

Zr and Ba edge phenomena in the scintillation intensity of fluorozirconate-based glass-ceramic X-ray detectors

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The energy-dependent scintillation intensity of Eu-doped fluorozirconate glass-ceramic X-ray detectors has been investigated in the energy range from 10 to 40 keV. The experiments were performed at the Advanced Photon Source, Argonne National Laboratory, USA. The glass ceramics are based on Eu-doped fluorozirconate glasses, which were additionally doped with chlorine to initiate the nucleation of BaCl₂ nanocrystals therein. The X-ray excited scintillation is mainly due to the 5*d*–4*f* transition of Eu²⁺ embedded in the BaCl₂ nanocrystals; Eu²⁺ in the glass does not luminesce. Upon appropriate annealing the nanocrystals grow and undergo a phase transition from a hexagonal to an orthorhombic phase of BaCl₂. The scintillation intensity is investigated as a function of the X-ray energy, particle size and structure of the embedded nanocrystals. The scintillation intensity *versus* X-ray energy dependence shows that the intensity is inversely proportional to the photoelectric absorption of the material, *i.e.* the more photoelectric absorption the less scintillation. At 18 and 37.4 keV a significant decrease in the scintillation intensity can be observed; this energy corresponds to the *K*-edge of Zr and Ba, respectively. The glass matrix as well as the structure and size of the embedded nanocrystals have an influence on the scintillation properties of the glass ceramics.

Keywords: X-ray detector; fluorozirconate glass ceramics; energy-dependent scintillation intensity.

1. Introduction

Traditional inorganic scintillators like CsI:Na, CsI:Tl, NaI:Tl, CdWO₄ and Bi₄Ge₃O₁₂ (BGO) (for reference, see van Eijk, 2001, 2002) have light yields larger than 10000 photons per MeV but decay times slower than 200 ns. On the other hand, the undoped halides BaF₂, CsF, CeF₃ and CsI, which have decay times in the range from 1 to 30 ns, have light yields of only a few thousand photons per MeV for the fast component. Other materials include cerium-doped inorganics, Lu₂SiO₅:Ce (LSO), Gd₂SiO₅:Ce (GSO), YAlO₃:Ce (YAP), LuAlO₃:Ce (LuAP), Lu₂Si₂O₇:Ce (LPS) and cerium-doped ⁶Li glass (van Eijk, 2001, 2002). As no existing scintillator material has all the desired properties, there has been a search for different materials.

Eu-doped fluorozirconate glasses, which were additionally doped with chlorine to initiate the nucleation of BaCl₂ nanocrystals therein, are promising candidates as X-ray detectors for digital radiography (Chen *et al.*, 2005; Chen, Johnson, Schweizer *et al.*, 2006; Johnson *et al.*, 2006). They can

be produced in any shape or size, including large-area detectors with very high resolution and adequate efficiency. The X-ray excited scintillation is mainly due to the 5*d*–4*f* transition of Eu²⁺ embedded in the BaCl₂ nanocrystals showing an intense luminescence band at 406 nm whereas Eu²⁺ in the glass does not luminesce (Schweizer *et al.*, 2006). Upon pouring the glass, no significant X-ray excited scintillation is observed. However, after annealing, at a temperature of 563 K, nanocrystals of BaCl₂ are formed, which show a pronounced X-ray excited scintillation. For relatively short annealing times the glass ceramics stay transparent, but upon further annealing the ceramics become opaque. The surprising result is that the fluorozirconate glass ceramic has a high sensitivity to X-rays (Chen *et al.*, 2005; Chen, Johnson, Schweizer *et al.*, 2006; Johnson *et al.*, 2006), considering that the nanocrystals have, at most, a volume fraction of approximately 20% (Schweizer *et al.*, 2005) of the ceramic volume. This implies that the nanocrystals have a sensitivity which is probably much larger than that for single-crystal BaCl₂ or their powders.

In this work we investigated whether the glass matrix is active in the scintillation process, *i.e.* whether it absorbs the X-rays and the electron–hole pairs then created are transferred to the nanocrystals and lead to scintillation therein. We need to study the scintillation intensity of the material as a function of X-ray energy, particle size and structure of the embedded nanocrystals. In particular, one must excite with X-rays at the edges (*K*, *L*, *M*) of the constituent atoms of the glass, especially the *K*-edge of the dominant high-atomic-number elements, Zr and Ba, where the biggest effect is expected. For this a bright monochromatic source is needed; the Zr *K*-edge is at about 18 keV, the Ba *K*-edge at about 37.4 keV.

2. Materials and methods

The Eu-doped fluorochlorozirconate (FCZ) glasses investigated are based on the well known ZBLAN composition (Aggarwal & Lu, 1991). The nominal composition of the FCZ glasses is $52\text{ZrF}_4\text{--}10\text{BaF}_2\text{--}10\text{BaCl}_2\text{--}20\text{NaCl}\text{--}3.5\text{LaF}_3\text{--}3\text{AlF}_3\text{--}0.5\text{InF}_3\text{--}1\text{EuF}_2$ (values in mole percent). The constituent chemicals were melted at the University of Paderborn in a glassy carbon crucible at 1013 K in an inert atmosphere of nitrogen and then poured into a brass mold that was at a temperature of 473 K, before being slowly cooled to room temperature. The samples were subsequently brought to a temperature of 563 K and held there for 0, 2.5, 5, 7.5, 10, 20 and 50 min in an inert nitrogen atmosphere (0 min implies that the sample was brought to 563 K for a few seconds). The visible appearance of the initial glass is clear, but after the 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 dimensions of the glass ceramic plates are approximately 10 mm × 5 mm × 0.5 mm.

The energy-dependent scintillation intensity measurements on the FCZ glass ceramics were performed at the 5-BMC beamline of the Advanced Photon Source (Argonne National Laboratory). The experimental set-up has been shown previously (Chen, Johnson, Weber *et al.*, 2006). A 6 mm (horizontal) × 4 mm (vertical) monochromatic X-ray beam ($\sim 10^{10}$ photons s^{-1} at 18 keV) is used as an imaging light source. The X-ray image on the sample is formed on a cooled charge-coupled-device (CCD) camera through a 4× objective lens. The CCD camera is a 1340 × 1300 pixel, 24 μm per pixel, and 16 bits per pixel camera manufactured by Roper Scientific.

The scintillation intensity is given as the average brightness value for a selected area of the scintillation image; for all samples an identical area has been chosen. The samples annealed for 10, 20 and 50 min show an afterglow signal which is of the order of a few percent after switching off the X-ray excitation. In order to keep the afterglow at a constant background level these samples were irradiated for several minutes with a photon energy of 40 keV until the afterglow was saturated. The average brightness value was corrected for the dark counts and normalized to acquisition time and X-ray

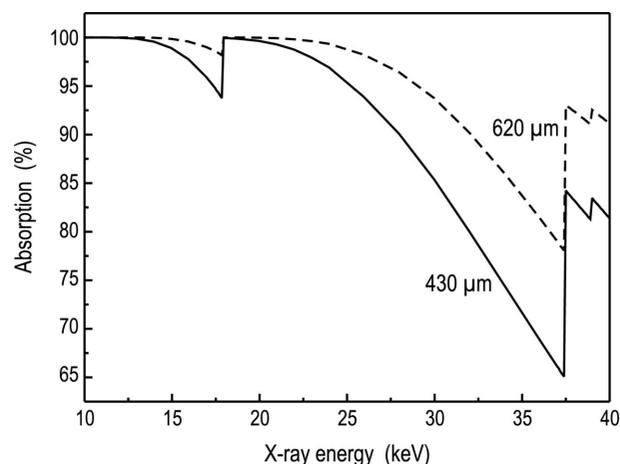


Figure 1

Calculated absorption (in %) of FCZ glass ceramics having a thickness of 430 μm (solid line) and 620 μm (dashed line), respectively. For the calculation we used the data from the National Institute of Standards and Technology (<http://physics.nist.gov/PhysRefData/Xcom/html/xcom1.html>).

flux. The acquisition time was between 2 and 10 s. The flux was determined by calculating the gas (air) absorption (<http://www.pnc.aps.anl.gov/cgi-bin/gasmix.cgi.pl>) and using this value to estimate the photon flux (<http://www.pnc.aps.anl.gov/cgi-bin/flux.cgi.pl>) at a given energy. In addition to all these corrections, we had to correct the scintillation intensity for the fact that the mass attenuation varies with X-ray energy. Fig. 1 shows how many of the incident X-ray photons are absorbed in the FCZ glass with the nominal formulation $\text{Zr}_{104}\text{--Ba}_{40}\text{--Na}_{40}\text{--La}_7\text{--Al}_6\text{--In}_1\text{--Eu}_2\text{--F}_{502}\text{--Cl}_{80}$, a density of 4.3 g cm^{-3} (Aggarwal & Lu, 1991) and a thickness of 430 and 620 μm , respectively; for the calculation of the total mass attenuation coefficient without coherent scattering we used the data from the National Institute of Standards and Technology (<http://physics.nist.gov/PhysRefData/Xcom/html/xcom1.html>). The lowest absorbance in this energy range is observed at 37.4 keV (Ba *K*-edge). For an absorbance of 99.8%, at this energy, the FCZ glass ceramic should have a thickness of at least 2500 μm . The investigated samples had thicknesses between 480 and 570 μm , *i.e.* a thickness correction is necessary, in particular for higher energies.

3. Results and discussion

Fig. 2 shows the scintillation intensity for a 50 min-annealed Eu-doped FCZ glass ceramic as measured (open squares) and after thickness correction (full squares); the sample had a thickness of about 480 μm . The energy-dependent scintillation intensity of all FCZ glass ceramics followed the same curve; it increases quasi-exponentially with X-ray energy. Note that deviations from the expected linear dependence have already been observed by Engelkemeir (1956) who investigated the non-linear response of NaI(Tl) to photons. The steps at 18 and 37.4 keV are caused by the zirconium and barium *K*-edge, respectively. The scintillation intensity at the Zr edge decreases whereas it increases at the Ba edge (Fig. 2, open

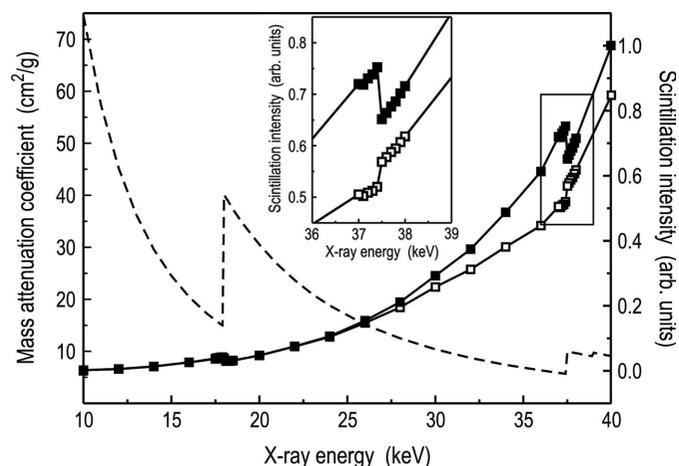


Figure 2 Scintillation intensity versus X-ray energy of the 50 min-annealed Eu-doped FCZ glass ceramic before (open squares) and after (full squares) absorption correction. The thickness of the sample was $\sim 480 \mu\text{m}$. For the correction, the original data (open squares) are divided by the absorption coefficient data shown in Fig. 1. The dashed curve shows the total mass attenuation coefficient without coherent scattering calculated from <http://physics.nist.gov/PhysRefData/Xcom/html/xcom1.html>. The inset shows the Ba K-edge at 37.4 keV.

squares). After an appropriate thickness correction (Fig. 2, full squares) in which the scintillation intensity is divided by the X-ray absorption, the sign of the Ba step is inverted (Fig. 2, inset). The experimentally observed scintillation intensity increases at the Ba edge were thus an artifact caused by the different X-ray absorption ‘before’ and ‘after’ the edge. The dashed curve shows the total mass attenuation coefficient without coherent scattering derived from <http://physics.nist.gov/PhysRefData/Xcom/html/xcom1.html>. The spectrum of the scintillation intensity is similar to the inverse mass attenuation coefficient.

The scintillation intensity around the zirconium K-edge can be seen in Fig. 3(a); in order to make a satisfactory comparison the spectra were normalized, *i.e.* divided by the scintillation intensity value at 18 keV. It is clear that the value of the scintillation intensity change varies with annealing time. The first regime is for annealing time intervals less than 5 min, where the zirconium K-edge step in the scintillation intensity is rather small. In the second time regime, FCZ glass ceramics were annealed for at least 5 min; here the step in the scintillation intensity becomes more pronounced. XRD experiments (Schweizer *et al.*, 2006) have shown that in the first time regime the BaCl₂ nanocrystals are in a hexagonal phase with a particle size in the range of 10 to 20 nm, whereas in the second time regime the nanocrystals have an orthorhombic structure with a particle size of 40 to 120 nm. Thus, the effect of decreasing scintillation intensity at the zirconium K-edge depends on the size and/or structure of the embedded nanocrystals. The step is not absolute, as one would expect, since all investigated FCZ glass ceramics have the same chemical composition; they differ only in their thermal treatment.

The same effect can also be seen in Fig. 3(b), where the value of the decrease of the scintillation intensity relative to

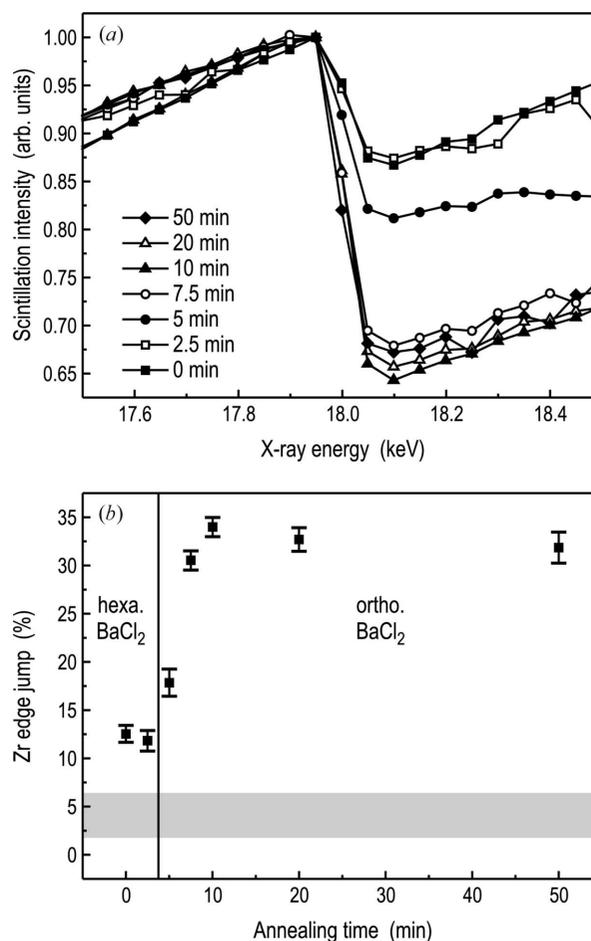


Figure 3 (a) Zirconium K-edge: scintillation intensity (normalized to the low-energy part of the edge) versus X-ray energy of Eu-doped FCZ glass ceramics annealed at a temperature of 563 K for various periods of time. The lines are a guide to the eye; the symbols represent the experimental data points. (b) Value of the decrease of the scintillation intensity at the zirconium K-edge relative to the scintillation intensity at 18 keV. The hexagonal phase BaCl₂ nanocrystals have a particle size of 10–20 nm, whereas the orthorhombic phase ones have a particle size of 40–120 nm. The grey bar gives the range of values for the zirconium K-edge step in the absorption for thicknesses from 430 (upper limit) to 620 μm (lower limit). The values are taken from Fig. 1.

the scintillation value at 18 keV is shown. The experimental error is mainly determined by the thickness measurement; although the experimental error for the thickness measurements is about $\pm 10 \mu\text{m}$, we assumed an uncertainty of $\pm 50 \mu\text{m}$ to show that the observed effect is not related to different X-ray absorption caused by different thicknesses. The error bar of the luminescence intensity is negligible. A similar step at the zirconium K-edge can be seen in the absorption spectrum (see Fig. 1). The value of the difference in the spectra depends on the thickness of the sample. The grey bar in Fig. 3 gives the range of values for this step in the absorption for thicknesses from 430 to 620 μm . The data points were normalized to the absorption at 18 keV.

The experimental data points of the scintillation intensity and their error bars are outside this bar and therefore the observed effect is not caused by the different thickness of the

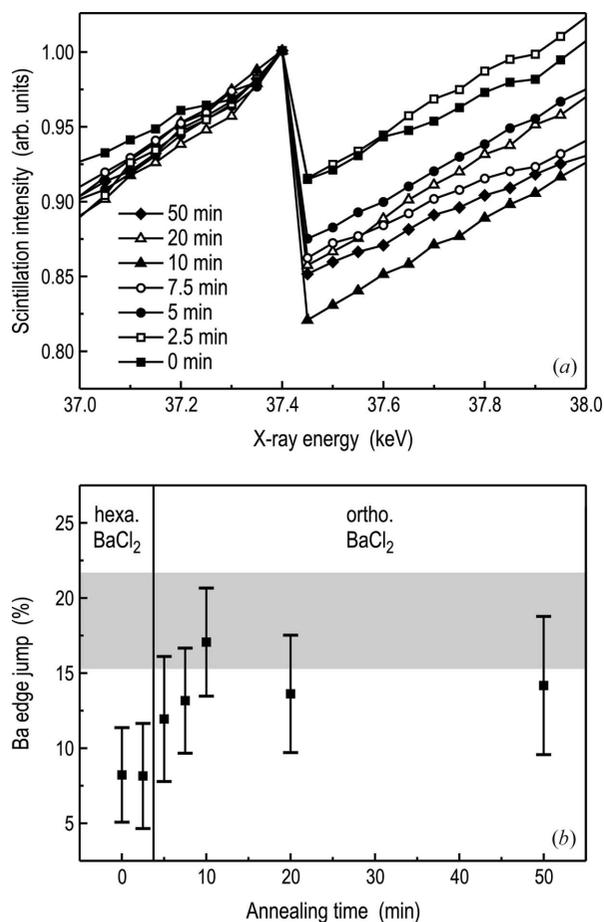


Figure 4

(a) Barium *K*-edge: scintillation intensity (normalized to the low-energy part of the edge) versus X-ray energy of Eu-doped FCZ glass ceramics annealed at a temperature of 563 K for various periods of time. The lines are a guide to the eye; the symbols represent the experimental data points. (b) Value of the decrease of the scintillation intensity at the barium *K*-edge relative to the scintillation intensity at 37.4 keV. The hexagonal phase BaCl₂ nanocrystals have a particle size of 10–20 nm, whereas the orthorhombic phase ones have a particle size of 40–120 nm. The grey bar gives the range of values for the barium *K*-edge step in the absorption for thicknesses from 430 (upper limit) to 620 μm (lower limit). The values are taken from Fig. 1.

samples. Surprisingly, the same curve has already been observed, when investigating the relative PSL efficiency for FCZ glass ceramics with different annealing times (Schweizer *et al.*, 2003). In that case the PSL efficiency increases with annealing time, but saturates for annealing times longer than 10 min.

Fig. 4(a) shows the energy-dependent scintillation around the barium *K*-edge; the spectra were normalized to the scintillation intensity at 37.4 keV, which is the onset of the step. This is needed to compare the size of the step for different annealing times. As already found for the Zr edge, the scintillation intensity decreases at the absorption edge. The value of these changes depends on the annealing time; for FCZ glass ceramics from the first time regime the change is rather small, whereas for the second time regime it is more pronounced.

Again, the effect strongly depends on the structure of the crystals embedded.

To clarify, the values of the scintillation change relative to the scintillation intensity at 37.4 keV are depicted in Fig. 4(b). The error bars are again given by the uncertainty in the thickness measurement. The grey bar gives the range of values for the barium *K*-edge step in the absorption for thicknesses from 430 to 620 μm. The experimental data points show that the value of the effect in scintillation at the barium *K*-edge saturates upon annealing. In this case the error bars are larger, because in this energy range the absorption differs much more with the thickness of the investigated glass ceramics. Nevertheless, the same saturation effect as in Fig. 3(b) can be seen.

4. Conclusion

The scintillation intensity of Eu-doped FCZ glass ceramics increases quasi-exponentially with the X-ray energy and is inversely proportional to the mass absorption coefficient, which is dominated by the photoelectric effect in the range from 10 to 40 keV. The zirconium *K*-edge as well as the barium *K*-edge is seen as a decrease in the scintillation intensity depending on the particle size and/or structure of the embedded BaCl₂ nanocrystals. The fact that the Zr edge is seen as changes in the scintillation intensity of the BaCl₂ nanocrystals in the glass indicates that the fluorozirconate-based glass matrix does have an influence on the scintillation mechanism therein; the change is more significant when the embedded nanocrystals are in the orthorhombic phase.

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