Eu oxidation state in fluorozirconate-based glass ceramics

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The influence of InF_3 doping and remelting on Eu-doped fluorozirconate-based glass ceramics was investigated using near-edge x-ray absorption and optical spectroscopy. It was found that the addition of InF_3 to the melt decreases the $\text{Eu}^{2+}/\text{Eu}^{3+}$ mole ratio, while remelting leads to a significant change in the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio in favor of Eu^{2+} . Photoluminescence spectroscopy shows that additional annealing steps lead to the formation of BaCl_2 nanoparticles in the glass. In as-made glass ceramics containing InF_3 , a phase transition of the nanoparticles from hexagonal to orthorhombic structure is observed. This phase transition is not observed in the remelted glasses studied here. © 2009 American Institute of Physics. [doi:10.1063/1.3259390]

I. INTRODUCTION

A class of europium-doped fluorochlorozirconate (FCZ) glass ceramics has been developed for ionizing radiation detection in medical imaging, homeland security, and nondestructive testing.^{1,2} The new materials are derived from a standard ZBLAN formulation. ZBLAN is a fluoride glass, made from zirconium, barium, lanthanum, aluminum, and sodium, as the name suggests. Several synthesis routes have been derived,³ many of which involve performing the synthesis in a halide gas to maintain zirconium in the 4+ state. Halide gases are corrosive and dangerous to work with; later work found that the addition of a small amount of indium fluoride helped to maintain Zr in the 4+ state, and hence the clarity of the glass.⁴ The glasses under investigation here were additionally doped with chlorine ions by partial substitution of barium fluoride for barium chloride and complete substitution of NaF by NaCl. This enabled precipitation of barium chloride nanocrystals within the glass upon appropriate annealing. Depending on the structural phase of the barium chloride, the glass-ceramic material can act either as a scintillator (able to convert ionizing radiation to visible light)¹ 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).² In both applications, Eu is added to the glass for optical activation showing an intense luminescence in the blue spectral region upon excitation with ultraviolet light or x rays. Note that Eu^{2+} does not luminesce in the glass matrix but in the BaCl_2 nanocrystals.^{5,6} For this reason, the crystalline structure of the barium chloride nanoparticles is critical to potential ap-

plications, as scintillators and storage phosphors require vastly different light collection methodologies, i.e., readout mechanisms.

For luminescence from these materials, the critical component is the Eu^{2+} , in particular the Eu^{2+} present in the barium chloride nanocrystals. However, photoluminescence (PL) and x-ray excited luminescence measurements^{1,6} have shown that there is always a significant amount of Eu^{3+} in the glass which reduces the performance of these systems as both scintillators and storage phosphors. Specifically, in Ref. 7 it was found that about half of the doped Eu exists as Eu^{3+} in the as-made FCZ sample, even though it was added as EuF_2 . X-ray absorption near edge structure (XANES) measurements showed that one source of oxygen was found to be in the as-bought EuF_2 , in which Eu^{2+} is oxidized to Eu^{3+} before and/or during glass melting. In this context, XANES gives detailed information on the electronic structure, chemical valence, and chemical composition of the embedded Eu. Upon remelting the samples with additional ammonium bifluoride (ABF), the Eu^{2+} -to- Eu^{3+} ratio changed significantly in favor of the Eu^{2+} , i.e., it increased to about 3:1. However, remelting with additional ABF doping also affected the phase transition induced by heat treatment of the as-made FCZ glasses: the ABF-undoped FCZ glass sample showed the typical phase transition from hexagonal to orthorhombic BaCl_2 upon increasing the annealing temperature, while the ABF-doped sample did not. The glasses containing hexagonal BaCl_2 act as a scintillator while those containing orthorhombic BaCl_2 act as a storage phosphor. In such a complex system the addition of each new chemical and each change in processing affects the material properties and so must be systematically investigated. The aim of this work is to increase luminescence in these materials; in Ref. 2 it was shown that an increase in luminescence by a factor of 2

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TABLE I. Nominal compositions of the Eu^{2+} -doped FCZ glasses (values in mol %).

Sample No.	In-doping level (mol %)	Composition (mol %)						
		ZrF ₄	BaF ₂	NaCl	LaF ₃	AlF ₃	InF ₃	EuF ₂
1	0	51.2	9.66	19.42	3.87	2.9	0	3
2	0.5	51.5	9.71	19.42	3.88	2.91	0.5	3
3	1	51.0	9.62	19.23	3.85	2.89	1	3

would lead to a commercially competitive image plate. This increase can be achieved by maintaining the europium in the divalent state. In this work we investigate the influence of adding InF_3 and remelting on the Eu^{2+} -to- Eu^{3+} ratio.

II. MATERIALS AND METHODS

The Eu-doped FCZ glasses investigated are based on the well-known ZBLAN composition.⁸ The nominal compositions of the FCZ glasses are given in Table I (values in mole percent). The EuF_2 doping level is kept at 3 mol % while the addition of InF_3 is compensated at the expense of all the other components. The constituent chemicals were melted in a glassy carbon crucible at 745 °C in an inert atmosphere of nitrogen and then poured into a brass mold that was at a temperature of 200 °C, before being slowly cooled to room temperature. Afterward, each glass is cut in half and one half is again melted in a glassy carbon crucible at 745 °C in an inert atmosphere of nitrogen. The as-made and remelted samples were subsequently brought to temperatures of 260, 270, 280, and 290 °C and held there for 20 min in an inert nitrogen atmosphere. The visible appearance of the as-made glass is mostly clear. For lower amounts of indium fluoride a large number of black spots can be found in the samples. After remelting the number and size of these spots increase, in particular for those glasses containing no InF_3 . After thermal processing there is evidence of crystallization in all of the glasses, ranging from a near-transparent glass, which was light yellow in transmitted light, to one which was opaque and milky white.

The XANES measurements on the FCZ glass ceramics were recorded in the vicinity of the Eu L_3 edge (6977 eV) at the 5-BM-D beamline of the Advanced Photon Source (Argonne National Laboratory) using a Si(111) double crystal monochromator with an energy resolution of 10^{-4} . A monochromator stabilizer was used to keep a constant photon flux. The spectra were recorded in fluorescence mode using an N_2 -filled ionization chamber and a Canberra 13-element solid state detector (SSD) for the detection of the incidence and fluorescence radiation, respectively. XANES spectra for all samples are isolated from the energy scans following subtraction of the pre-edge background absorption, approximated as a linear function, and normalization of the edge jump (average between 7080 and 7130 eV) to unity using the IFEFFIT-software package.⁹ In order to quantify the white-line intensity in these spectra, curve fitting is accomplished by modeling the experimental data using pseudo-Voigt (for the white-line resonances) and arctan (for the edge steps) functions. The arctan width is set to the natural Eu L_3 linewidth.¹⁰

The differential scanning calorimetry (DSC) was performed with a DSC 204 F1 Phoenix instrument (Netzsch) and the PL measurements with a FluoroLog-3 spectrophotometer (Horiba Jobin Yvon).

III. RESULTS

A. Europium oxidation state

Figure 1 shows the normalized Eu L_3 XANES spectrum of the as-made Eu-doped FCZ glass without InF_3 doping. In the pre-edge region two maxima can be clearly seen: one is located at about 6975 eV, and the other is at about 6983 eV. These two resonances are associated with a dipole-allowed transition from a $2p_{3/2}$ core level into an empty $5d$ state and they are characteristic white lines (WLs) of Eu^{2+} and Eu^{3+} .¹¹ The WL of the Eu^{2+} species is approximately 8 eV lower than the WL of Eu^{3+} species. The relative intensity of the two WLs is an indication of the Eu^{2+} -to- Eu^{3+} ratio.^{12,13} To obtain quantitative information about these WLs and to determine the Eu^{2+} -to- Eu^{3+} ratio, a pseudo-Voigt function and an arctan function were used to fit each WL and the absorption edge, respectively. The fitted curve (dashed curve) and the individual fitted components (dotted curves) are shown in the same graph, and the fitting results of the WLs are listed in Table II. It is known that the area ratio (A_{Eu}) between the Eu^{2+} and Eu^{3+} WLs is related to the mole ratio (M_{Eu}) through $M_{\text{Eu}} = RA_{\text{Eu}}$, where R is a constant that is related to the $2p \rightarrow 5d$ transition probabilities of Eu^{2+} and Eu^{3+} .¹³ In a dilute system (e.g., an aqueous solution), the R value for Eu is about 1.5, determined from an *in situ* XANES analysis of electrochemical conversion between Eu^{2+} and Eu^{3+} in an

FIG. 1. Normalized XANES spectra of the as-made, indium-free, Eu-doped FCZ 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).

TABLE II. Fitting results of Eu^{2+} and Eu^{3+} L_3 WLs from as-made and remelted FCZ glasses with and without InF_3 doping.

InF ₃ doping	Species	Edge resonance				Edge step		M_{Eu}	Fraction
		Height (a.u.)	Position (eV)	FWHM (eV)	Area (a.u.)	Height (a.u.)	Position (eV)		
As-made									
0 mol%								1.85 ±0.05	
	Eu ^{II}	1.91 ±0.02	6975.0 ±0.1	4.58 ±0.04	11.6 ±0.2	0.54	6975.6 ±0.1		0.65 ±0.01
	Eu ^{III}	1.55 ±0.02	6983.3 ±0.1	4.99 ±0.04	9.4 ±0.2	0.32	6986.2 ±0.1		0.35 ±0.01
0.5 mol%									
								0.87 ±0.02	
	Eu ^{II}	1.38 ±0.02	6975.1 ±0.1	4.71 ±0.04	8.5 ±0.2	0.38	6977.2 ±0.1		0.47 ±0.01
	Eu ^{III}	2.29 ±0.02	6983.3 ±0.1	5.10 ±0.04	14.6 ±0.2	0.43	6986.2 ±0.1		0.53 ±0.01
1 mol%									
								1.03 ±0.03	
	Eu ^{II}	1.56 ±0.02	6975.1 ±0.1	4.67 ±0.04	9.4 ±0.2	0.43	6977.2 ±0.1		0.51 ±0.01
	Eu ^{III}	2.18 ±0.02	6983.3 ±0.1	5.06 ±0.04	13.7 ±0.2	0.40	6986.2 ±0.1		0.49 ±0.01
Remelted									
0 mol%								4.99 ±0.18	
	Eu ^{II}	2.48 ±0.02	6975.1 ±0.1	4.67 ±0.04	15.3 ±0.2	0.67	6977.1 ±0.1		0.83 ±0.01
	Eu ^{III}	0.86 ±0.02	6983.4 ±0.1	5.06 ±0.04	4.6 ±0.2	0.25	6986.2 ±0.1		0.17 ±0.01
0.5 mol%									
								1.61 ±0.04	
	Eu ^{II}	1.86 ±0.02	6975.1 ±0.1	4.71 ±0.04	11.3 ±0.2	0.52	6977.5 ±0.1		0.62 ±0.01
	Eu ^{III}	1.73 ±0.02	6983.3 ±0.1	4.97 ±0.04	10.5 ±0.2	0.33	6986.2 ±0.1		0.38 ±0.01
1 mol%									
								1.79 ±0.05	
	Eu ^{II}	1.91 ±0.02	6975.1 ±0.1	4.70 ±0.04	11.8 ±0.2	0.51	6977.2 ±0.1		0.64 ±0.01
	Eu ^{III}	1.63 ±0.02	6983.3 ±0.1	5.00 ±0.04	9.9 ±0.2	0.34	6986.1 ±0.1		0.36 ±0.01

EuCl_3 solution.¹³ Since the Eu content is only 3 mol % in our samples, the system can be considered dilute. Therefore, in our study, we use an R value of 1.5 to determine M_{Eu} , which is used to calculate the mole fraction of Eu ions (the result is listed in the final column of Table II).

The XANES spectra depend significantly on the InF_3 doping. Figure 2 shows the normalized Eu L_3 XANES spectra of as-made FCZ glass ceramics without (solid curve) and with 0.5 (dashed curve) and 1 mol % InF_3 (dotted curve). A significant shift in the energy of the XANES WLs is not evident in any of the spectra. The height of the Eu^{2+} and Eu^{3+} WLs and therefore the Eu^{2+} -to- Eu^{3+} ratio changes significantly upon increasing the InF_3 doping level. The Eu^{2+} WLs of the InF_3 -doped samples are less intense than in the indium-free sample, whereas the Eu^{3+} WLs are more intense. The Eu^{3+} WLs of both the InF_3 -doped samples have about

FIG. 2. Normalized XANES spectra of the as-made Eu-doped FCZ glasses without (solid curve) and with 0.5 (dashed curve) and 1 mol % InF_3 (dotted curve).

FIG. 3. Normalized XANES spectra of the indium-free Eu-doped FCZ glass, as-made (solid curve), and remelted (dashed curve).

the same height, the Eu^{2+} WL of the 0.5 mol % InF_3 -doped sample is slightly less intense than the one of the 1 mol % sample. The complete analysis of all spectra is summarized in Table II.

Remelting the samples without any additional chemicals leads to significant changes in the Eu^{2+} -to- Eu^{3+} mole ratio. The normalized XANES spectra of the indium-free sample before and after a remelting step can be seen in Fig. 3. For the original sample the WLs of Eu^{2+} and Eu^{3+} are about the same height, whereas after the remelting process the WL of Eu^{2+} is significantly higher than the Eu^{3+} WL, i.e., the Eu^{2+} WL increases in height and the Eu^{3+} WL height decreases.

Figure 4 shows the Eu^{2+} -to- Eu^{3+} mole ratio of the Eu-doped FCZ glass ceramics versus the annealing temperature. Thermal annealing has no influence on the Eu^{2+} -to- Eu^{3+} mole ratio (XANES spectra are not shown). The glasses containing InF_3 always show a ratio of approximately 0.85 (0.5 mol %) and 1 (1 mol %). Remelting of these glasses leads to an increase in the Eu^{2+} -to- Eu^{3+} mole ratio to values between 1.5 (0.5 mol %) and 1.7 (1 mol %). The indium-free glass has an Eu^{2+} -to- Eu^{3+} mole ratio of about 1.8 before the remelting process. Upon remelting this value increases to about 4.6, i.e., more than 80% of the europium ions are divalent.

B. Crystallization behavior

As shown in Sec. III A, the Eu oxidation state is significantly affected by the addition of indium and subsequent

FIG. 4. Eu^{2+} -to- Eu^{3+} mole ratio vs annealing temperature.

FIG. 5. DSC results for as-made and remelted Eu-doped FCZ glasses.

remelting. Further investigation focuses on the influence of indium and/or remelting on the crystallization; this was done using DSC and PL. DSC provides information on the onset of the BaCl_2 crystallization whereas PL infers the structure of the BaCl_2 nanocrystals.⁵

The DSC data of Eu-doped FCZ glasses with and without 0.5 mol % InF_3 are shown in Fig. 5. The glass transition temperature is approximately 230 °C and does not change upon increasing InF_3 content or when the sample is remelted. A first exothermic peak can be found at 271 and 269 °C for glasses with and without 0.5 mol % InF_3 , respectively. For the glass containing 1 mol % InF_3 the first crystallization peak is found at 277 °C (not shown). In Ref. 5 this peak is attributed to the crystallization of BaCl_2 nanoparticles. For the remelted samples the crystallization peak is smaller and shifted to higher temperatures, i.e., 281, 287, and 293 (not shown) for glasses with 0, 0.5, and 1 mol % InF_3 , respectively. The large crystallization peak at 330 °C is associated with a partial crystallization of the glass matrix.⁸

PL spectra of differently annealed FCZ samples (with and without 0.5 mol % InF_3) are plotted in Fig. 6. The samples were annealed for 20 min at temperatures between 260 and 290 °C. Note that all spectra have been normalized to their most intense emission.

The as-made, indium-free sample annealed at 260 °C (top left, dashed-dotted curve) shows the typical PL spectrum for a glass ceramic containing predominantly hexagonal phase BaCl_2 particles.⁵ 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. A similar band near 485 nm was reported in fluorozirconate glass ceramics containing small hexagonal phase BaBr_2 crystallites.^{14,15} The 485 nm emission has only been observed in glass ceramics containing hexagonal phase BaCl_2 nanoparticles. When annealing up to 290 °C, 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 Refs. 5 and 16, even though the heat treatment at 290 °C was well above the temperature of formation of the nanocrystals (see Fig. 5, solid curve).

The 0.5 mol % InF_3 doped sample (top right) shows the hexagonal phase after annealing at 260 °C, but annealing at 290 °C leads to the formation of orthorhombic phase BaCl_2 :

FIG. 6. Normalized PL of spectra of as-made and remelted Eu-doped FCZ glass ceramics annealed at 260 (dashed-dotted), 270 (dotted), 280 (dashed), and 290 °C (solid curve) for 20 min. The PL was excited at 280 nm.

the 406 nm band is shifted to 401 nm, i.e., to the bulk BaCl_2 value,¹⁷ while the 485 nm band is almost gone.

When the as-made sample without indium is remelted and subsequently annealed at different temperatures (bottom left), the 485 nm peak is the most intense one, but the 406 nm peak increases upon heat treatment and after the 290 °C annealing step, both bands have the same intensity. However, it seems that there is also no phase transformation from hexagonal phase to orthorhombic phase BaCl_2 although the annealing temperature of 290 °C is again above the crystallization peak of the BaCl_2 nanocrystals (see Fig. 5, dotted curve). On remelting the as-made sample that contained 0.5 mol % InF_3 (see Fig. 6, bottom right), the 485 nm band is as intense as the 406 nm band after the 260 °C annealing step, but the spectra after the 270, 280, and 290 °C anneal are all very similar with the 485 nm band slightly less in intensity than the 406 nm one.

IV. DISCUSSION

The results show that the Eu^{2+} -to- Eu^{3+} ratio in Eu-doped FCZ glasses depends significantly on the quantity of InF_3 added and on the melting process. Without the InF_3 additive, a higher fraction of Eu^{2+} is produced. Interestingly, the Eu^{2+} content can be further increased by a factor of about 2 upon remelting the glasses. 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 num-

ber of black precipitates on the surface. After remelting, the number and size of these precipitates increase, in particular for those glasses without InF_3 .

The black specks in the glass ceramics are Zr^{3+} , which is reduced from Zr^{4+} .¹⁸ 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+} . This does not seem to depend on the amount of InF_3 added to the glass. Both glasses containing InF_3 have the same Eu^{2+} -to- Eu^{3+} ratio within experimental error (see Table II).

The interactions within the material between the multiple cations and the halides are very complex. It is known that fluorine and chlorine¹⁹ evaporate during the melting process; exact measurements are ongoing but preliminary ion chromatography results show that this could be up to 25% by weight. In the remelting process, it is likely that further halide is lost and so the redox conditions could change as there is less fluorine and chlorine to bond to the cations.

The indium additive and the melting process also affect the crystallization properties of the FCZ glasses. The BaCl_2 crystallization peak shifts to higher temperature upon increasing the amount of InF_3 and upon remelting. In all annealed samples, crystallization of hexagonal phase BaCl_2 can be found, but only for as-made InF_3 -containing glass ceramics a phase transformation to orthorhombic phase BaCl_2 is observed. Indium is required to produce the desirable orthorhombic phase for the material to work as a storage phosphor. As stated in our recent work,²⁰ *in situ* transmission electron microscopy (TEM) measurements are ongoing to examine the growth kinetics at the interface between the nanoparticles and the glass matrix. DSC results give some insight into the mechanism. When the as-made glass is heated for the first time, an exothermic peak appears as the nanocrystals form. If the material is cooled to room temperature and heated again the nanoparticles do not precipitate. As the nanocrystals are already crystallized in the first heating and there is no thermodynamic impetus to reverse this reaction upon cooling, it is plausible that this is why no nanocrystal precipitation takes place on the second heating. The hexagonal phase is formed at temperatures below 290 °C, above this temperature the orthorhombic phase is formed. It is anticipated that the high resolution TEM will allow observation of the structural phase change and that this hypothesis will be proved.

This work is a step on the road to identify the role of each chemical component and to improve the material for x-ray imaging. InF_3 has both advantages and disadvantages: 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 storage phosphor applications. Without the addition of In, no phase transformation from hexagonal to orthorhombic phase BaCl_2 nanoparticles can be found. While subsequent remelting of the glass has proved to have a detrimental effect on storage properties, the performance of the glass ceramics for scintillator applications, where hexagonal phase BaCl_2 and a high

Eu²⁺ content are needed, is significantly improved by a remelting step. Experiments are ongoing to improve the glass ceramics both for scintillator and storage phosphor applications, such as a two-step preparation process and/or the addition of codopants such as divalent samarium.

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