

Structural phase changes in barium bromide nano-crystals in a fluorobromozirconate glass-ceramic x-ray storage phosphor

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 6259

(<http://iopscience.iop.org/0953-8984/13/28/308>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 13:57

Please note that [terms and conditions apply](#).

Structural phase changes in barium bromide nano-crystals in a fluorobromozirconate glass-ceramic x-ray storage phosphor

A Edgar¹, M Secu², G V M Williams³, S Schweizer², and J-M Spaeth²

¹ School of Chemical and Physical Sciences, Victoria University, Wellington, New Zealand

² Department of Physics, University of Paderborn, D-33095 Paderborn, Germany

³ Industrial Research Limited, Lower Hutt, Wellington, New Zealand

Received 18 April 2001

Published 29 June 2001

Online at stacks.iop.org/JPhysCM/13/6259

Abstract

The structural changes in a fluorobromozirconate glass ceramic containing a ratio of 5% bromine to fluorine ions, following thermal annealing in the range 240–300 °C, are reported. The changes were monitored through x-ray diffraction, and the photoluminescence (PL) and electron paramagnetic resonance of Eu²⁺ dopant ions. In the range of 240–275 °C, the barium and bromine ions in the glass precipitate to form the metastable hexagonal phase of barium bromide. The Eu²⁺ PL spectrum comprises a narrow band at 410 nm, and a weaker broad band centred at 485 nm. The 410 nm band is assigned to two unresolved $4f^65d^1 \rightarrow 4f^7$ emissions from Eu²⁺ ions at the two Ba²⁺ sites in this phase, whilst the 485 nm band is assigned to an impurity associated site or cluster. On annealing at 290 °C, the hexagonal phase transforms to the stable orthorhombic phase, and the PL spectrum comprises a single narrow band centred at 404 nm, assigned to a $4f^65d^1 \rightarrow 4f^7$ emission from Eu²⁺ ions at the single Ba²⁺ site in the orthorhombic phase.

1. Introduction

X-ray storage phosphors [1] are alternatives to conventional silver-based film for industrial and medical radiography. The storage principle is that incident x-rays generate electron–hole pairs in a solid storage phosphor; these pairs are separately trapped and are stable at room temperature. Subsequent irradiation with visible light, typically using a raster-scanned red laser beam, can liberate one or other trapped charge carrier, and electron–hole recombination can follow, resulting in the emission of a photon of near band-gap energy at a nearby doped activator ion such as Eu²⁺ or Ce³⁺. The process is referred to as photostimulated luminescence (PSL). The most commonly used x-ray storage phosphor is powdered crystalline BaFBr doped with about 1000 ppm of Eu²⁺.

In some recent work [2–4] it was reported that PSL effects can also be observed in glasses, specifically fluoroaluminate and borate glasses doped with Eu^{2+} or Ce^{3+} ions. The magnitude of the effect compared to crystalline materials was not stated, but our own unpublished measurements on fluoroaluminate glasses show only a negligible effect at room temperature. However, we have recently observed photoluminescence (PL) and a significant room temperature PSL effect in x-irradiated fluorozirconate glasses which were co-doped with either cerium and bromine ions, or europium and bromine ions, and have given preliminary accounts of our observations [5]. We found that the PSL effect in our first glasses was about 4000 times weaker than in $\text{BaFBr}:\text{Eu}^{2+}$. We have proposed earlier [5] that the PSL effect arises not directly from the glass, but from a precipitate of BaBr_2 crystals, resulting in a glass ceramic. Thus it is important to develop an understanding of the conditions which affect crystallite growth in these glass ceramic systems, and of the origins of the PL and PSL in rare-earth doped material. In this paper we present the results of an x-ray diffraction (XRD), PL, and electron paramagnetic resonance (EPR) investigation of barium bromide crystallization in europium and bromine doped fluorozirconate glass, and report on an unusual phase transition. The influence of the phase transition on the PSL will be discussed in a forthcoming paper.

2. Crystal structure

The stable phase of barium bromide at room temperature has the orthorhombic PbCl_2 structure (space group D_{2h}^{16} , $Pnma$) with the lattice parameters $a = 8.276 \text{ \AA}$, $b = 4.956 \text{ \AA}$, and $c = 9.919 \text{ \AA}$ [6]. Ba^{2+} ions occupy four crystallographically equivalent positions of point group symmetry C_S as shown in figure 1(a), each has nine nearest neighbour Br anions at distances given in table 1. There are two crystallographically distinct bromine sites, one with four nearest neighbour barium ions, and one with five such ions.

A second, hexagonal, phase which is metastable at room temperature has been reported by Liu and Eick [7]. This has the anti- Fe_2P structure (space group D_{3h}^3) with $a = 8.4826 \text{ \AA}$ and $c = 4.824 \text{ \AA}$. There are three Ba^{2+} sites in the unit cell, two with D_{3h} point group symmetry, and the other with C_{3v} ; both of these are nine-fold coordinated to bromine ions in very similar BaBr_9 structures (figure 1(b), table 1), with the angle made between the c -axis and the out-of-plane Ba–Br bond being 46.8° (site I) and 42.0° (site II). In table 1 we have used the lattice constants of Liu and Eick [7], but the structural parameters $u = 0.2563$, $u' = 0.5918$ determined by Beck [8] for BaI_2 since these have not been determined for BaBr_2 . These parameter values should be adequate for BaBr_2 since those for the prototype Fe_2P structure (0.256, 0.594) and other isostructural compounds show little variation [9]. The hexagonal phase, which could only be produced in a powder form by a chemical solvation procedure starting with a $\text{Ba}_9\text{Ln}_5\text{Br}_{33}$ ($\text{Ln} = \text{La}, \text{Nd}$) precursor, was metastable at room temperature, but could be 50% transformed into the orthorhombic phase by annealing at 400°C for 7 hours [7].

3. Experiment

The investigations were performed on Eu^{2+} -doped fluorobromozirconate glasses (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 glasses were melted in a glassy carbon crucible at 740°C , in an inert atmosphere of argon or nitrogen, and then crucible quenched or poured into a mould which was at a temperature below the glass temperature of 260°C . They were subsequently annealed at temperatures between 235°C and 290°C in an inert atmosphere of argon or nitrogen. The physical appearance of the pre-

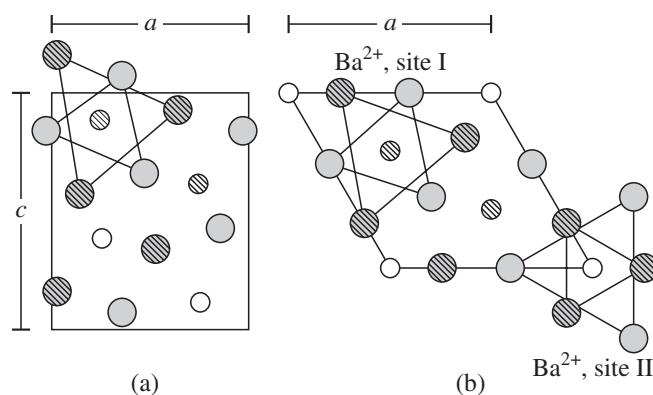


Figure 1. Lattice structure of (a) orthorhombic and (b) hexagonal BaBr_2 projected on the ac and ab plane, respectively. The small white and large grey circles denote Ba^{2+} and Br^- ions, respectively. The ions distinguished by hatched circles lie in a different mirror plane than the non-hatched ones. The close relationship between the orthorhombic site and the hexagonal site I can be judged by translating figure (a) onto (b) such that the triangles approximately coincide.

Table 1. Barium-bromine distances in hexagonal and orthorhombic phases of barium bromide [6–8]. All values are given in Å.

	Hexagonal		Orthorhombic
	site I	site II	
Out of plane	3.52	3.25	3.24
	3.52	3.25	3.38
	3.52	3.25	3.83
In plane	3.20	3.46	3.21
	3.20	3.46	3.26
	3.20	3.46	3.32

annealed glass was clear, but after annealing some of the glasses showed a light yellow colour in transmitted light but blue in scattered light, consistent with the Rayleigh scattering expected for a semi-transparent glass ceramic.

X-ray diffraction studies on these glasses were made using a standard Philips powder diffractometer equipped with a copper tube. There was evidence of surface attack by water vapour on some of the bromide-doped glasses after a few months storage, and so the XRD patterns were generally recorded using polished solid blocks of glass rather than with powder since the patterns had to be recorded for several hours to obtain a satisfactory signal-to-noise ratio for these glasses, which have only about 5% at the most of crystalline BaBr_2 content. High temperature XRD studies were made with a second Philips system using a cobalt tube which was equipped with an Anton Paar heated platinum-strip furnace accessory. In this case the glasses were first powdered in a ball mill and then attached to the strip using absolute alcohol, and the patterns recorded with the sample in an inert nitrogen atmosphere. To follow the formation of the hexagonal phase, a 1° anti-scatter slit was used as the receiving slit which permitted an integration of the XRD intensity from the unresolved (300), (002), and (211) diffraction peaks near 37° (for a copper tube).

The EPR measurements were performed with a conventional x-band (9.5 GHz) EPR spectrometer (Bruker ESP300). The sample temperature could be varied with a continuous flow cryostat (Oxford Instruments) between 4.2 and 300 K.

The ultraviolet-excited PL spectra were recorded with a single-beam spectrometer, in which two 0.25 m double monochromators (Spex) were used, with a xenon lamp as excitation source. The emission spectra were detected using a photomultiplier and single photon counting. The spectra were not corrected for spectral sensitivity of the experimental setup.

4. Experimental results

4.1. X-ray diffraction

The XRD pattern (figure 2(a)) for Cu $K\alpha$ radiation for glass quenched to temperatures of around 200 °C show only broad diffraction maxima at 25 and 47° characteristic of fluorozirconate glass. However, for annealing at temperatures above 235 °C and below about 275 °C, sharper lines appear superimposed on the broad lines, as shown in figure 2(b). The line positions agree with those predicted from the published structural data [7] for the metastable hexagonal phase of BaBr₂, but the line widths, typically 0.5 to 1°, are greater than expected given an instrumental resolution of 0.1°. Consequently, some expected reflections, such as those for the (300), (002), and (211) planes which are predicted to lie within 1° of each other at $\approx 37^\circ$ cannot usually be resolved in such patterns. The unit cell constants calculated from the five most prominent single reflections were $a = 8.500(6)$ Å, $c = 4.860(4)$ Å, compared with $a = 8.4826(6)$ Å, $c = 4.824(1)$ Å found by Liu and Eick [7] for hexagonal BaBr₂ prepared by the solvation process.

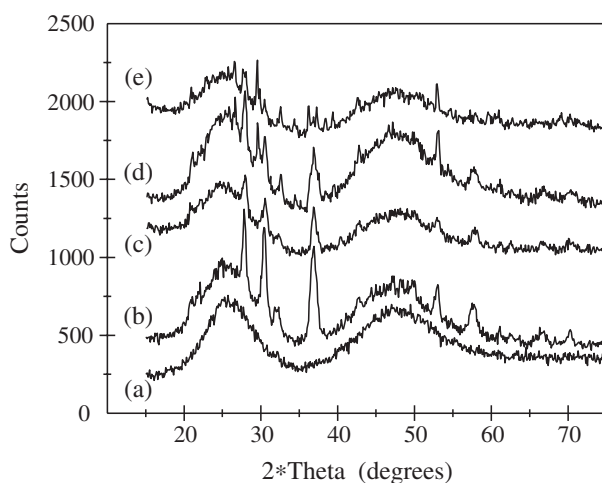


Figure 2. XRD patterns for (a) a sample of europium-doped fluorobromozirconate glass before annealing (b) a sample annealed at 265 °C, recorded at room temperature with a copper tube. Curves (c) to (e) show the XRD patterns after annealing at 290 °C for 0, 5, and 10 minutes. The curves have been offset for clarity.

In figure 3 we show the intensity of the combined (300), (002) and (211) peak as a function of temperature as the sample is heated at a rate of 1 K minute⁻¹. Before heating, this glass showed only the broad diffraction pattern of the glass (figure 2(a)), which forms the initial background count of approximately 6600 counts. The figure shows that crystal growth is rapid above 250 °C, but that it has stopped by about 265 °C, presumably due to the exhausted concentration of bromine ions in the glass. Figure 4 shows the time dependence of the peak intensity when the sample is held at 235 °C or 240 °C for 70 minutes, and then the temperature

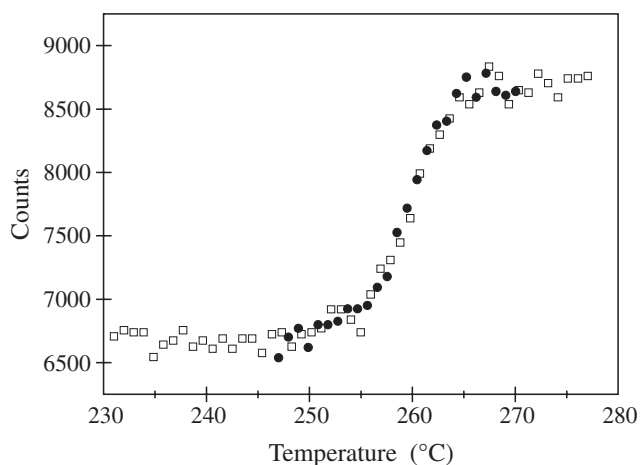


Figure 3. Integrated XRD line intensity for the unresolved (300), (002), and (211) peaks of hexagonal BaBr_2 crystallites as a function of temperature, as the sample is heated at a rate of 1 K/minute. Circles and squares indicate data from two different experiments demonstrating the degree of repeatability.

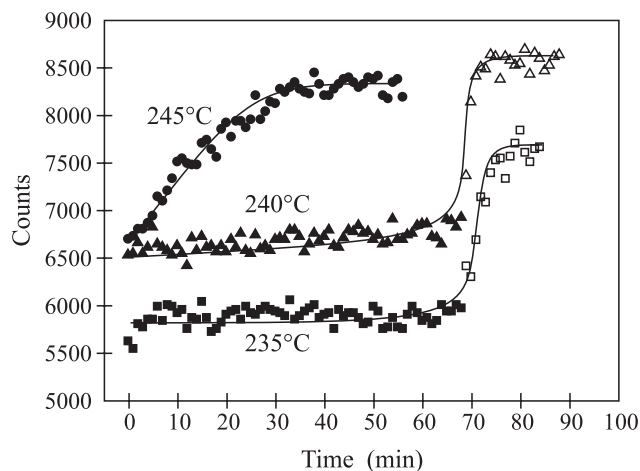


Figure 4. Integrated XRD intensities for the unresolved (300), (002), and (211) peaks as a function of time at various temperatures. For clarity, the 240 °C and 245 °C curves have been offset by 1000 counts. After 70 minutes at 235 °C and 240 °C, the temperature was rapidly raised to 265 °C (hollow symbols). The curves are a guide to the eye.

is rapidly increased to 265 °C to complete precipitation. We also show the peak intensity as a function of time for 245 °C, where the rate of growth is much more rapid. The general form of the growth judged from this curve is approximately exponential, with the first stage being closely linear in form. The time constants for the crystal growth process, as measured from this initial slope, are 33, 550 and 3600 minutes for temperatures of 245, 240 and 235 °C respectively.

For higher annealing temperatures up to 265 °C, the hexagonal phase forms too rapidly to follow in this way, but the appearance of the XRD pattern is the same and the line widths are also substantially unchanged. However, above about 275 °C, the intensity and line width of the

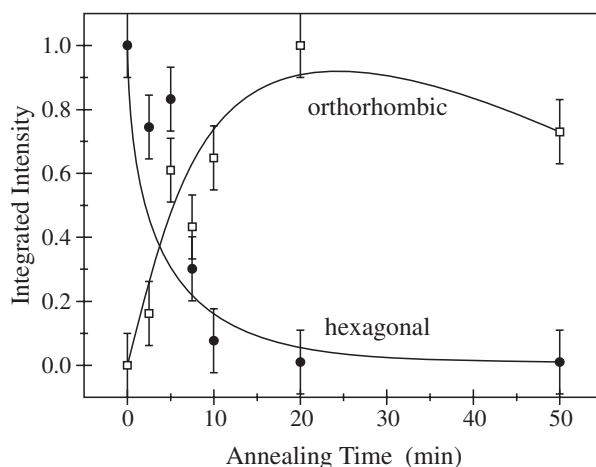


Figure 5. Integrated intensity of single XRD lines versus annealing time at 290 °C for the two phases of microcrystalline barium bromide in fluorozirconate glass. The curves are a guide to the eye.

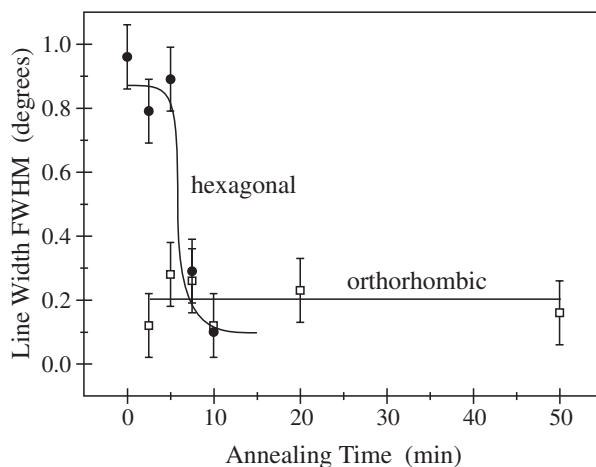


Figure 6. Line width versus annealing time at 290 °C for the two phases of microcrystalline barium bromide in fluorozirconate glass. The curves are a guide to the eye.

hexagonal phase pattern both decrease, and a new pattern characteristic of the orthorhombic phase appears, generally but not always accompanied by the appearance of another pattern corresponding to sodium bromide. To follow these developments, we annealed different samples of the same glass at 290 °C for periods of 0, 2.5, 5, 7.5, 10, 20 and 50 minutes, (where zero minutes implies that the sample was brought to 290 °C for a few seconds), and recorded the XRD patterns, the photoluminescence, and the EPR spectra. Figures 2(c)–(e) show the XRD patterns after 0, 5, and 10 minutes. Figure 5 shows the integrated intensities of the XRD patterns for the two BaBr₂ phases, relative to that of the broad glass peak at 47°, and based on the (201) reflection for the hexagonal phase and the (211) reflection for the orthorhombic phase, chosen for minimal overlap with other lines. Figure 6 shows the

associated line widths. The figures show that after approximately 10 minutes, the hexagonal phase has completely disappeared, whilst at the same time the orthorhombic phase rapidly grows. Before the hexagonal phase disappears, the line width narrows, becoming comparable with the instrumental resolution (0.1°).

4.2. Photoluminescence

The glass before annealing shows no Eu^{2+} PL emission [10]. After annealing at temperatures up to 265°C a PL spectrum appears comprising a narrow band centred at 410 nm at room temperature, together with a less intense and broader band centred at 485 nm (figure 7(a), see below). Annealing the samples at 290°C for intervals up to 50 minutes leads to a small shift in the position of the 410 nm band to 404 nm (figure 7(a)–(b)), whilst the 485 nm band disappeared after about 10 minutes of annealing. The PL spectrum of the sample annealed at 265°C is identical to that shown in figure 7(a). The shift of the luminescence position versus the annealing time is depicted in figure 8. For comparison, figure 7 also shows the fluorescence spectrum we recorded for a polycrystalline sample of orthorhombic europium-doped BaBr_2 (figure 7(c)), the fluorescence being similar to that reported by Iwase *et al* [11].

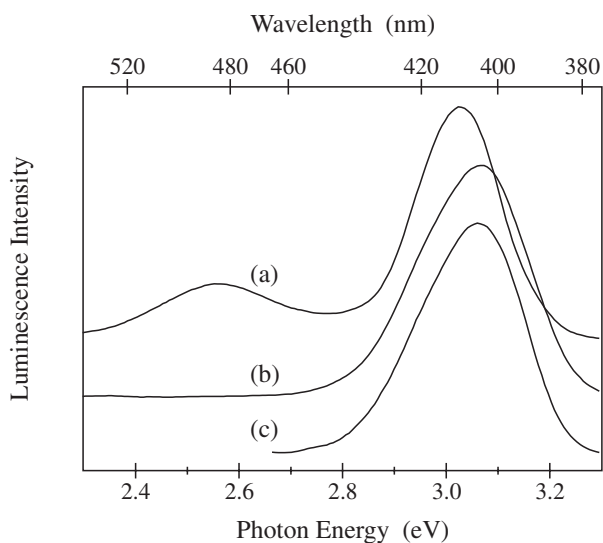


Figure 7. PL spectra of Eu-doped fluorobromozirconate glasses annealed at 290°C for (a) 0 minutes and (b) 50 minutes. Curve (c) shows the PL of polycrystalline $\text{BaBr}_2:\text{Eu}^{2+}$ for comparison. The PL was excited at 280 nm and recorded at room temperature. The spectra have been offset for clarity.

4.3. Electron paramagnetic resonance

The EPR spectra of the glass before annealing show only the ubiquitous U-spectrum of Eu^{2+} characteristic of this ion in most amorphous materials [10, 12]. Figure 9 shows the effect of annealing at 290°C for various time intervals on the spectrum. Sharper features which are characteristic of a crystalline environment are apparent around the $g = 2$ region of 300–400 mT. The spectra for an annealing period of 0 and 5 minutes are very similar (where 0 min implies that the sample was brought to 290°C for a few seconds), whereas there is a clear change in character after a 10 min annealing period. A comparison between a powdered orthorhombic

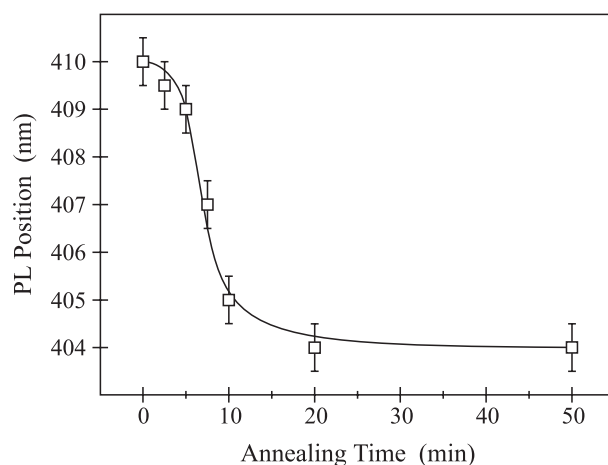


Figure 8. Shift of the luminescence position versus annealing time of Eu-doped fluorobromozirconate glasses annealed at 290 °C.

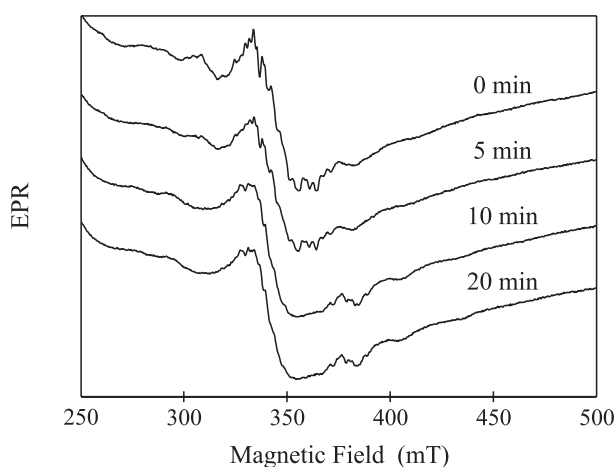


Figure 9. EPR of Eu-doped fluorobromozirconate glasses annealed at 290 °C for 0, 5, 10, and 20 min, respectively. The spectra were recorded at 20 K in X-band (9.5 GHz).

BaBr₂ single-crystal and the spectra for an annealing period of 10 min and 20 min, respectively, yields that there is a good agreement between the two spectra [13]. In the absence of single crystals for the meta-stable hexagonal phase, we are unable to do a direct comparison between a powdered crystal and the glass ceramic EPR spectra for an annealing period of 0 and 5 min.

5. Discussion

Our XRD results in figures 3 and 4 show that the hexagonal phase of BaBr₂ begins to nucleate and grow below the ZBLAN glass temperature of $T_g \approx 265$ °C, and the PL results indicate that the crystals contain europium ions. This suggests that the network modifying ions barium and divalent europium, and the bromine ion have a significant mobility below T_g . The europium ions have a clear effect on crystal growth, since samples grown without europium under

the same temperature conditions were quite opaque, indicating large BaBr₂ crystallite sizes. However, only a small fraction of the divalent europium ions are actually incorporated in the crystals, since the EPR spectra in figure 9 are dominated by the well-known U-spectrum [10, 12], characteristic of ⁸S_{7/2} ground state ions in a glassy environment, whilst the spectral features characteristic of Eu²⁺ ions in the crystallites in the region around $g = 2$ are relatively minor.

The optical transparency of the europium-doped glass ceramic samples which were annealed at temperatures below about 270 °C suggests that the hexagonal phase crystallite sizes are in the nanometer rather than the micrometer region, since only minimal blue light scattering is observed. Particle sizes in the nanometer range result in broadened XRD lines, as observed here, but the lines can also be broadened by lattice strains, as discussed by Klug and Alexander [14] for example. The latter effect may be effective in the present case since the crystals are grown in a polyatomic glass, and impurity ions such as sodium and fluorine may be incorporated giving rise to lattice strain. The two broadening effects would give rise to an overall linewidth W given by

$$W - w = \frac{K\lambda}{D \cos \theta} + L \tan \theta \quad (1)$$

where w is the instrumental linewidth, λ is the wavelength, D the average particle diameter, θ is the angle of diffraction, and K and L are particle geometry and strain parameters respectively. This simple formula assumes a Lorentzian XRD lineshape. The two effects can thus be distinguished [14] through a plot of $(W - w) \cos \theta$ versus $\sin \theta$. In the present case, this shows that the dominant effect is size broadening. On this basis, the average particle sizes in the sample annealed at 290 °C range from about 10–20 nm after a few seconds of annealing to 100 nm after a few minutes, beyond which the contribution to the linewidth becomes too small for reliable estimates. The line widths for samples annealed at around 265 °C correspond to particle sizes of around 20–30 nm. Preliminary transmission electron microscope measurements [22] on a powdered sample of such a glass annealed at 270 °C show needle-like crystals of about 50 nm in diameter. We note that the line width of the hexagonal phase (201) reflection was always some 20% greater than that for the other reflections, but have been unable to relate this [14] to any of the usual crystal morphologies, hexagonal needles in particular.

Given that the stable phase of bulk BaBr₂ is the orthorhombic one, it is surprising that the phase which initially forms in fluorozirconate glass is the metastable hexagonal phase. The line width and intensity results (figure 5 and 6) for the 290 °C anneal indicate that as the anneal proceeds, the hexagonal phase crystals increase in size, but decrease in volume fraction, whilst at the same time the orthorhombic phase crystals grow in volume fraction but appear to commence growth with a large size. Dunning has noted just this sort of phenomenon in his review of ripening and ageing processes in precipitates [15], where the initial appearance of an unstable phase is attributed to a more rapid nucleation or growth rate for that phase. Alternatively, the effect may be due to a difference in surface energy between the two phases which opposes and exceeds the difference in bulk free energy. In either model, as applied to the present case, the growth proceeds from the precipitation of small hexagonal crystals through Ostwald ripening [15]; small particles will re-dissolve, and the larger ones will grow from this fresh nutrient until they reach a size where they undergo a phase transition to the orthorhombic phase. Eventually, all the particles will end up as relatively large orthorhombic phase particles. This particle growth model is consistent with our qualitative observations of light scattering, which reflects particle sizes; it is possible to make transparent glass ceramics containing only the hexagonal phase, but samples annealed at 290 °C show a continuous variation from transparent but blue in back-scattered light for an annealing time of 0 and 2.5 minutes, to completely opaque for 20 and 50 minutes.

Our initial and tentative interpretation of the two observed PL bands attributed them to europium ions occupying the two different barium sites in hexagonal barium bromide [5]. However, this seems unlikely since the two sites have very similar ligand geometries (table 1), which in turn are closely related to that in the orthorhombic phase. In the latter case, Iwase *et al* [11] report a single PL band peaking at 400 nm, and it appears empirically that the emission of europium in many bromides is insensitive to the particular crystal field, usually giving an emission band at around (410–420) nm, except in the case of very large perturbations such as in the Suzuki phases in alkali halides. For example, for the alkali bromides, the host dependence for the cation-vacancy-associated site results in emission peaks at 428 nm (NaBr [16]), 423 nm (KBr [17]) to 418 nm (RbBr [18]). Europium bromide itself emits at 420 nm [19]. Therefore we consider that the two emissions from the two barium sites are unresolved within the 410 nm band. The annealing experiments at 290 °C show that the band at 410 nm shifts to 404 nm after about 10 minutes annealing, reflecting the phase change from hexagonal to orthorhombic evident in figures 2(c)–(e). The phase transition could also be monitored by EPR. There is a clear change in character after a 10 minute annealing period (figure 9).

This assignment leaves the question of the origin of the 485 nm band. Two interpretations are possible; it may be an impurity associated Eu^{2+} site with a perturbed crystal field, or an Eu^{2+} bound exciton emission, similar to that proposed [20, 21] to explain the anomalous yellow emission in Eu-doped barium fluoride. However, the latter explanation relies on the combination of Madelung energy at the Eu site and the band gap being such as to push all the Eu^{2+} excited states into the conduction band, resulting in photo-ionisation on excitation, and emission only from excitonic recombination. However, it is difficult to see why this phenomenon should not also occur in the structurally similar orthorhombic phase where no equivalent band is seen [11].

We therefore favour the interpretation based on an impurity-related site or cluster. The absence of a 485 nm band in the orthorhombic phase can be explained by crystal purity. We expect the hexagonal phase to contain a significant fraction of impurities from the glass, as discussed earlier, but the orthorhombic phase may well be purer: the crystals grow by dissolution of hexagonal phase material from small particles during the Ostwald ripening process, followed by re-growth on larger particles. The apparent saturation of the XRD lines of the hexagonal phase (figures 3 and 4) during growth at relatively low temperatures (≤ 270 °C) suggests all the bromine is removed from the glass, whilst the appearance of NaBr in the XRD patterns during growth at temperatures greater than ≈ 280 °C is consistent with bromine returning to the glass from dissolving small particles. Re-growth in the higher temperature region can lead to a more pure compound on average if the parameters such as atomic diffusion coefficients show differences in their temperature dependence; in the case of sodium impurities the local sodium concentration will certainly decline as a consequence of the growth of NaBr.

6. Conclusions

Fluorozirconate glass which is co-doped with bromine and europium ions can be prepared by suitable thermal annealing to contain either the hexagonal phase of barium bromide as a transparent glass ceramic, or the orthorhombic phase as an opaque glass ceramic. Nucleation first occurs as the hexagonal phase, but as the crystallites grow a transformation to the orthorhombic phase occurs, with consequent changes in the PL and EPR spectra, and in the XRD patterns.

Acknowledgments

This work is partially supported by the Deutsche Forschung Gemeinschaft and the Foundation for Research, Science and Technology (New Zealand).

References

- [1] Spaeth J-M, Hangleiter Th, Koschnick F-K and Pawlik Th 1995 *Radiat. Eff. Defects Solids* **135** 1
- [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] Brackett E B, Brackett T E and Sass R L 1963 *J. Phys. Chem.* **67** 2132
- [7] Liu G and Eick H A 1989 *J. Less Common Met.* **149** 47
- [8] Beck H P 1983 *J. Solid State Chem.* **47** 328
- [9] Wyckoff R W G 1964 *Crystal Structures vol 2* (New York: Interscience)
- [10] MacFarlane D R, Newman P J, Cashion J and Edgar A 1999 *J. Non-Cryst. Solids* **256&257** 53
- [11] Iwase N, Tadaki S, Hidaka S and Koshino N 1994 *J. Lumin.* **60&61** 618
- [12] Furniss D, Harris E A and Hollis D B 1987 *J. Phys. C: Solid State Phys.* **20** L147
- [13] Schweizer S, Corradi G, Edgar A and Spaeth J-M 2001 *J. Phys.: Condens. Matter* **13** 2331
- [14] Klug H P and Alexander L E 1974 *X-Ray Diffraction Procedures* (New York: Wiley)
- [15] Dunning W J 1972 *Particle Growth in Suspension* ed A L Smith (London: Academic) pp 3–28
- [16] Lopez F J, Murrieta H S, Hernandez J A and Rubio J O 1981 *J. Lumin.* **26** 129
- [17] Aguilar G M, Rubio O J, Lopez F J, Garcia-Sole J and Murrieta H S 1982 *Solid State Commun.* **44** 141
- [18] Sastry S B S and Sapru S 1981 *J. Lumin.* **23** 281
- [19] Brixmer L H 1976 *Mater. Res. Bull.* **11** 269
- [20] Moine B, Pedrini C, and Courtois B 1991 *J. Lumin.* **50** 31
- [21] Dujardin C, Moine B, and Pedrini C 1993 *J. Lumin.* **54** 259
- [22] Assmann S, 2000 private communication