu-doped FCZ and FBZ glasses depends significantly on the addition of InF_3 . Without the InF_3 additive, a higher fraction of Eu^{2+} is produced. However, the quality of the glasses also depends on the addition of indium and the melting process. Samples with lower amounts of InF_3 show a large number of black precipitates on the surface. These black specks in the glass ceramics arise from Zr^{3+} , which is reduced from Zr^{4+} [8]. This problem is alleviated in the presence of InF_3 as InF_3 acts as a mild oxidizer. If any Zr^{3+} does form, the In^{3+} oxidizes it back to Zr^{4+} , and in this process indium is reduced to In^{1+} . It appears that while InF_3 is added as an oxidizer to maintain Zr in the 4+ state, it also oxidizes some of the Eu^{2+} to Eu^{3+} .

In all annealed samples, crystallization of hexagonal phase BaCl_2 and BaBr_2 , respectively, can be found. The indium additive, however, affects the crystallization properties of the FCZ and FBZ glasses: Analogous to previous work [6], for the InF_3 -containing FCZ glass ceramics a phase transformation from hexagonal to orthorhombic phase BaCl_2 is observed. Here, indium is required to produce the desirable orthorhombic phase for the material to work as a storage phosphor. The hexagonal phase is formed at temperatures below 290 °C, above this temperature the orthorhombic phase is formed. Contrary to the FCZ glasses, the InF_3 -containing FBZ glasses do not show a phase transformation to orthorhombic BaBr_2 , but the indium-free FBZ glass ceramics do.

This work is a step on the road to identify the role of each chemical component and to improve the material for luminescence applications such as ionizing radiation detection. InF_3 has both advantages and disadvantages. For example, it has proved to be essential to glass quality. Without indium, the quantity of black precipitates (reduced Zr) is unacceptably high. In addition, InF_3 is also important for the phase transformation: Without the addition of In, no phase transformation from hexagonal to orthorhombic phase BaCl_2 nanoparticles can be found in FCZ glass ceramics, while for FBZ glass ceramics it is vice versa. Experiments are ongoing to improve the glass ceramics both for ionizing radiation detection and frequency conversion, such as a two-step preparation process and/or the addition of codopants such as divalent samarium.

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Figure 1. Normalized XANES spectra of the as-made, indium-free, Eu-doped FBZ glass. A pseudo-Voigt function (dashed curve) and an arctan function (dotted curve) were used to fit each of the characteristic WLs of Eu^{2+} and Eu^{3+} and the absorption edge, respectively (see inset).

Figure 2. Normalized XANES spectra of the as-made Eu-doped FBZ glasses without (solid curve) and with 1.5 mol% InF_3 (dotted curve).

Figure 3.
 Eu^{2+} -to- Eu^{3+} mole ratio vs. annealing temperature.

Figure 4.

Normalized PL spectra of Eu-doped FCZ and FBZ glass ceramics annealed at 270, 280, 290 °C and 280, 290, 300 °C, respectively, for 20 min (270 °C – dotted, 280 °C – dashed, 290 °C – solid, 300 °C – dashed-dotted). The PL was excited at 280 nm. All spectra have been normalized to their most intense emission.