

## Mössbauer spectroscopy of europium-containing glasses: optical activator study for x-ray image plates

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**Abstract** A fluorozirconate glass (ZBLAN) containing BaCl<sub>2</sub> nanocrystals doped with divalent Eu is a promising material for x-ray image plates for medical diagnosis. Since it is known that Eu<sup>2+</sup> readily oxidizes to Eu<sup>3+</sup>, which reduces fluorescence efficiency of the image plates, <sup>151</sup>Eu Mössbauer spectroscopy was used in this work to monitor the Eu oxidation state of the samples during degradation over time in the presence of ambient humidity. In addition, Mössbauer spectroscopic experiments show that the oxidation state has already changed during the glass melt: The sample made from 5 mol% EuCl<sub>2</sub> contained 78 % EuCl<sub>2</sub> + 22 % EuCl<sub>3</sub> deduced from the relative areas of the absorption lines. The sample made from 2.5 mol% EuCl<sub>2</sub> + 2.5 mol% EuCl<sub>3</sub> contained 37 % EuCl<sub>2</sub> + 63 % EuCl<sub>3</sub>, i.e. 26 % of the original EuCl<sub>2</sub> was oxidized to EuCl<sub>3</sub>.

**Keywords** Mössbauer · Glass ceramics · Rare-earths · Medical imaging

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## 1 Introduction

Fluorochlorozirconate (FCZ) glass ceramics are being developed to detect x-rays for biomedical imaging. The materials are based on a standard ZBLAN formulation. ZBLAN (zirconium, barium, lanthanum, aluminum, and sodium) is a fluoride glass in its original form. These glasses however, under investigation for mammography image plates, are additionally doped with chlorine ions by total substitution of barium chloride for barium fluoride and the addition of europium (II) chloride as an optical activator. Upon appropriate thermal annealing, barium chloride nanocrystals precipitate within the glass and take up the divalent europium. Upon x-ray irradiation, electron-hole pairs are created, which are stable until stimulated by a laser, at which time the electron-hole pairs recombine followed by a luminescence signal. This luminescence produces the image. It is critical to mammography image plates that the europium remains in the 2+ state inside the barium chloride nanocrystals. However, photoluminescence and x-ray excited luminescence measurements [1] have shown that there is always a significant amount of  $\text{Eu}^{3+}$  in the glass, which reduces the performance of the material as an image plate. Some of the trivalent europium comes from the source material, some from oxidation after removal from the inert atmosphere where the material is stored and some from redox reactions within the glass melt.

Ball et al. [2] showed that  $\text{EuCl}_2$  can be produced by heating  $\text{EuCl}_3$  above 300 °C in a vacuum. The reaction proceeds according to the equation  $\text{EuCl}_3 \leftrightarrow \text{EuCl}_2 + 1/2\text{Cl}_2$ . The goal of this work is to investigate the oxidation of  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  in the raw material as a function of time using Mössbauer spectroscopy and also to investigate the redox reaction in the glass melt by the same technique. Deeper understandings of this issue will feedback to an improved synthesis of the modified ZBLAN glass plates. Previous Mössbauer studies of Eu-doped FCZ glass ceramics have been reported by Newman et al. [3].

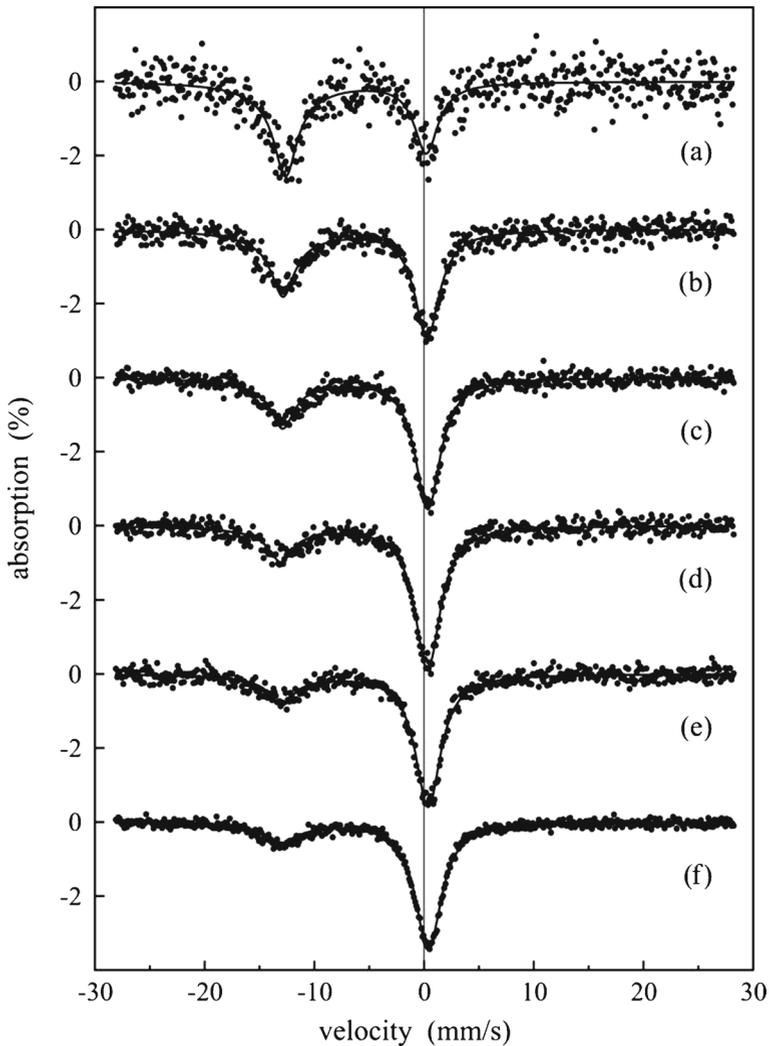
## 2 Experimental

The two modified ZBLAN glasses measured consist of  $51\text{ZrF}_4\text{-}17\text{BaCl}_2\text{-}20\text{NaF}\text{-}3.5\text{LaF}_3\text{-}3\text{AlF}_3\text{-}0.5\text{InF}_3\text{-}X$  ( $X = 5 \text{ mol\% EuCl}_2$  or  $2.5 \text{ mol\% EuCl}_2 + 2.5 \text{ mol\% EuCl}_3$ ). They were made by heating the constituent chemicals in a platinum crucible in a furnace at 750 °C inside a glove box with an argon atmosphere. Then they were poured into a 200 °C hot brass mold and slowly cooled down to room temperature linearly over 4 h. During these preparation steps oxygen and water vapor were continuously monitored and found to be <0.1 ppm; this prevents oxidation of the melt. Plates of dimensions 5 mm × 5 mm were cut and ground to 0.2 mm thickness.

Mössbauer measurements were made on samples at room temperature using a spectrometer manufactured by SEE Co, Edina, Mn, USA. The  $^{151}\text{Eu}$  Mössbauer spectra were measured using a  $^{151}\text{SmF}_3$  source, which was accelerated through a  $\pm 30 \text{ mm/s}$  range of velocities using a linear motor. The transmitted 21.7 keV  $\gamma$ -rays were detected with a Kr-filled proportional counter. The resulting spectra were fitted with a Mössbauer fitting program for the  $^{151}\text{Eu}$  resonance.

## 3 Results and discussion

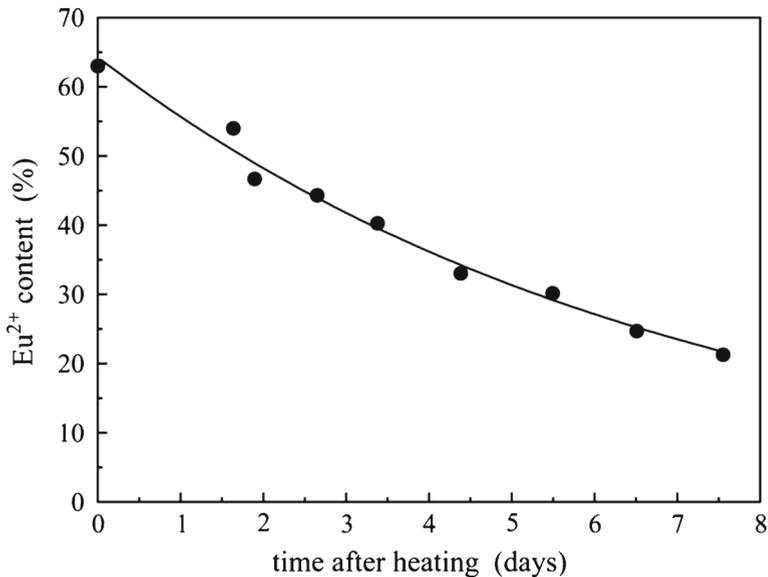
For the investigation of the raw materials, 99.9 % cation purity  $\text{EuCl}_3$  obtained from Aldridge Chemical Company was heated at 700 °C for 1 h and the resulting spectrum is



**Fig. 1** Room temperature Mössbauer spectra of finely powdered  $\text{EuCl}_3$  heated at  $700^\circ\text{C}$  for 1 h, (a) directly, (b) 2.9 days (c) 4.8 days (d) 6.9 days (e) 15.9 days, and (f) 19.9 days after the heat treatment

shown in Fig. 1a. Initially,  $\text{EuCl}_2$  is formed but is unstable; the subsequent decay, as a function of time after heating, is shown in Fig. 1b to f. The spectra show the variation in  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  contributions. Analysis of the area under the  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  absorption curves yield that the amount of  $\text{Eu}^{2+}$  decreases and  $\text{Eu}^{3+}$  increases with time. The resulting product is identified as  $\text{Eu}_2\text{O}_3$  from its isomer shift (see later). The  $\text{Eu}^{2+}$  degradation can be described by  $2\text{EuCl}_2 + 2\text{H}_2\text{O} + 1/2\text{O}_2 \rightarrow \text{Eu}_2\text{O}_3 + 4\text{HCl}$ . Figure 2 shows a fitted exponential decay curve; the  $\text{Eu}^{2+}$  has a half life of approximately 7 days.

The two glass samples were made with 5 mol% europium doping in order to provide sufficient Mössbauer signal to obtain spectra over a reasonable time scale. One sample was made with 5 mol%  $\text{EuCl}_2$ , the other with 2.5 mol%  $\text{EuCl}_2$  and 2.5 mol%  $\text{EuCl}_3$ . The

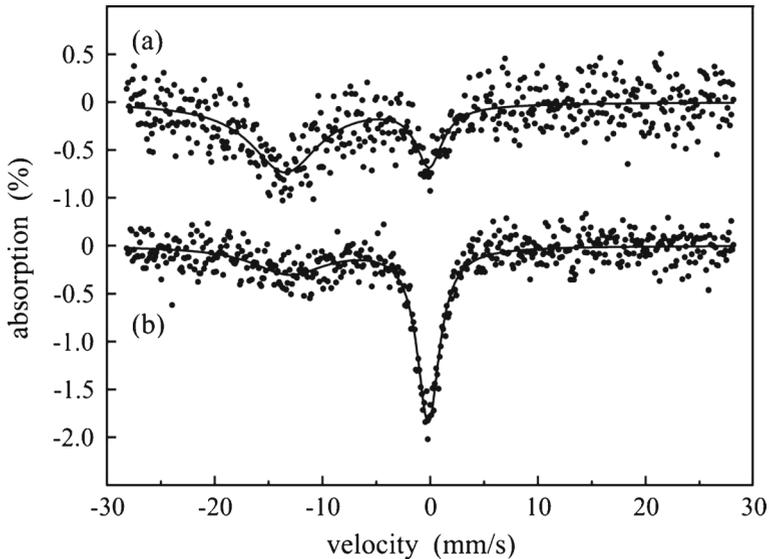


**Fig. 2** Percentage of  $\text{Eu}^{2+}$  in  $\text{EuCl}_3$  heated over time. The data were fitted by  $y(t) = 64.3 \cdot \exp(-t/7.0)$

Mössbauer spectra are shown in Fig. 3a and b. The absorption is small and difficult to observe, partly because of the small amount of europium and partly because the 21.7 keV  $\gamma$ -rays are strongly absorbed by the more abundant zirconium which has an L x-ray edge close by, thereby reducing the signal/noise ratio. The  $\text{Eu}^{2+}$  line is especially difficult to observe as it is broad ( $\text{FWHM} = 7.7$  mm/s). Coey et al. [4] have observed such broadening in fluoride glasses and attributed it to a spread in isomer shifts due to the different Eu-F environments in a glass. It is more likely to be caused by slow electron spin relaxation rates which arise from the weak interactions between the paramagnetic  $\text{Eu}^{2+}$  ions due to their low concentration; such broadening has been observed in  $\text{Eu}^{2+}$  diluted (2 mol%) in  $\text{CaF}_2$ [5]. This reduces the depth of the absorption relative to that of the narrower  $\text{Eu}^{3+}$  line ( $\text{FWHM} = 2.6$  mm/s), and combined with the low Debye temperature adds to the difficulty of observing the spectrum at room temperature. The Mössbauer spectrum (Fig. 3a) of the sample made from 5 mol%  $\text{EuCl}_2$  showed that it also contained some  $\text{EuCl}_3$ , the relative areas of the lines  $\text{Eu}^{2+}:\text{Eu}^{3+}$  being 78:22. This supports conclusions from photoluminescence and x-ray excited luminescence. Similar results were found by Coey et al. [4] in Mössbauer spectra of  $\text{ZrF}_4\text{-BaF}_2\text{-ThF}_4$  glasses. They made measurements at low temperatures and deduced the Debye temperatures of the two valence states to be 145 K ( $\text{Eu}^{2+}$ ) and 261 K ( $\text{Eu}^{3+}$ ). Using Coey's data the relative amount of  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  92:8, i.e. the glass contained 4.6 %  $\text{Eu}^{2+}$  and 0.4 %  $\text{Eu}^{3+}$ .

In the sample made from 2.5 mol%  $\text{EuCl}_2$  and 2.5 mol%  $\text{EuCl}_3$  the areas of the spectra showed an  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  ratio of 37:63. Correcting for the different Debye-Waller factors the glass contained 3.25 %  $\text{Eu}^{2+}$  and 1.75 %  $\text{Eu}^{3+}$ , i.e. 30 % of the original  $\text{EuCl}_3$  was reduced to  $\text{EuCl}_2$ .

The shift of the  $\text{Eu}^{3+}$  was close to 0 mm/s, so that unlike the result of heating  $\text{EuCl}_3$  followed by oxidation in air (Fig. 1f) the  $\text{Eu}^{2+}$  has oxidized to  $\text{EuCl}_3$ . Presumably the oxygen and water vapor in the air does not penetrate the plates, whereas it can react extensively with powdered samples (Fig. 2).



**Fig. 3** Mössbauer spectra of 0.2 mm thick plates of ZBLAN:Eu with (a) 5 mol%  $\text{EuCl}_2$  and (b) 2.5 mol%  $\text{EuCl}_2$  and 2.5 mol%  $\text{EuCl}_3$

#### 4 Conclusion

$\text{EuCl}_2$  in the raw oxidizes to  $\text{Eu}_2\text{O}_3$  whereas  $\text{EuCl}_2$  in the glass oxidizes to  $\text{EuCl}_3$ . This is because there is a chlorine source in the glass. The interior of the plate is protected by the outer surface and inward diffusion of oxygen and moisture is slow. With a diffusion coefficient of  $10^{-16} \text{ cm}^2/\text{s}$  at  $25^\circ\text{C}$  for moisture/oxygen in the glass, internal oxidation would proceed at a rate of approximately 10  $\mu\text{m}/\text{year}$ .

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