Structural properties of fluorozirconate-based glass ceramics doped with multivalent europium

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The structure/property relationships of fluorochlorozirconate glass ceramics as a function of divalent and trivalent europium (Eu) co-doping and thermal processing have been investigated; the influence of doping ratio on the formation of barium chloride (BaCl_2) nanocrystals therein was elucidated. X-ray absorption near-edge structure spectroscopy shows that the post-thermal annealing changes the Eu valence of the as-poured glass slightly, but during the melting process Eu^{3+} is more strongly reduced to Eu^{2+} , in particular, when doped as a chloride instead of fluoride compound. The Eu^{2+} -to- Eu^{3+} doping ratio also plays a significant role in chemical equilibrium in the melt. X-ray diffraction measurements indicate that a higher Eu^{2+} fraction leads to a BaCl_2 phase transition from hexagonal to orthorhombic structure at a lower temperature. © 2011 American Institute of Physics. [doi:10.1063/1.3662148]

I. INTRODUCTION

Fluorozirconate (FZ)-based glasses and glass ceramics are known for their potential as image plates in medical diagnostics and up- or down-conversion layers for solar cells.^{1–5} In contrast to conventional silicate glasses, FZ-based glasses have the advantage of low phonon energies reducing the probability for non-radiative decay processes and, hence, lead to an increased luminescence output when doped with fluorescent activators like rare-earth (RE) ions such as Eu^{2+} .⁶ A further increase can be achieved by additional doping with barium halides (in our case BaCl_2) and post-annealing of the “as-poured” glass to form BaCl_2 nanocrystals in the glass matrix, which incorporate some of the RE dopants. The small nanocrystal sizes of a few hundred nanometers allow even smaller phonon frequencies, leading to enhanced fluorescence efficiencies of the glasses.⁷

Currently, there is a serious shortage of rare-earth minerals; Beijing cut its export quotas by 72% in the latter half of 2010 and by a further 35% during the first half of 2011 in an effort to ostensibly address its environmental problems. Whatever the reason, China has doubled or, in some cases, tripled the cost of rare-earth materials in recent times and a crisis is predicted to be reached in 2014 and 2015.⁸ China has about one-third of the global rare-earth deposits but produces around 95% of the world’s supply. The rare-earth portion of the image plate is, therefore, the most expensive part, Eu^{2+} being particularly costly.

In this paper, focus is put on the amount of divalent and trivalent Eu chloride and fluoride additives, because it is known that the expensive Eu^{2+} can be synthesized by melting the cheaper Eu^{3+} raw material.^{9–11} The effect of multivalent

Eu doping on the BaCl_2 crystallization is discussed. X-ray absorption near-edge structure (XANES) and x-ray diffraction (XRD) investigations were performed to evaluate the accurate Eu^{2+} -to- Eu^{3+} ratios, as well as the upcoming corresponding crystal phases. A clear understanding of the chemical processes during melting and of crystallization is essential to tailor the properties of the FZ glass ceramics to maximize the luminescence output for the particular applications discussed here.

II. MATERIALS AND METHODS

The Eu-doped fluorochlorozirconate (FCZ) glasses are based on the well-known ZBLAN composition,¹² which consists of a mixture of zirconium, barium, lanthanum, aluminum, and sodium fluorides. The nominal composition of the FCZ glasses investigated is $51\text{ZrF}_4\text{--}20\text{BaCl}_2\text{--}20\text{NaF--}3.5\text{LaF}_3\text{--}3\text{AlF}_3\text{--}0.5\text{InF}_3\text{--}x\text{EuCl}_2\text{--}(2\text{--}x)\text{EuCl}_3$ ($x=0, 0.4, 0.8, 1.6, 2.0$) (values in mol%) for the chloride series, and $51\text{ZrF}_4\text{--}20\text{BaCl}_2\text{--}20\text{NaF--}3.5\text{LaF}_3\text{--}3\text{AlF}_3\text{--}0.5\text{InF}_3\text{--}x\text{EuF}_2\text{--}(2\text{--}x)\text{EuF}_3$ ($x=0, 0.4, 0.8, 1.6, 2.0$) (values in mol%) for the fluoride series. All glasses were prepared inside a glovebox with an inert-argon atmosphere to avoid oxygen and moisture contamination. Both amounts remained below 0.1 ppm during the preparation. The compositions were melted in a two-step process, which significantly decreases the evaporation of the chlorides from the melt. The first step involves mixing and melting only the metal fluorides together at a temperature of 800 °C for 60 min. After this initial step, the melt is cooled to room temperature and the chlorides added. The mixture is placed back into the furnace and remelted at a temperature of 745 °C for 60 min before it is poured into a heated brass mold at 200 °C and then cooled to room temperature at 50 °C per hour. Subsequently, the as-made glasses are heat treated in an inert-argon atmosphere at temperatures of 250 to 290 °C in 10 °C steps for 20 min.

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X-ray absorption near-edge structure (XANES) experiments were performed at the bending-magnet beamline 5-BM-D (DuPont-Northwestern-Dow Collaboration Access Team, DND-CAT) at the Advanced Photon Source (Argonne National Laboratory, IL). The spectra were recorded in the vicinity of the Eu L_{III} edge (6977 eV, Ref. 13). To suppress higher harmonics of the fundamental energy, the crystals of the Si(111) double-crystal monochromator were continuously detuned to about 70% of the maximum peak intensity of their rocking curve. The monochromator was calibrated using the Fe K edge (7112 eV, Ref. 13). XANES spectra were recorded in fluorescence mode using an energy-dispersive four-pixel silicon-drift detector (Vortex-ME4, SII NanoTechnology USA Inc.). The region of interest was set to include the Eu^{2+} and Eu^{3+} L_{III} emission lines only. The incident photon flux was measured by means of an Oxford IC Spec ionization chamber filled with a gas mixture of He (600 Torr) and N_2 (160 Torr). For each single XANES spectrum, background correction, normalization, and curve fitting were performed individually with WinXAS 3.0.¹⁴ The pre-edge background fluorescence was subtracted from the raw data by approximating a linear function. This was followed by normalization of the edge jump to unity. Each corrected spectrum was fitted with two pseudo-Voigt functions and two arctangent functions to account for the white-line (WL) resonances and the electron excitation into unbound states, respectively. The width of both arctangent functions, however, was kept constant for each XANES spectrum and set to the natural Eu L_{III} linewidth of 3.91 eV.¹⁵ The residual degrees of freedom of the fit, in particular, the position of the pseudo-Voigt function and the height of the arctangent function, were obtained as a result of the fitting process. To quantify the WL intensities of both europium oxidation states, the area of each peak function was calculated based on the resulting fit parameters.

XRD measurements were performed in the Bragg-Brentano focusing geometry using an AXS D8 Advanced Diffractometer (Bruker) with a Cu tube operating at 40 kV and 40 mA.

III. RESULTS AND DISCUSSION

A. X-ray absorption near-edge structure

Figure 1 shows the normalized Eu L_{III} XANES spectrum of the as-poured, nominal 100% EuCl_3 -doped FCZ glass. The two resonances located at approximately 6975 eV and 6983 eV are caused by a dipole-allowed transition from a $2p_{3/2}$ core level into an empty $5d$ state and are associated to the characteristic WLs of Eu^{2+} and Eu^{3+} , respectively.¹⁶ The Eu^{2+} -to- Eu^{3+} ratios can be determined by building the relative intensity ratios of the two WLs via fitting each WL by a pseudo-Voigt and arctangent function (see Fig. 1).^{17,18} The mole ratio, M_{Eu} , is obtained by $M_{\text{Eu}} = R \cdot A_{\text{Eu}}$, where R is a constant that is related to the $2p \rightarrow 5d$ transition probabilities of Eu^{2+} and Eu^{3+} ,¹⁸ and A_{Eu} is the area ratio between the Eu^{2+} and the Eu^{3+} WL. For diluted systems, as in this case for the relatively low 2 mol% Eu doping, the R value for Eu was determined to be 1.5 from an in situ XANES analysis

FIG. 1. Normalized XANES spectrum of the as-made, nominal 100% EuCl_3 -doped FCZ glass. A pseudo-Voigt function and an arctan function (dashed curves) were used to fit each of the characteristic white lines of Eu^{2+} and Eu^{3+} and their absorption edges, respectively. The inset shows the normalized XANES spectrum of the as-made, nominal 100% EuCl_2 -doped FCZ glass for comparison.

of electrochemical conversion between Eu^{2+} and Eu^{3+} in an EuCl_3 solution.¹⁸

Figure 2 shows the measured Eu^{2+} fractions for different ratios of EuCl_2 -to- EuCl_3 in FCZ glasses versus annealing temperature. The actual Eu^{2+} content differs from the nominal Eu^{2+} doping and also shows a slight decrease when the annealing temperature is increased within each doping series, in contrast to previous work that showed no trends.¹⁹ In this work, the heat treatment was done in an inert-argon atmosphere, whereas it was previously done in nitrogen. Another difference is that the studied samples here were exposed to air for several days before the heat treatment. In Ref. 11, Weber *et al.* evaluated Mössbauer measurements on an Eu^{2+} - Eu^{3+} mixed powder and attributed the decrease in Eu^{2+} , after 10 weeks exposure in air, to oxidation. The observed behavior here is, therefore, likely caused by a small partial and diffusion-limited oxidation of Eu^{2+} on and near the oxygen-contaminated glass surfaces during the annealing step. The diffusion coefficient in solids at different temperatures is well known to be proportional

FIG. 2. Measured Eu^{2+} fraction for differently EuCl_2 -to- EuCl_3 -doped FCZ glasses vs. annealing temperature. The linear fits are a guide to the eye.

to $\exp(-E_A/RT)$, with the activation energy for diffusion E_A , the universal gas constant R , and the temperature T of the solid. Therefore, higher annealing temperatures lead to slightly larger diffusion distances of oxygen and moisture for the same annealing time, leading to a decrease in the actual Eu^{2+} content.

The melting process is even more influential. When doped with pure EuCl_3 , about 40% of the Eu^{3+} is reduced to Eu^{2+} . Looking at the thermodynamics and at the primary-phase equilibrium for changing the Eu oxidation state, this result fits well to the theory. The reaction equation during heat treatment above 570 K is given by:²⁰

and the corresponding equilibrium constant is given by:

$$K = e^{\frac{-G^\ominus}{RT}} = \frac{a[\text{EuCl}_2]p^{1/2}[\text{Cl}_2]}{a[\text{EuCl}_3]}, \quad (2)$$

with the free energy of the reaction $G^\ominus$ at process temperature T and the gas constant R . In Ref. 10, Massot *et al.* calculated K to be 0.811 for an operating temperature of 800 °C via an electrochemical study. For pure EuCl_3 doping, this would result in an equilibrium consisting of 45% Eu^{2+} and 55% Eu^{3+} , confirming the measured data for the ZBLAN: EuCl_3 melt, i.e., the sample with nominal 0% Eu^{2+} fraction in the as-made state.

However, doping with pure EuCl_2 shows the possible Eu^{2+} doping limit for the above explained melting process to be slightly more than 90% for the as-made glass (see Fig. 2). It is known that the InF_3 additive acts as a mild oxidizer preventing a reduction from Zr^{4+} to Zr^{3+} for reasons of glass quality, but at the same time also oxidizes some Eu^{2+} to Eu^{3+} .¹⁹ Moreover, even minimal oxygen contamination in the used raw materials and the above-mentioned long air exposure could lead to this oxidation process and the 90% limit, respectively.

Unlike all other series, the nominal pure 2 mol% EuCl_2 -doped series shows a significant downward trend to lower Eu^{2+} fractions with higher annealing temperatures (78% for 20-min annealing at 290 °C) synonymous with an increased conversion from Eu^{2+} into Eu^{3+} . The reason is not completely understood yet, but could be related to a higher Eu fraction near the surface caused by a not fully homogeneously blended melt and glass, respectively, making an interaction with oxygen during air exposure more probable.

Looking at the measured Eu^{2+} fractions and their corresponding theoretical Eu^{2+} fractions, it is noticeable that the difference between them is not linear in all regions. Figure 3 shows the measured Eu^{2+} fraction for Eu^{2+} -to- Eu^{3+} chloride- (squares) and fluoride- (triangles) doped FCZ glasses. During melting, more Eu^{2+} is formed when the glasses are doped with EuCl_3 as opposed to EuF_3 . Thus, for the chloride series and from nominal Eu^{2+} fractions between 0 and 80%, an even higher Eu^{2+} amount is found because of the reduction of the additional Eu^{3+} dopant. A saturation is observed at nominal Eu^{2+} fractions of more than 80% because of the above-mentioned effects of InF_3 and oxygen contamination. These effects are confirmed when looking at

FIG. 3. Measured Eu^{2+} fraction for Eu^{2+} -to- Eu^{3+} chloride- (squares) and fluoride- (triangles) doped FCZ glasses vs. their nominal Eu^{2+} fraction. The polynomial fits are a guide to the eye.

the fluoride series, where the measured Eu^{2+} fraction also saturates at almost the same mean value of about 83% (Eu^{3+} fraction of about 17%) for a nominal pure EuF_2 -doped glass. In the following text, all nominal Eu fractions are replaced by their measured equivalent.

B. X-ray diffraction

Figure 4 shows a typical XRD pattern for a 2 mol% EuCl_3 -doped FCZ glass. The as-poured glass does not show any crystalline phases, whereas annealing at 250 °C for 20 min leads to the formation of hexagonal phase BaCl_2 nanocrystals (space group P2m (189), see bottom bar pattern). Whereas up to an annealing temperature of 270 °C only diffraction peaks related to hexagonal BaCl_2 are detectable, a phase transition to the orthorhombic BaCl_2 structure (space group Pnam (62), see top bar pattern) can be observed upon annealing at 290 °C. In addition, two reflections arise at 26.3° and 50.1°, which are not yet identified. Figure 5 focuses on the crystalline phases and their transition

FIG. 4. XRD patterns of a pure 2 mol% EuCl_3 -doped FCZ glass as-made and annealed at temperatures from 250 °C to 290 °C for 20 min. The XRD patterns of hexagonal (bottom, PDF 45-1313) and orthorhombic BaCl_2 (top, PDF 24-0094) are shown for comparison.

FIG. 5. BaCl_2 nanocrystal phases depending on the Eu valence fraction and annealing temperature of the chloride (solid symbols) series: hexagonal phase (squares), mixed phase (triangles), and orthorhombic phase (circles).

temperatures for different Eu^{2+} fractions. It can be seen that the temperature at which the phase transition from hexagonal to orthorhombic structure occurs, depends on the Eu valence, i.e., a higher amount of divalent Eu leads to a less stable hexagonal BaCl_2 phase. When doped with nominally pure EuCl_2 , a phase transition from hexagonal to orthorhombic structure is completed at 270 °C. For Eu^{2+} fractions between 54% and 83% the transition takes place at 280 °C, whereas, for pure 2 mol% EuCl_3 doping, a fully transformed orthorhombic BaCl_2 phase is not found before annealing at 290 °C for 20 min.

In comparison to the chlorides, the fluorides (not shown for reasons of clarity) show that the phase transition takes place at a higher temperature. Figure 6 shows XRD patterns of an Eu^{2+} - Eu^{3+} fluoride FCZ glass series annealed at 270 °C for 20 min. Compared to the nominal 100% EuCl_2 -doped sample, which already shows a completely ortho-

FIG. 6. XRD patterns of an Eu^{2+} - Eu^{3+} fluoride FCZ glass series annealed at 270 °C for 20 min. The percentages correspond to the measured Eu^{2+} fraction of the total Eu doping. The XRD patterns of hexagonal (bottom, PDF 45-1313) and orthorhombic BaCl_2 (top, PDF 24-0094) are shown for comparison.

rhombic BaCl_2 phase at 270 °C, the nominal 100% EuF_2 -doped glass still contains a clear measurable amount of both phases. Furthermore, within the fluoride series a phase mixture at 270 °C is not observed prior to 40% Eu^{2+} being present, whereas it is observed at 20% within the chloride series. Because the base-glass compositions (except Eu^{2+} and Eu^{3+} chlorides and fluorides) remain constant, there are two possible reasons for this behavior: First, because of the slightly decreased chlorine content in the Eu fluoride series, higher energies and temperatures are needed, respectively, to initiate nucleation and phase transition. Second, the XANES measurements show that, compared to the chloride series, the Eu^{3+} in the fluoride series is more stable for the same melting process. From the previous results on chlorides (see Fig. 3) it is known that a lower amount of Eu^{2+} leads to a more stable hexagonal BaCl_2 phase, explaining the later phase transition at higher temperatures for the fluoride series.

IV. CONCLUSION

XANES measurements show that, during the glass-melting process, Eu^{3+} is partially reduced to Eu^{2+} . Because the measured Eu^{2+} fraction in the glass saturates with higher doping ratio (only 13% difference between nominal 60% and 100% Eu^{2+} fraction), usage of the cheaper EuCl_3 for this region would reduce costs without lowering the Eu^{2+} luminescence significantly. These results also show that europium chloride converts more Eu^{3+} into the divalent valence state than their fluoride counterparts and, therefore, are the preferred choice for this method. Furthermore, a slight oxidation of Eu^{2+} during annealing was observed. It is recommended to heat treat the samples soon after the cutting and polishing steps.

The different chemical equilibria of the multivalent Eu-doped FCZ glass melts significantly influence the luminescence output, which is important for BaCl_2 crystallization. XRD measurements show that a higher amount of divalent Eu leads to an earlier (in terms of temperature) phase transition from hexagonal to orthorhombic BaCl_2 . As XANES results suggest, the phase transition takes place at higher temperatures for Eu-fluoride compounds than for their chloride equivalents.

In conclusion, and in terms of a price reduction for image plates for medical diagnostics and down-conversion layers for solar cells, multivalent Eu doping of ZBLAN glasses and glass ceramics could be a technically and financially feasible route.

Future work will focus on further routes to improve glass-ceramic luminescence output while reducing production costs. Co-doping with other REs for energy transfer to Eu^{2+} , as well as a two-step annealing process, are promising ways.

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