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Mössbauer spectroscopy of europium-doped fluorochlorozirconate glasses and glass ceramics: optimization of storage phosphors in computed radiography

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Abstract

Eu²⁺-doped fluorochlorozirconate (FCZ) glasses and glass ceramics, which are being developed for medical and photovoltaic applications, have been analysed by Mössbauer spectroscopy. The oxidation state and chemical environment of the europium ions, which are important for the performance of these materials, were investigated. Routes for maximizing the divalent europium content were investigated. By using EuCl₂ instead of EuF₂ in the starting material a fraction of about 90% of the europium was maintained in the Eu²⁺ state as opposed to about 70% when using EuF₂. The glass ceramics produced by subsequent thermal processing contain BaCl₂ nanocrystals in which Eu²⁺ is incorporated, as shown by the narrower linewidth in the Mössbauer spectrum. Debye temperatures of 147 K and 186 K for Eu²⁺ and Eu³⁺, respectively, were determined from temperature dependent Mössbauer measurements. The f-factors were used to obtain the Eu²⁺/Eu³⁺ ratio from the area ratio of the corresponding absorption lines.

1. Introduction

Fluorozirconate (FZ)-based glasses containing rare-earth ions have uses for various optical devices such as fiber lasers and amplifiers [1, 2] and colour displays [3]. Recently, they also attracted interest as up-converting and down-converting glass layers for solar cells [4, 5, 6]. Our interest in these glasses arises because they are promising candidates for x-ray detection, being used as x-ray storage phosphors or scintillators. X-ray imaging may be performed when these materials are doped with europium and chlorine and heat-treated [7, 8]; the Eu is present dilutely in BaCl₂ nanocrystals that are precipitated during heat treatments [9, 10]. Europium exists in two oxidation states, namely 2+ and 3+. In contrast to Eu³⁺, Eu²⁺ does not fluoresce in the FZ base glass, although it is known from electron paramagnetic resonance [11] and Mössbauer spectroscopy [12] that both Eu²⁺ and Eu³⁺ are present in the glass. During annealing some Eu²⁺ ions are incorporated into the BaCl₂ nanocrystals, enabling a strong fluorescence when excited accordingly. Depending on the annealing conditions, the BaCl₂ nanocrystals crystallize in a hexagonal or an orthorhombic

structure. Glass ceramics with hexagonal phase crystallites can be used as scintillators [7] while the orthorhombic phase is suitable for storage phosphors [8].

Eu^{2+} is extremely sensitive to oxidation to Eu^{3+} . Indeed, commercially supplied samples usually contain large amounts of Eu^{3+} unless they are specially sealed in glass ampoules containing an inert gas. Glasses containing Eu^{2+} always contain some Eu^{3+} [13]; it is important for imaging applications to be able to measure the oxidation state and maximize the amount of Eu^{2+} .

The oxidation states of Eu in Eu-doped fluorochlorozirconate (FCZ) glasses have previously been studied by x-ray absorption near-edge structure (XANES) [14]. As-made samples contained 65% Eu^{2+} which increased to 83% by re-melting. It was found to be beneficial for making clear glasses to add a few mole per cent of InF_3 which prevented reduction of Zr^{4+} to Zr^{3+} , though this resulted in a decrease in the amount of Eu^{2+} both in the as-made (51%) and re-melted (64%) glasses.

Initial Mössbauer measurements on Eu-doped FCZ glasses were presented in [15]. It was shown that in fluorochlorozirconate glasses, synthesized in a two-step melting process, where the europium was added to a pre-melted mixture of fluorides, only a small amount of Eu^{2+} oxidizes during the melting process.

Here, a continuation of the work presented by Weber *et al* [15] was performed. In addition to the room temperature measurements described in [15] low temperature Mössbauer spectroscopy was used to determine the oxidation state in Eu-doped FCZ glasses and glass ceramics as well as to investigate the best route to maximize the Eu^{2+} content. EuF_2 - and EuCl_2 -doped FCZ glasses are compared. Furthermore, glass ceramics were analysed, in which the Cl ions in the glass compositions initiate the growth of the BaCl_2 nanocrystals upon thermal processing. Mössbauer spectra of as-made and thermally treated glasses are compared. The temperature dependence of the Mössbauer spectra was measured in order to determine the Lamb-Mössbauer factors (f-factors) and the Debye temperatures of Eu^{2+} and Eu^{3+} in the glass ceramics, and hence correct the Eu^{2+} -to- Eu^{3+} ratio deduced from the spectra for the different f-factors.

2. Experimental

The measurements were done with a Mössbauer spectrometer manufactured by SEE Co, Edina, MN, USA. 21.7 keV γ -rays from a $^{151}\text{SmF}_3$ source were used for the ^{151}Eu Mössbauer spectroscopy. The source was accelerated with a linear motor through a velocity range of ± 36 mm/s. The samples were placed in a closed cycle cryostat (Janis, Wilmington, MA and SEE Co), which enables cooling of the samples at temperatures down to 6 K. The detection was carried out with a Kr-filled proportional counter; the integration time was 3–5 days. The resulting spectra were fitted with a custom Mössbauer fitting program for the ^{151}Eu (21.7 eV) resonance; a Lorentzian line profile was used in the fitting procedure.

All glasses were prepared inside a glove box with an inert argon atmosphere to avoid oxygen and moisture contamination. A glass of the composition $51\text{ZrF}_4\text{-}17\text{BaCl}_2\text{-}20\text{NaF}\text{-}3.5\text{LaF}_3\text{-}3\text{AlF}_3\text{-}0.5\text{InF}_3\text{-}5\text{EuF}_2$, which is close to the standard ZBLAN formulation but with BaCl_2 substituted for BaF_2 , was compared to a glass of the composition $51\text{ZrF}_4\text{-}17\text{BaCl}_2\text{-}20\text{NaF}\text{-}3.5\text{LaF}_3\text{-}3\text{AlF}_3\text{-}0.5\text{InF}_3\text{-}5\text{EuCl}_2$, i.e. EuCl_2 was used instead of EuF_2 . All values are given in mol%. The EuF_2 -doped FCZ glass is henceforth abbreviated with FCZ – 5 mol% EuF_2 , while the acronym for the EuCl_2 -doped sample is FCZ – 5 mol% EuCl_2 .

The glasses were melted in a two-step process in order to avoid evaporation of chlorides from the melt. In the first step, the metal fluorides were mixed and melted at 800 °C. The resulting melt was cooled down to form a crystalline product. In the second step, the chlorides and the europium halide were added and the mixture was remelted at 750 °C. The melt was poured into a brass mould that was at a temperature of 200 °C, before being slowly cooled to room temperature. Subsequently, the glasses were annealed for 5 minutes at 300 °C to initiate the growth of BaCl₂ therein. Each sample was powdered and uniformly distributed on the sample holder area (60 mg/cm₂) in an inert argon atmosphere, before being quickly put into the cryostat to avoid oxidation.

3. Results and discussion

In Figure 1 the 260 K and 6 K Mössbauer spectra of an as-made EuCl₂-doped FCZ glass are compared. The corresponding fitting parameters of the Eu²⁺ Mössbauer line are given in Table 1. The Eu²⁺ and Eu³⁺ Mössbauer lines have shifts (isomer plus second order Doppler) of about −14 mm/s and 0 mm/s, respectively. According to theory, the absolute value of the second order Doppler shift increases as the temperature is lowered. The expected effect of the temperature on the shift is about -10^{-4} mm/(s·K) [16], and is within the experimental error (see Table 1) and can thus not be observed.

The linewidth of the Eu²⁺ resonance (about 8–9 mm/s) is broad mainly because of paramagnetic relaxation and partly because of the different sites associated with the disorder in the glass. This may be compared with that of the Eu³⁺ (about 3 mm/s), which has a non-magnetic ground state. The measurements do not show a significant influence of the temperature on the linewidths.

The Mössbauer effect increases as the temperature is decreased. The enhanced absorption at low temperature is clearly visible in Figure 1. Beside this, low temperature Mössbauer spectroscopy has the further advantages that it prevents the sample from oxidizing. Without a cryostat the powdered samples oxidized very quickly. A partial break-through to obtain spectra from Eu²⁺ in the glasses was making polished plates as used in [15], which oxidized more slowly. The measurements presented here were done on powdered samples installed in a closed-cycle cryostat in which both the low temperature and the vacuum prevented oxidation.

The main reason for going to low temperatures is to achieve a good quantitative analysis of the Eu²⁺-to-Eu³⁺ ratio. The ratio of the areas under the Eu²⁺ and Eu³⁺ absorption lines is 70 : 30 and 88 : 12 at 260 K and at 6 K, respectively. The Eu²⁺-to-Eu³⁺ ratio increases on cooling, because the Mössbauer effect increases more for Eu²⁺ than for Eu³⁺ resulting from its weaker binding strength (see below). The relative area of each line does not give directly the amount of each oxidation state present. The low temperature values of the f-factors are limited by the mean square zero-point vibrations. The ratio measured at the lowest temperature would be the closest to the true value. An analysis of the f-factors shows that the estimated relative area at 6 K is already a very good estimate for the real value (see below).

In Figure 2 low temperature Mössbauer spectra of the as-made FCZ – 5 mol% EuF₂ and FCZ – 5 mol% EuCl₂ samples are compared (for the fitting parameters see Table 1). The isomer shift depends on the glass composition; the fit of the Eu²⁺ Mössbauer line gives −14.0 mm/s for EuF₂-doping and −14.3 mm/s for EuCl₂-doping. The difference between F and Cl is barely significant, but it shows the expected tendency. Mössbauer studies of different Eu(II)-halides [16] suggest that the absolute value of the isomer shift increases as the covalency increases, i.e. in the order F < Cl. There is only a small difference between the linewidths of the FCZ – 5 mol% EuCl₂ and FCZ – 5 mol% EuF₂ samples.

The relative absorption strengths are strongly affected by the europium halide used for doping. An analysis of the relative areas under the absorption lines yields that using EuCl_2 instead of EuF_2 significantly improves the Eu^{2+} -to- Eu^{3+} ratio. A replacement of EuF_2 by EuCl_2 increases the relative Eu^{2+} area from 70% to 88%. EuCl_2 is preferable for keeping the Eu^{2+} fraction high having a lower free energy in an FCZ glass than EuF_2 . This advantage of EuCl_2 is confirmed by XANES measurements giving 88% and 83% relative Eu^{2+} content for EuCl_2 and EuF_2 doping, respectively [17]. Note, that europium doping level was only 2 mol% in those XANES measurements. The following investigations were done with the EuCl_2 -doped FCZ glasses, having the highest Eu^{2+} fraction. The growth of BaCl_2 nanocrystals in the glasses was achieved by annealing the glasses for 5 minutes at 300 °C. The glasses were annealed in either air or argon to determine if it is necessary to anneal in an inert atmosphere to keep the Eu^{2+} fraction high.

The Mössbauer spectra of the as-made glass, the glass annealed in air and the glass annealed in argon are compared in Figure 3. While the isomer shift is not influenced by the thermal treatment of the glasses (see Table 1), the linewidth is significantly reduced from 8.3 mm/s to about 7 mm/s after annealing, suggesting that the Eu is now in an ordered, i.e. crystalline, state. This can be explained by the formation of the BaCl_2 nanocrystals in the glasses containing the europium ions. The Eu^{2+} fraction remains almost the same after both annealing in air and annealing in an argon atmosphere. In particular, annealing in an inert-argon atmosphere does not affect the Eu^{2+} -to- Eu^{3+} ratio. This result is confirmed by [14], in which the Eu^{2+} -to- Eu^{3+} ratio was also found to be unchanged after annealing in an inert-argon atmosphere. On the contrary, the relative Eu^{2+} content of the sample that was annealed in air decreased slightly (but barely significant) by about 5%, which is consistent with a previous XANES study giving the same decrease after annealing in air [17]. Thus, it cannot be excluded that Eu^{2+} is partially oxidized on annealing the glasses in air. It should also be noted that heating can reduce EuCl_3 to EuCl_2 [15].

The temperature dependence of the Mössbauer spectra was studied for the FCZ –5 mol% EuCl_2 sample annealed in an argon atmosphere. In Figure 4 the Mössbauer spectra are shown for a set of different temperatures of the glass ceramic. The comparison clearly shows the continuous increase of the Mössbauer absorption strengths with decreasing sample temperature as described for the as-made glass (Figure 1). Beside this, the ratio of the areas under the Eu^{2+} -to- Eu^{3+} absorption lines changes with temperature. Starting at an Eu^{2+} -to- Eu^{3+} ratio of 78 : 22 at 275 K, it increases up to about 90 : 10 at 6 K. The errors for the line shifts and the linewidths in the table are the standard errors of the Lorentz fit parameters. The errors for the area fractions were estimated on the basis of the errors for the absorption strengths and the linewidths. For the presented low temperature Mössbauer measurements the errors for the Eu^{2+} -fractions are mostly about 4 %. For longer integration times the errors are reduced to about 1–2 % comparable to the errors achieved in XANES studies [14]. The temperature dependence can be described in terms of the Lamb-Mössbauer factor (or f-factor), which is the recoil free fraction determining the intensity of the Mössbauer effect.

The f-factor depends on the amplitude, x , of vibrations of the nuclei. For a harmonic oscillator the Lamb Mössbauer factor f can be described by

$$f = \exp \left(-\frac{E_\gamma^2}{(\hbar c)^2} \langle x^2 \rangle \right) \quad (1)$$

where E_γ is the energy of the emitted γ -radiation, $\hbar$ is the reduced Planck constant, and c is the velocity of light.

In Figure 5, the temperature dependence of the f-factors deduced from the areas of absorption lines is shown for Eu^{2+} and Eu^{3+} . It is seen from the temperature dependence that the Mössbauer effect increases more for Eu^{2+} than for Eu^{3+} due to the lower binding strength of Eu^{2+} . According to Equation 1 the f-factor decreases exponentially with the mean square amplitude of the vibrations. Eu^{2+} is less strongly bound so starting from absolute zero the amplitude of the thermal vibrations increases more rapidly than for the more strongly bound Eu^{3+} .

Describing the vibrations within the Debye model (as a first approximation) yields [18]

$$f = \exp \left(-\frac{3E_R}{2k_B\theta_D} \left[1 + 4 \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x}{e^x - 1} dx \right] \right) \quad (2)$$

with E_R the recoil energy, k_B the Boltzmann constant, T the temperature, and θ_D the Debye temperature. Least square fits were applied to the temperature dependence of the f-factors using Equation 2 and the recoil energy of ^{151}Eu , which is $E_R = 0.0017$ eV. The fits, shown in Figure 5, yielded Debye temperatures of $\theta_D = 147$ K and 186 K for Eu^{2+} and Eu^{3+} , respectively. The estimated Debye temperatures for the Eu^{2+} and Eu^{3+} in the glass ceramic are typical for those found for europium compounds [13, 19]. However, it should be pointed out that this estimation of the Debye temperatures is just a rough approximation. The errors for the f-factors, especially for Eu^{3+} are large. Beside experimental uncertainties, some simplifying assumptions in the Debye model, for example that an isotropic monatomic crystal lattice is present, are not satisfied.

At high temperatures ($T \gg \theta_D$) Equation 2 can be written as

$$\ln f = -\frac{6E_R T}{k_B \theta_D^2} \quad (3)$$

i.e., $\ln f$ decreases linearly with increasing temperature, which is seen from the high temperature data in Figure 5. According to Equation 2 the linear slope goes through $f = 1$ at $T = 0$ K. This enabled the f values to be deduced from the measured areas. Due to zero-point energy the amplitude of vibrations remains finite (i.e. $f < 1$). The slope decreases at low temperatures.

At room temperature, the f-factors are low, about 0.4 for Eu^{3+} and only about 0.2 for Eu^{2+} . Thus, at room temperature the absorption areas are small and comparable in size for both, Eu^{3+} and Eu^{2+} , although the concentration of Eu^{2+} is much higher in the samples. By contrast, at low temperatures the f-factors are high and comparable. The f-factors extrapolated to $T = 0$ K are 0.818 and 0.853 for Eu^{2+} and Eu^{3+} , respectively. The Eu^{2+} -to- Eu^{3+} ratio of 89.4 : 10.6 extracted directly from the 6 K spectra changes only slightly upon correction with the corresponding f-factors (0.816 for Eu^{2+} and 0.852 for Eu^{3+}); after correction a Eu^{2+} -to- Eu^{3+} ratio of 89.8 : 10.2 is obtained. In case of the room temperature spectra, however, the Eu^{2+} -to- Eu^{3+} ratio before f-factor correction (0.219 for Eu^{2+} and 0.382 for Eu^{3+}) is 77.8 : 22.2 where it becomes 85.9 : 14.1 after correction. This means, deducing the Eu^{2+} -to- Eu^{3+} ratio directly from the ratio of the areas under the absorption lines is already a good estimate, i.e. the f-factor correction is negligibly small, unlike at room temperature.

4. Conclusion

The relative Eu^{2+} and Eu^{3+} contents were successfully measured in FCZ glass ceramics. It was found that the use of EuCl_2 instead of EuF_2 as a starting material resulted in 20% more of the europium in a divalent state. The results also showed that annealing in air or an inert atmosphere did not significantly affect the Eu^{2+} content. After annealing, the Mössbauer spectrum linewidth was narrowed indicating that Eu^{2+} moved to a more ordered (crystalline) environment. Debye temperatures of 147 K and 186 K were deduced for Eu^{2+} and Eu^{3+} in the glass ceramics, respectively. The present work shows that the fractions of each oxidation state cannot be directly extracted from the area ratio of the absorption lines at room temperature; a correction with the corresponding f-factors is necessary. For an exact quantitative analysis, low temperature measurements are essential.

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Figure 1. Mössbauer spectra of an as-made FCZ – 5 mol% EuCl₂ glass measured at (a) 260 K and (b) 6 K.

Figure 2. Mössbauer spectra of (a) as-made FCZ – 5 mol% EuF₂ and (b) FCZ – 5 mol% EuCl₂ glasses, both measured at 6 K.

Figure 3. Mössbauer spectra of FCZ – 5 mol% EuCl_2 glasses (a) as-made, (b) annealed at 300 °C in air, and (c) in an argon atmosphere. All spectra were measured at 6 K.

Figure 4. Mössbauer spectra of a FCZ – 5 mol% EuCl₂ glass annealed at 300 °C in argon atmosphere measured at different temperatures between 275 K and 6 K.

Figure 5. Natural logarithm of the f-factors of Eu^{3+} (open circles) and Eu^{2+} (full squares) in a FCZ – 5 mol% EuCl_2 glass annealed at 300 °C in an argon atmosphere versus the sample temperature. The solid lines are fits with $\theta_D = 147$ K and 186 K for Eu^{2+} and Eu^{3+} , respectively. The dashed lines show the exponential temperature dependencies valid at high temperatures.

Table 1

Fitting parameters of the Eu^{2+} Mössbauer spectra in different FCZ glasses, measured at 6 K, the values at 260 K are given in brackets.

sample composition	treatment	area fraction (%)	line shift (mm/s)	line width (mm/s)
FCZ – 5 mol% EuF_2	as-made	69.6 ± 4.6	-14.3 ± 0.2	8.9 ± 0.5
FCZ – 5 mol% EuCl_2	as-made	88.0 ± 1.8 (75.4 ± 8.5)	-14.0 ± 0.1 (-14.3 ± 0.3)	8.3 ± 0.2 (8.9 ± 0.9)
FCZ – 5 mol% EuCl_2	annealed at 300 °C in air	84.2 ± 3.6	-14.0 ± 0.1	7.0 ± 0.3
FCZ – 5 mol% EuCl_2	annealed at 300 °C in Ar	89.4 ± 3.7 (77.8 ± 9.8)	-14.1 ± 0.1 (-14.1 ± 0.2)	7.3 ± 0.3 (7.5 ± 0.5)