Photostimulated luminescence from a fluorobromozirconate glass-ceramic and the effect of crystallite size and phase

Photostimulated luminescence from a fluorobromozirconate glass-ceramic and the effect of crystallite size and phase

M Secu[1], **S Schweizer**[1,4], **J-M Spaeth**[1], **A Edgar**[2], **G V M Williams**[3] **and U Rieser**[2]

[1] Department of Physics, University of Paderborn, D-33095 Paderborn, Germany
[2] The MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University, PO Box 600, Wellington, New Zealand
[3] Industrial Research Limited, PO Box 31310, Lower Hutt, Wellington, New Zealand

E-mail: schweizer@physik.upb.de

Abstract

We report a systematic study of the photoluminescence (PL), photostimulated luminescence (PSL) and thermostimulated luminescence (TSL) from europium- and bromine-doped fluorozirconate glass-ceramics. Eu^{2+} ions in the as-prepared glass show no PL, but after suitable thermal annealing hexagonal phase and orthorhombic phase barium bromide crystallites are precipitated and PL is observed from Eu^{2+} ions in these crystallites. Room temperature PSL is observed from the orthorhombic phase, with an efficiency which is up to 9% of the well known crystalline storage phosphor $BaFBr:Eu^{2+}$. The emission is at 404 nm, and there is a maximum in the stimulation at 580 nm. We associate the PSL with an optically quenchable peak in the glow curve, which has an activation energy of 1.20 eV and attribute this feature to a perturbed F centre. Room temperature PSL from glass-ceramics containing predominantly the hexagonal phase of $BaBr_2$ has a relative efficiency of less than 0.07%. The resultant trap depth determined from the glow curve is 0.60 eV, which suggests that this trap does not arise from a perturbed F centre. We find that the PSL efficiency systematically decreases with decreasing hexagonal $BaBr_2$ nanocrystallite size and there is no detectable PSL from nanocrystallites smaller than 10 nm. However, below 100 K, the PSL efficiency for the hexagonal phase is nearly as high as for the orthorhombic phase and the concomitant electron traps are perturbed F centres. The measured low temperature emission was at 409 nm and an additional stimulation peak was observed at 700 nm. The PSL in this case is thermally bleached above about 150 K.

[4] Author to whom any correspondence should be addressed.

1. Introduction

Photostimulated luminescence (PSL) is a phenomenon displayed by some materials following irradiation with x-rays or other ionizing radiation. The PSL is detected by post-irradiation illumination with low-energy visible or infrared light that stimulates luminescent emission, typically in the blue region of the spectrum. This effect arises from the optically stimulated recombination of locally trapped electrons and holes that are generated by the irradiation process, and it is the basis for digital x-ray storage phosphor imaging plates. The most common commercial x-ray storage phosphor is powdered crystalline BaFBr doped with europium (Eu^{2+}).

A storage phosphor effect has recently been found in certain glasses [1–4] although the magnitude of the effect was not reported. Storage phosphor glasses have the practical advantage over powdered crystals of improved spatial resolution, since inter-grain scattering of the focused laser beam used for image read-out is eliminated. In an earlier work [5] we reported a storage phosphor effect in bromine and europium co-doped fluorozirconate glasses that was approximately 1/4000th that of BaFBr:Eu^{2+}, and we showed that the glasses were in fact glass-ceramics comprising hexagonal phase barium bromide crystals in a fluorozirconate glass matrix. Subsequently, we have reported [6] that, by various thermal annealing processes, it is possible to transform the glass-ceramic from a transparent form containing nano-crystals of the hexagonal phase (which is metastable as a bulk crystal), into an opaque form that contains larger crystals of the stable orthorhombic phase. We argued that there was a cross-over in the relative stabilities of the two phases with increasing particle size, and that this was the basis for the observed phase transformation as the particles grew in size through annealing-induced Ostwald ripening. One important physical property that has not been studied is the effect of the crystallite size on the resultant PSL.

In this paper, we report the results from a systematic study of the PSL effect from europium-doped fluorozirconate glass-ceramics containing hexagonal and orthorhombic phases of $BaBr_2$ as the crystallites sizes are increased. We show there is no room temperature PSL from small hexagonal $BaBr_2$ nanocrystallites (<10 nm in diameter) in the glass-ceramic. Furthermore, our results are consistent with the room temperature PSL being dominated by the orthorhombic phase of $BaBr_2$.

2. Experimental details

2.1. Sample preparation

The typical composition of the glasses investigated is 53% ZrF_4, 20% BaF_2, 5% NaF, 15% NaBr, 3% AlF_3, 1.5% LaF_3, 1.5% YF_3 and 1% EuF_2. The total number of bromine ions was close to 5% of the total number of anions. The preparation method is described in the previous paper [6], but briefly the glasses were melted in a glassy carbon crucible at 740 °C, in an inert atmosphere of argon or nitrogen, and then the crucible was quenched or the glass poured into a mould which was at a temperature below the glass temperature of 260 °C. The samples were subsequently annealed at various temperatures between 250 and 290 °C in an inert atmosphere of argon or nitrogen. The physical appearance of the pre-annealed glass was usually clear, but after annealing some of the glasses showed a light yellow colour in transmitted light and blue in scattered light, consistent with the Rayleigh scattering expected for a semi-transparent glass-ceramic. X-ray diffraction (XRD) measurements revealed the presence of hexagonal phase $BaBr_2$ microcrystallites which, during the annealing at 290 °C, transform to the stable orthorhombic phase [6].

We have studied a large number of samples produced under varying annealing combinations of temperature (230–305 °C) and time (<1 min to 14 days), and find that our samples fill a continuum between two extremes. Low temperature and/or short time annealing (<270 °C for hours, <300 °C for a few minutes) of initially transparent glass results in transparent glass-ceramics containing hexagonal phase $BaBr_2$ with an average particle diameter of up to 20 nm. High temperature, long anneals (>275 °C, >1 h) resulted in an opaque glass-ceramic containing predominantly the orthorhombic phase with particle diameters generally in excess of 20 nm. Particle sizes were estimated from the XRD linewidths using the Scherrer formula applied to the (201) reflection for the hexagonal phase and the (211) reflection for the orthorhombic phase.

2.2. Experimental set-up

Optical absorption spectra were recorded at room temperature using a Shimadzu 2101 double beam spectrometer with a resolution of 0.5 nm. Photoluminescence (PL), PL excitation spectra and PSL spectra were measured at room temperature with a Perkin-Elmer LS-5B spectrometer with a resolution of 2.5 nm, and at temperatures between 10 K and room temperature with a system based on two 0.25 m focal length Spex double monochromators, photon counting electronics, deuterium lamp and xenon lamp excitation sources and a continuous flow refrigerator.

The PSL and PSL stimulation spectra were recorded following x-irradiation at 15 K or at room temperature using tungsten (50 kV, 30 mA) or molybdenum (40 kV, 20 mA) tubes. We have studied the dependence of the PSL efficiency, computed as the area under the whole decay curve recorded under optical bleaching, on annealing time and irradiation time, and compared the results with a standard sample of BaFBr doped with 1000 ppm of Eu^{2+}. The temporal behaviour of the PSL following a light pulse was measured using a flash lamp.

A Risø TL-DA15 TL/OSL reader was used to record thermostimulated luminescence (TSL) curves between room temperature and 270 °C using heating rates between 1 and 20 K s^{-1}. The samples were first subject to a dose of between 0.17–1 Gy from a $^{90}Sr/^{90}Y$ beta irradiation source. TSL was recorded in a nitrogen atmosphere from small grains (∼500 μm diameter) of the glass-ceramic in good thermal contact (via silicone oil) with the instrument's heater plate. Schott BG39 and Kopp 5–58 optical filters selected the principal emission peaks close to 404 nm. Delayed scanning and erasure with 840 nm light were used to help to resolve individual peaks in composite glow curves. Activation energies were determined using both the peak shape method and the Hoogenstraaten method (peak shift with heating rate) [7].

3. Experimental results

3.1. Photoluminescence

It was noted earlier that the basic glass, before annealing, shows no fluorescence from Eu^{2+} ions, which was attributed to quenching by Zr^{3+} ions in the glass network [8]. However, the glass-ceramics generated after annealing do fluoresce and we have shown that the PL spectrum of a glass-ceramic containing the orthorhombic phase $BaBr_2$ comprises a single peak at 404 nm (3.06 eV), whilst a glass-ceramic containing the hexagonal phase has a slightly shifted peak at 410 nm (3.02 eV), together with a broader and weaker band centred near 485 nm (2.55 eV) [6]. The PL spectrum from the orthorhombic phase in the glass-ceramic was essentially identical to that from Eu^{2+} ions in single crystals of orthorhombic $BaBr_2$. A fluorescence lifetime of (0.70 ± 0.02) μs was measured in both cases. We previously assigned the 410 nm band to an
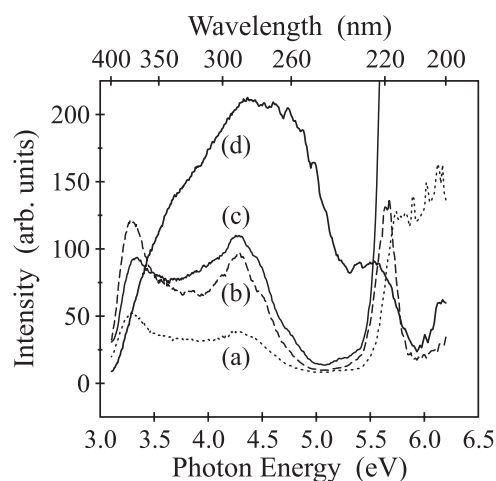
Figure 1. PL excitation spectra recorded at room temperature for (a) transparent glass-ceramic containing the hexagonal phase of $BaBr_2$, monitored at 485 nm, (b) opaque glass-ceramic containing the orthorhombic phase, monitored at 404 nm, (c) transparent glass-ceramic containing the hexagonal $BaBr_2$ phase, monitored at 410 nm, and (d) (orthorhombic) single-crystal $BaBr_2$, monitored at 404 nm.

unresolved emission from Eu^{2+} ions at two crystallographically inequivalent sites in hexagonal $BaBr_2$ and the 485 nm band to an impurity related site [6]. The fluorescence lifetimes at room temperature of (0.62 ± 0.02) μs for the 410 nm band and (1.06 ± 0.02) μs for the 485 nm band are typical for the 5d–4f transition of Eu^{2+} in dihalide hosts [9].

The PL excitation spectra from the glass-ceramic, plotted in figure 1, is significantly different from that observed in single-crystal europium-doped $BaBr_2$ (figure 1(d)). The PL excitation spectrum, in principle, should map out the excited states of the $4f^6 5d^1$ configuration. However, we do not believe that the three-band structure at 218 nm (5.68 eV), 290 nm (4.27 eV) and 375 nm (3.30 eV) evident in figure 1, which is commonly observed for these glass-ceramics, represents a crystal field splitting of the $4f^6 5d^1$ excited configuration of Eu^{2+} in the $BaBr_2$ crystals. Rather, it is a consequence of optical absorption by Eu^{2+} and Eu^{3+} ions primarily located in the glass matrix. The multi-peak structure is, in any case, inconsistent between the bulk and the microcrystalline forms of the orthorhombic phase, as is clear from figure 1, and the peaks at 218 and 375 nm do not appear in all samples. The europium ions present in the glass, which also include a fraction of Eu^{3+} ions, are known to strongly absorb ultraviolet light [8]. We have confirmed that the glass matrix does retain a significant fraction of Eu^{2+}, as shown by EPR measurements [6, 8]. In figure 2 we show the optical absorption spectrum from europium ions in a thinned sample of a fluorozirconate glass that contained 0.2% Eu^{2+} and no bromine. Particularly noticeable is a peak in the absorption coefficient near 260 nm (4.8 eV), which probably accounts for the significant decrease in the intensity of the PL excitation spectra over a comparable wavelength range.

Annealing the glass initially results in nanocrystals of the hexagonal phase that grow by Ostwald ripening. Further annealing is accompanied by a phase transition to the orthorhombic phase when the crystallites exceed a certain size. The PL intensity increases by nearly one order of magnitude during this process for crystallites larger than 10 nm, as can be seen in the upper section of figure 3. Initially only the hexagonal phase is apparent in the XRD data, followed by a regime where the XRD data contains both phases. Finally, only the orthorhombic phase can be seen in the XRD data. All of the points for the orthorhombic phase, plotted in figure 3,
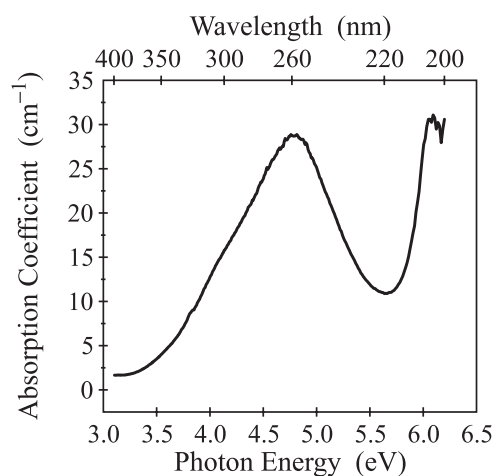
Figure 2. Optical absorption spectrum for a fluorozirconate glass containing 0.2% europium.
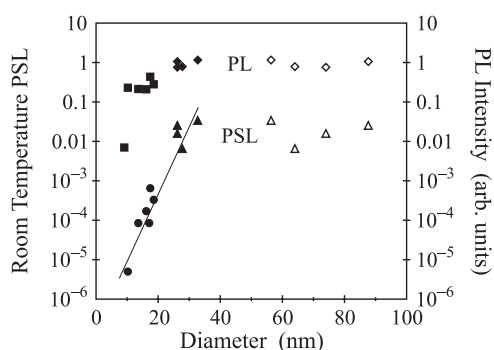

Figure 3. Room temperature PSL (left axis, circles and triangles) relative to BaFBr:Eu^{2+} and PL (right axis, squares and diamonds) plotted versus crystallite diameter determined from the XRD linewidth of the (201) reflection for the hexagonal phase (full symbols) and the (211) reflection for the orthorhombic phase (open symbols). The full circles and squares are from glass-ceramics containing only hexagonal BaBr$_2$, while the full triangles and diamonds are from glass-ceramics that contain a mixture of hexagonal and orthorhombic BaBr$_2$. The PL intensity is in arbitrary units. The line is a guide to the eye.

lie in the intermediate regime and both hexagonal and orthorhombic phase sizes are plotted. It is clear that the orthorhombic phase crystallites are significantly larger than the hexagonal ones in this intermediate regime. Finally, when the hexagonal phase intensities are too small for a reliable estimate, the orthorhombic phase XRD linewidths approach the instrumental linewidths, making a size estimate also unreliable for this phase.

The changes in the room temperature PL spectra are typified by the normalized spectra plotted in figure 4. Initial annealing leads to broad and weak PL, although there is no evidence of BaBr$_2$ crystallites in the XRD data. Further annealing results in an increase in intensity and a shift in the PL peak wavelength from 413 to 400 nm as well as a systematic decrease in the intensity of the 485 nm peak. These changes are also accompanied by a change in the transparency, where glasses containing crystallites with diameters less than 20 nm are transparent.
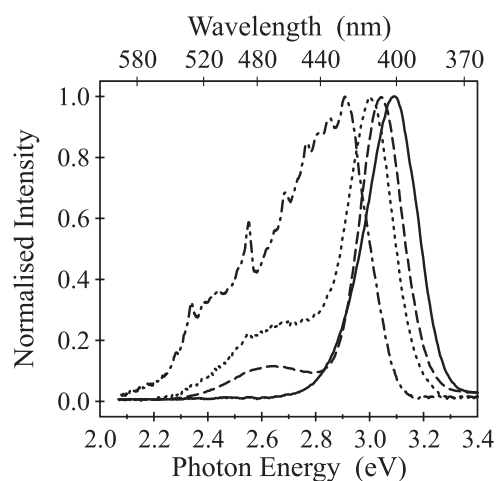
Figure 4. Room temperature PL versus wavelength for glass-ceramics containing large orthorhombic $BaBr_2$ crystallites (>10 nm, full curve), hexagonal $BaBr_2$ crystallites with diameters of 18 nm (broken curve) and 10 nm (dotted curve). Also shown is the PL from an annealed glass where the crystallites are too small to be observed by XRD (chain curve). The spectra have been normalized to the same peak value.

3.2. Photostimulated luminescence

Following x-irradiation at room temperature, we observed an afterglow at around 400–413 nm, but not from the 485 nm band. PSL measurements were performed when the afterglow had subsided, generally a few minutes after irradiation. PSL was then observed at around 400–413 nm when the sample was irradiated with red light in the region of 450–800 nm. We did not observe any PSL associated with the 485 nm band.

In the lower part of figure 3 we present the PSL efficiency for a large number of samples annealed under different conditions as a function of the crystallite diameter where the diameters were determined from the XRD linewidths. Samples annealed for 88 h at 287 °C and for 120 h at 286 °C contained only orthorhombic $BaBr_2$ and the PSL efficiencies were 9 and 6%, respectively, but the XRD linewidths were too small to obtain reliable estimates of the crystallite sizes. Interestingly, these samples also showed a PL peak at 400 nm, which is a lower wavelength than that for bulk $BaBr_2:Eu^{2+}$ (or for $NaBr:Eu^{2+}$, [10]). Possibly the long annealing times have resulted in an enhanced infusion of defects, such as F^- ions, with a resulting strain-induced shift in the line position. One sample containing only small hexagonal $BaBr_2$ crystallites (10 nm diameter) did not show a PSL effect above the detectable limit (10^{-5}% relative to the $BaFBr:Eu^{2+}$ standard).

In figure 5, we show the PSL stimulation spectra recorded at 15 K following irradiation at room temperature and compare them with the corresponding stimulation spectra for a powdered $BaBr_2:Eu$ single crystal. No temperature dependence of the PSL intensity was observed during the cooling down to 15 K. Although the room temperature PSL from the glass-ceramic containing only the hexagonal phase in the XRD data is very weak, we find that irradiation of the same material at low temperatures results in a relatively large PSL effect. However, it is unstable, decaying above about 150 K.

In figure 6, we show the PSL stimulation and PSL spectra for x-irradiation and measurement at 15 K, for samples that show either predominantly the hexagonal (annealed 290 °C, <1 min) or predominantly the orthorhombic phase (annealed 290 °C, 20 min). The
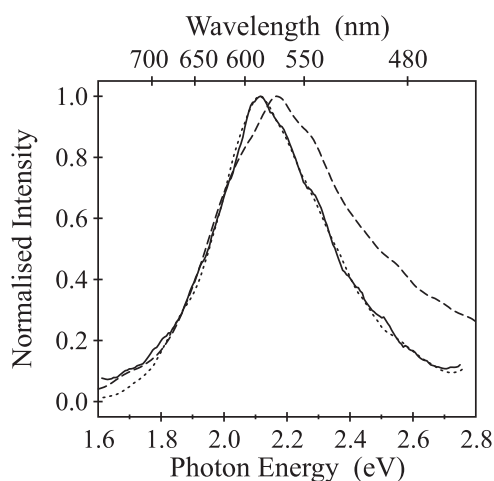
Figure 5. PSL stimulation spectra for glass-ceramics containing the hexagonal (full curve) and orthorhombic phases (dotted curve) of $BaBr_2$ and powdered $BaBr_2$:Eu (broken curve). The PSL stimulation was detected at 403 nm. The spectra were recorded at 15 K after x-irradiation at RT.
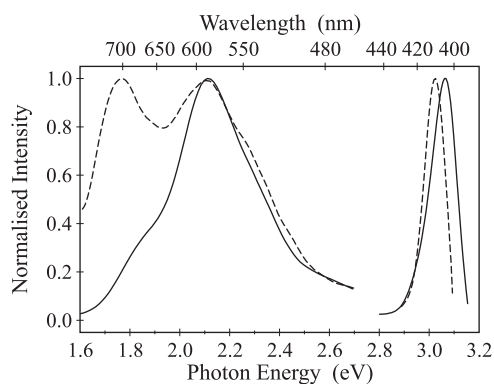

Figure 6. Normalized PSL and PSL stimulation spectra of Eu-doped fluorobromozirconate glasses annealed at 290 °C for less than 1 min (hexagonal phase, broken curve) and 20 min (orthorhombic phase, full curve). The PSL stimulation was detected at 409 nm (<1 min) and 403 nm (20 min), respectively; the PSL was stimulated at 590 nm. All spectra were recorded at 15 K after x-irradiation at 15 K.

PSL stimulation spectrum for the glass-ceramic containing orthorhombic $BaBr_2$ shows a peak at 590 nm and a weak shoulder at 680 nm. This can be contrasted with the glass-ceramic containing hexagonal $BaBr_2$ that displays a peak at 590 nm as well as an additional stimulation peak at 700 nm. The PSL stimulation was detected at 409 nm for glasses containing predominantly the hexagonal phase of $BaBr_2$ and at 403 nm for glasses containing predominantly the orthorhombic phase.

For practical storage phosphors, it is important to know the image lifetime and the characteristic read-out time. The image lifetime was obtained by measuring the PSL efficiency after a variable time delay. We find that the time for the PSL efficiency to fall to $1/e$ was approximately 1 h. The characteristic readout time is the time for the PSL to decrease to $1/e$ following a pulse of stimulation light. At room temperature, we measured a PSL
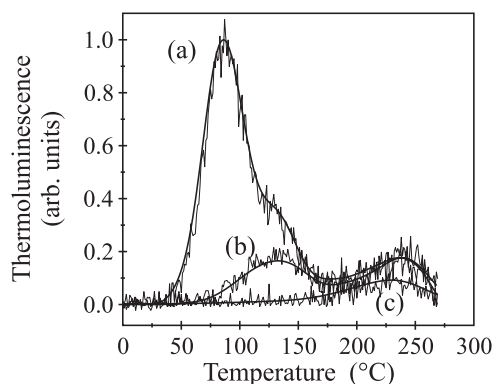
Figure 7. Glow curves for a glass-ceramic containing the hexagonal BaBr$_2$ phase recorded (a) 10 min after electron irradiation, (b) 2 h after irradiation and (c) 2 h after irradiation and after 5 min of illumination with 840 nm light.

readout time for the glass-ceramics of (0.70 ± 0.02) μs. After x-irradiation at 15 K, the readout time for the glass-ceramics sample containing predominantly the hexagonal phase was (0.82 ± 0.02) μs when stimulating with 575 nm light and (0.49 ± 0.02) μs when stimulating with 705 nm light. The measurement process was checked against BaFBr:Eu^{2+}, where the readout time at room temperature is (0.80 ± 0.02) μs, which agrees with previous measurements [11].

3.3. Thermostimulated luminescence

Glow curves were recorded above room temperature at a heating rate of 5 K s^{-1} up to the glass temperature $T_g = 265\,°C$ for two glass-ceramic samples containing predominantly the hexagonal phase and predominantly the orthorhombic phase. The samples came from the same glass batch, but one was annealed at 268 °C for one hour and contained only the hexagonal BaBr$_2$ in the XRD pattern, whereas the other was annealed at 305 °C for 30 min and contained predominantly the orthorhombic phase of BaBr$_2$. The TSL from the former sample was rather weak, whilst that from the latter was orders of magnitude more intense. Both showed a significant afterglow and so the first recordings were made ten minutes after irradiation to let the afterglow subside.

For the glass-ceramic containing the hexagonal phase, the TSL is still dominated after ten minutes by the afterglow which appears as a peak at about 90 °C, as can be seen in figure 7, with a shoulder at around 135 °C. The afterglow is not optically quenchable. For a delay of 2 h, the 90 °C peak has completely decayed and the shoulder is clearly resolved as a peak at 135 °C, which shows that it does not belong to the afterglow. This peak has an activation energy of (0.56 ± 0.06) eV as determined by the peak shape method, and it is optically quenchable, as can be seen in figure 7. The peak shift method on a different sample gave a similar activation energy of (0.60 ± 0.06) eV. A higher temperature peak at 240 °C is not significantly optically quenchable.

For the glass-ceramic containing the orthorhombic phase of BaBr$_2$, the principal peak in the TSL after a 2 h delay occurs at 145 °C, as can be seen in figure 8. This peak is optically quenchable and the peak shape method yields an activation energy of (0.94 ± 0.10) eV, while the Hoogenstraaten (peak shift with heating rate) method yields an activation energy of (1.20 ± 0.12) eV. Measurements with other delays show that there is a weak shoulder near 137 °C, and so the different values probably result from the composite nature of the peak;
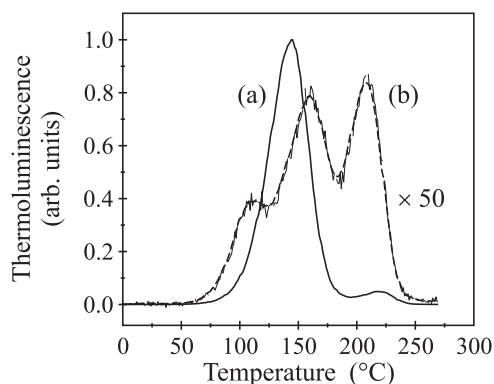
Figure 8. Glow curves for a glass-ceramic containing the orthorhombic BaBr$_2$ phase recorded (a) 2 h after irradiation and (b) 2 h after irradiation and after 5 min of illumination with 840 nm light.

the peaks are too close to resolve thermally. Given that the peak shape method will be more strongly influenced by additional shoulders, the Hoogenstraaten estimate of activation energy for the 145 °C peak is likely to be more reliable. Peak cleaning with 840 nm light shows that there are additional secondary peaks at 160 and 210 °C, that are not readily quenchable by light, at least at 840 nm. The optical stimulation resulted in some retrapping into the glow peak at 110 °C that is responsible for the afterglow.

4. Discussion

We interpret the increase in the PL intensity following annealing to a size effect. As the crystallites in the glass-ceramic grow, so on average the Eu^{2+} ions become more distant, both from the defective crystallite/glass interface and from the host glass, and thus from the luminescence quenching processes that take place in both regions. This, along with disorder effects, is particularly noticeable in glass-ceramics containing hexagonal BaBr$_2$ crystallites less than 10 nm, where the PL peak wavelength is higher than that for hexagonal BaBr$_2$. Preliminary investigations on polycrystalline, hexagonal BaBr$_2$ powder have shown that the Eu-related PL peaks at 410 nm. For crystallites larger than 10 nm, there is a systematic decrease in the PL peak wavelength that arises from a transition from hexagonal BaBr$_2$ to a mixture of hexagonal BaBr$_2$ and orthorhombic BaBr$_2$ and finally to orthorhombic BaBr$_2$ that possibly contains a small amount of fluorine. The increase in crystallite size is accompanied by a change in transparency, from a transparent glass-ceramic for crystallites less than 20 nm to an opaque glass-ceramic. Transparency has also been observed for other glass-ceramics containing small crystallites (<15 nm) and has been attributed to coherent scattering [14].

The origin of the 485 nm band in the PL spectra is not clear although, since it displays no PSL effect, it has no direct consequences for storage phosphor operation. This band is most prominent in samples that contain small nanocrystals with diameters slightly above 10 nm and it diminishes in intensity relative to the main peak near 410 nm as annealing proceeds. It is possible that, as we have previously suggested, the 485 nm band arises from a Eu^{2+} ion associated with an impurity in the hexagonal phase where, in the process of Ostwald ripening, the smaller impure crystals dissolve, leading to larger and purer BaBr$_2$ crystallites. Another possibility is that the band may arise from nucleation centres for the precipitation process. Evidence for this can be seen in figure 4, where the glass-ceramic containing very small BaBr$_2$ crystallites that cannot be detected by XRD has a very broad PL spectra, extending from 390

to above 600 nm. It is also possible that there are small crystallites of a third phase [12, 13] of $BaBr_2$, a high-pressure monoclinic phase, which is known to have an emission in the region 480–580 nm, depending on pressure [15]. However, the pressure required for such a shift is more than one order of magnitude higher than the usual internal pressures observed in glass-ceramics. Thus, this possibility does not appear to be likely, especially as there is no evidence for it in the XRD data.

One of our most interesting observations is that, at room temperature, there is a strong increase in the PSL efficiency with increasing hexagonal $BaBr_2$ crystallite size. This is not due to an increasing crystallite volume fraction because there is no corresponding significant increase in the XRD integrated intensity. The simplest explanation is that there is no room temperature PSL from small hexagonal $BaBr_2$ crystallites in the glass-ceramic and the increase in the room temperature PSL is due to an increasing fraction of orthorhombic $BaBr_2$ that is below the detection limit in the XRD data. It is unlikely that the small or nil room temperature PSL efficiency in small hexagonal $BaBr_2$ crystallites is due to the separation between electron and hole traps being comparable to the crystallite diameter. This is because PSL measurements at low temperatures on a glass-ceramic containing predominantly small hexagonal $BaBr_2$ crystallites reveal a low temperature PSL efficiency that is comparable to that from glass-ceramics containing predominantly larger orthorhombic $BaBr_2$ crystallites.

The PSL stimulation spectra arise from optical transitions from the electron and/or hole trapping centres to the conduction or valence bands respectively, or to shallow excited trapped states from which tunnelling recombination is possible. The consensus for the intensively studied case of $BaFBr:Eu^{2+}$ is that electron traps are F centres, although the hole centre remains a matter of controversy. After room temperature irradiation our glass-ceramics containing both $BaBr_2$ phases and powdered $BaBr_2:Eu$ single crystals have almost identical PSL stimulation spectra and comparable readout times. The low temperature PSL stimulation spectra has a maximum at 570 nm for $BaBr_2:Eu$ and it is slightly shifted to 590 nm for the glass-ceramics. For bulk $BaBr_2:Eu$, the PSL effect has recently been attributed to the optical stimulation of F centres [17]. Since only a single dominant optically quenchable peak is seen in the glow curve for glass-ceramics containing orthorhombic $BaBr_2$, we ascribe the peak to the same basic defect, which therefore has a trap depth of about 1.2 eV, typical of F centres in $BaFBr:Eu^{2+}$. The difference between the thermal energy and the optical stimulation peak energy (2.1 eV) is attributed to lattice relaxation around the centre following optical stimulation, in accordance with the Franck–Condon principle. Houlier [18] and Moreno [19] have reported the optical absorption spectra of F centres in electrolytically coloured $BaBr_2$ and a perturbed F centre for $BaBr_2$ doped with potassium. The absorption spectra of perturbed F centres shows peaks at 785 nm (1.58 eV), 685 nm (1.81 eV), 663 nm (1.87 eV) and 588 nm (2.11 eV), and a similar spectrum, shifted to higher energies, peaking at 730 nm (1.70 eV), 600 nm (2.06 eV), 575 nm (2.16 eV) and 520 nm (2.38 eV) for the F centre. In the present case, the crystals grow in a poly-ionic glass flux, and so there are many possibilities for impurity uptake and perturbed F centre energies. It therefore seems reasonable to adopt as a working model that the electron trap involved in the present case is a perturbed F centre.

Since in the temperature range from 10 to 300 K no thermal dependence of the PSL signal intensity could be observed for the orthorhombic phase, this indicates a tunnelling recombination mechanism followed by the characteristic radiative decay of the Eu^{2+} activator. The duration of the complete process is 0.70 μs and it is mainly determined by the Eu^{2+} excited state lifetime.

Two of the glow curve peaks reported here (145, 210 °C) for the glass-ceramic containing orthorhombic $BaBr_2$ occur at essentially the same temperature as the two peaks observed in bulk $BaBr_2:Eu^{2+}$ (135, 200 °C [17]) if the difference in heating rates is considered, and so

we attribute them to the same basic defects, which are therefore not specifically induced by the annealing process or the glass environment. The 160 °C peak was not observed in bulk $BaBr_2$:Eu^{2+} crystals. One interesting point is that the 200 °C peak in bulk $BaBr_2$:Eu^{2+} was found to be optically quenched by sunlight [17], but it is apparent in figure 8 that 840 nm light does not significantly quench the similar peak in glass-ceramics.

Glasses whose XRD pattern shows only hexagonal phase $BaBr_2$ crystals of size $\sim$20 nm display a weak TSL (figure 7) which is characterized by a quite different activation energy (0.6 eV) from that (1.2 eV) for the strong TSL from glasses containing orthorhombic phase crystals, and so must come from a different centre. The PSL results suggest that this centre is absent or ineffective in smaller hexagonal crystals.

5. Conclusion

In conclusion, we have found that the room temperature PSL efficiency from a fluorozirconate glass-ceramic can be increased to up to 9% of that in the commercial x-ray storage phosphor, $BaFBr$:Eu^{2+}. Our results are consistent with the room temperature PSL in the glass-ceramics being dominated by orthorhombic $BaBr_2$ crystallites and there is no detectable room temperature PSL from small hexagonal $BaBr_2$ nanocrystallites ($<$10 nm in diameter). When the small crystallite volume fraction is accounted for ($<$7%), the maximum room temperature PSL from the crystallites is nearly 1.3 times that observed in $BaFBr$:Eu^{2+}. The peak PSL stimulation energy and the TSL activation energy for orthorhombic $BaBr_2$ crystallites in the glass-ceramics are consistent with the electron trap being a perturbed F centre. The situation for small hexagonal $BaBr_2$ nanocrystallites is not so clear. The low temperature PSL efficiency is comparable to that from orthorhombic $BaBr_2$ crystallites in the glass-ceramics and the readout time for 575 nm stimulation is comparable to that observed in $BaFBr$:Eu^{2+}. Consequently, it is likely that the low temperature trap is also a perturbed F centre. However, the room temperature TSL activation energy for glass-ceramics containing hexagonal $BaBr_2$ nanocrystallites is too small for the TSL to be associated with a perturbed F centre.

Acknowledgments

References

[1] Qiu J, Shimizugawa Y, Iwabuchi Y and Hirao K 1997 *Appl. Phys. Lett.* **71** 43
[2] Qiu J, Shimizugawa Y, Iwabuchi Y and Hirao K 1997 *Appl. Phys. Lett.* **71** 759
[3] Qiu J, Shimizugawa Y, Sugimoto N, Iwabuchi Y and Hirao K 1997 *J. Non-Cryst. Solids* **209** 200
[4] Qiu J, Shimizugawa Y, Sugimoto N and Hirao K 1997 *J. Non-Cryst. Solids* **222** 290
[5] Edgar A, Spaeth J-M, Schweizer S, Assmann S, Newman P J and Macfarlane D R 1999 *Appl. Phys. Lett.* **75** 2386
[6] Edgar A, Secu M, Williams G V M, Schweizer S and Spaeth J-M 2001 *J. Phys.: Condens. Matter* **13** 6259
[7] McKeever S W S 1985 *Thermoluminescence of Solids* (Cambridge: Cambridge University Press)
[8] MacFarlane D R, Newman P J, Cashion J D and Edgar A 1999 *J. Non-Cryst. Solids* **256/257** 53
[9] Kobayasi T, Mroczkowski S and Owen J F 1980 *J. Lumin.* **21** 247
[10] Lopez F J, Murrieta H S, Hernadez J A and Rubio J O 1981 *J. Lumin.* **26** 129
[11] von Seggern H, Voigt T, Knüpfer W and Lange G 1988 *J. Appl. Phys.* **64** 1405
[12] Leger J M, Haines J and Atouf A 1995 *J. Appl. Crystallogr.* **28** 416
[13] Leger J M, Haines J and Atouf A 1995 *Phys. Rev.* B **51** 3902
[14] Tick P A 1998 *Opt. Lett.* **23** 1904

[15] Tröster T, Schweizer S, Secu M and Spaeth J-M 2002 *J. Lumin.* **99** 343
[16] Zhang H and Banfield J F 2000 *J. Phys. Chem.* **104** 3481
[17] Secu M, Kalchgruber R, Schweizer S, Spaeth J-M and Edgar A 2002 *Radiat. Eff. Defects* **157** 957–62
[18] Houlier B 1977 *J. Phys. C: Solid State Phys.* **10** 1419
[19] Moreno M 1977 *Cryst. Lattice Defects* **7** 27