Published in final edited form as:

J Am Ceram Soc. 2013 November 1; 96(11): 3617–3621. doi:10.1111/jace.12540.

Nanocrystallization in Fluorochlorozirconate Glass-Ceramics

Carlos J. Alvarez^{†,‡,§}, Yuzi Liu[§], Russell L. Leonard[¶], Jacqueline A. Johnson[¶], and Amanda K. Petford-Long^{†,§}

[‡]Materials Science and Engineering Department, Northwestern University, Evanston, Illinois 60208

[§]Nanoscience and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

[¶]Mechanical, Aerospace and Biomedical Engineering Department, University of Tennessee Space Institute, Tullahoma, Tennessee 37388

Abstract

Heat treating fluorochlorozirconate (FCZ) glasses nucleates nanocrystals in the glass matrix, resulting in a nanocomposite glass-ceramic that has optical properties suitable for use as a medical imaging plate. Understanding the way in which the nanocrystal nucleation proceeds is critical to controlling the optical behavior. The nucleation and growth of nanocrystals in FCZ glass-ceramics was investigated with *in situ* transmission electron microscopy heating experiments. The experiments showed the nucleation and growth of previously unreported BaF₂ nanocrystals in addition to the expected BaCl₂ nanocrystals. Chemical analysis of the BaF₂ nanocrystals shows an association with the optically active dopant previously thought only to interact with BaCl₂ nanocrystals. The association of the dopant with BaF₂ crystals suggests that it plays a role in the photoluminescent (PL) properties of FCZ glass-ceramics.

I. Introduction

Fluoride glasses, such as ZrF₄–BaF₂–LaF₃–AlF₃–NaF (ZBLAN) have traditionally been studied as possible lasing windows and waveguides because of their low infrared attenuation.^{1–3} As they were primarily studied for applications as optical components, preventing crystallization during fabrication led to extensive investigation of the heat-treatment and devitrification processes.^{2,4–12} In 1999, Edgar *et al.* explored controlling the devitrification process to fabricate a functional glass-ceramic from a modified ZBLAN glass for use as an imaging plate in medical X-ray systems.¹³ This modified ZBLAN glass is known as fluorochlorozirconate (FCZ) glass because of the addition of chloride ions. When FCZ glasses, doped with the appropriate rare earth element, undergo partial crystallization, they can develop the desired photostimulated luminescence (PSL) properties that make them suitable for use as a storage phosphor plate in high-resolution X-ray systems.^{14,15} FCZ glass-ceramics have also shown potential for use in photovoltaic applications.¹⁶

X-ray diffraction (XRD) studies by Schweizer *et al.* were used to analyze the crystalline phase formation in FCZ glasses as a function of heat-treatment conditions. It was found that heat treating FCZ glass nucleates BaCl₂ nanocrystals in the glass matrix, with the nanocrystal phase being a function of heat-treatment temperature.^{15,17} The BaCl₂ nanocrystals form in a metastable hexagonal phase at ~260°C, but at temperatures above 270°C the BaCl₂ can transform to the orthorhombic phase. This transformation is very

significant, changing the optical properties dramatically: hexagonal BaCl_2 leads to scintillation, whereas orthorhombic BaCl_2 gives the desired storage phenomenon when the material is irradiated with X-rays. During the nucleation and growth of BaCl_2 , an additional, unknown phase had been shown to form for heat treatments at temperatures $>280^\circ\text{C}$. This unknown phase had been reported multiple times, but never identified.^{15,17–19} Heat treating at temperatures greater than $\sim 310^\circ\text{C}$ leads to crystallization of the entire glass matrix, a process that is equivalent to conventional ZBLAN glass devitrification, with the formation of crystalline $\beta\text{-BaZrF}_6$, $\text{BaZr}_2\text{F}_{10}$, and additional phases. The formation of any large crystals, other than BaCl_2 , is seen as undesirable because they produce increased optical scattering and therefore reduced PSL.^{10,20,21} To understand the nucleation, growth, and phase transitions of the nanocrystals that are critical to the optical behavior, a technique that allows analysis of small local regions of the material, such as transmission electron microscopy (TEM), is essential.

In this study, we conducted *in situ* TEM heating experiments to explore the earliest stages of nanocrystal formation, which are inaccessible by XRD. We observed the formation of BaF_2 nanocrystals in FCZ glass-ceramics concurrent with the formation of BaCl_2 nanocrystals. The BaF_2 nanocrystals are shown to associate with the optically active Eu dopant. The morphology and strain is dependent on the type of crystal. Both BaF_2 and BaCl_2 form spheroid-like shapes in the later stages of growth.

II. Experimental Procedure

The FCZ glass fabrication technique is described in previous work by Johnson *et al.*²² The FCZ glass composition explored here is: $51.0\text{ZrF}_4\text{--}20.0\text{BaCl}_2\text{--}3.5\text{LaF}_3\text{--}3.0\text{AlF}_3\text{--}20.0\text{NaF--}0.5\text{InF}_3\text{--}x\text{EuF}_2\text{--}(2.0 - x)\text{EuF}_3$, where $0 \leq x \leq 2.0$ with values in mol%. Table I indicates the Eu content of the glass for the samples analyzed. A mixture of Eu valence states (2^+ and 3^+) is added to the initial glass composition to assess the photoluminescence emission spectrum as a function of oxidation state of the Eu. Studies of the valence state of Eu after heat treatment have shown the formation of Eu (III) from heating of bulk Eu (II).²³ We are therefore interested in analyzing the influence of the change in oxidation state on the crystallization process. TEM specimens were prepared by one of the following methods: crushing in ethanol using a mortar and pestle and then depositing on a lacey carbon grid, or using a conventional TEM specimen preparation technique. In the conventional method, bulk FCZ glass was cut into 3 mm squares with a diamond saw and then mechanically polished and dimpled and mounted onto molybdenum TEM grids. Thinning to electron transparency was carried out using ion milling at -50°C , to prevent any crystallization during the thinning process.

Specimens were heat-treated either *ex situ* prior to TEM analysis or *in situ* using a heating holder. The *ex situ* heat-treated specimens were prepared in a Thermolyne 21100 Tube Furnace (Barnstead International, Dubuque, IA), with the temperature monitored using a K-type thermocouple. First, the specimens were heated to 200°C at a rate of 25 K/min on a hot plate, to prevent thermal shock in the glass. The 200°C is just below the transition glass temperature (T_g) of FCZ glass, which is around 210°C . The specimens were then transferred to a furnace set to the heat-treatment temperature and held for 5 min. After the 5 min hold, the specimens were cooled to room temperature and prepared for TEM analysis, as described above. The *in situ* TEM heat-treatment experiments were carried out in a FEI Tecnai F20 (Hillsboro, OR) with a Gatan heating holder operated at 200 kV. Before heating, the specimens were analyzed in dark-field TEM mode to ensure that they had remained amorphous during TEM specimen preparation. The dark-field TEM image seen in Fig. 1(a) shows uniform contrast typical of an amorphous region, and the inset selected area diffraction pattern shows only amorphous rings, confirming that no crystallization has

occurred during the specimen preparation process. The specimens are then heat-treated using the same heating protocol as for the *ex situ* heat-treated specimens. Care was taken to limit the cooling rate when returning to room temperature, due to the small volume of the specimen.

III. Results

During *in situ* TEM heating, nanocrystals nucleated throughout the glass at $\sim 260^{\circ}\text{C}$ with the nucleation sites occurring in clustered regions. Some of the nucleated crystals began to coalesce and grow, but many remained as individual nanoparticles in the clustered regions. The bright and dark contrast regions seen in the dark-field TEM image of Sample 2 shown in Fig. 1(b) are the nanocrystals that formed during heat treatment; the image shows the variation in nanocrystal size and the clustering of the nanocrystals. The circled region contains both small nanocrystals that are clustered together, and a larger crystalline region formed by coalescence of several smaller nuclei. The clusters often produce significant strain contrast and Moiré fringes are observed as a result of nanocrystals that overlap through the thickness of the TEM specimen. In addition to the formation of nanocrystals, voids ($\sim 10\text{--}100\text{ nm}$ in diameter) form as a result of the production of gas during heating; these voids are observed in both *in situ*- and *ex situ*-heated specimens and tend to form in regions close to the nanocrystals. The nanocrystal formation was not influenced by the variation in the initial Eu oxidation state between sample compositions.

High-resolution electron microscopy (HREM) was used to determine the phase of individual nanocrystals in the heat-treated FCZ glass. Digital fast Fourier transforms (FFT) of localized regions of the HREM images were calculated and compared against simulated electron-diffraction patterns, to determine the specific nanocrystalline phases present in the heat-treated material. The experimental patterns match the simulated patterns within 1° for the angles between the planes, and have less than 5% difference in d-spacing. The small differences in d-spacing are attributed to slight changes in the values of the objective lens used to obtain the HREM images. The HREM images in Fig. 2 are from Sample 2, heat-treated under different conditions. Figure 2(a) shows a nanocrystal of hexagonal BaCl_2 at an early stage of nucleation together with the inset digital FFT, following heat treatment to 265°C . This is the same phase that was previously observed from XRD analysis of the bulk material following heat treatment at temperatures below 270°C . Figure 2(b) displays an orthorhombic BaCl_2 nanocrystal from a specimen heat-treated at 300°C . However, the TEM analysis of individual nanocrystals showed that this is not the only nanocrystalline phase present. All samples analyzed, no matter the composition or heat-treatment temperature, also contained orthorhombic and face-centered cubic (FCC) BaF_2 nanocrystals, as shown in Figs. 2(c) and (d). The FCC BaF_2 nanocrystal formed with a twin plane. The twin planes for the FCC BaF_2 are highlighted by black or white circles corresponding to each set of planes in the FFT of Fig. 2(d). Nanocrystalline BaF_2 has not previously been observed in FCZ glass-ceramics and this is an important observation: as BaF_2 is not one of the components in the original glassmelt, as shown in Table I, its formation had to occur during heat treatment. The size range for the BaF_2 nanocrystals is $30\text{--}80\text{ nm}$, which is consistent with that of the BaCl_2 nanocrystals during the early stages of nucleation. However, the distribution of the two materials throughout the heat-treated FCZ material is very different. The BaF_2 nanocrystals are observed to form in clustered regions that exhibit significant strain contrast and Moiré fringes, whereas the BaCl_2 nanocrystals are more isolated. The same nanocrystal structures and morphologies are observed for each sample composition, indicating that the oxidation state of the optically active dopant does not influence their nucleation and growth process.

In addition, the morphology and structure of the crystals were analyzed in dark-field TEM imaging mode, with the use of nanobeam diffraction (NBD) and energy-dispersive X-ray

spectrometry (EDX). The nanocrystals formed randomly oriented spheroid structures up to 150 nm in size, as shown in Fig. 3(a) for Sample 1. The circled regions 2–4 in Fig. 3(a) correspond to the NBD patterns shown in Figs. 3(b)–(d), respectively. The patterns seen in Figs. 3(b) and (c) are from orthorhombic BaCl₂ nanocrystals, whereas the pattern in Fig. 3(d) is from FCC BaF₂. The nonuniform contrast in the image of the BaF₂ nanocrystal results from the overlap of several nanocrystals. The identification of these crystals is supported by EDX analysis at each of the circled locations shown in Fig. 3(e). The spectra from the BaCl₂ crystals have large Cl and Ba peaks, whereas the spectrum from the BaF₂ crystal has large Ba and F peaks. The spectrum indicated by (1) corresponds to the glass matrix region, and shows only large Zr and F peaks. The lack of Ba and Cl in the matrix suggests that the majority of these elements are incorporated into the nanocrystals leaving a matrix mostly comprised of Zr, Na, and F.

IV. Discussion

The observation of BaF₂ nanocrystals in partially crystallized FCZ glasses has not previously been reported. Therefore, it has not been considered as a potential factor influencing the optical properties of the material. However, bulk crystalline BaF₂ acts as an effective scintillator, a property that had been associated in the FCZ materials with the formation of hexagonal BaCl₂.^{24–26} Previous literature reports suggested that Eu is associated with the BaCl₂ nanocrystals, but this has not been confirmed experimentally. However, the presence of previously unidentified BaF₂ nanocrystals could alter this preconception and play a critical role in the resulting optical properties of the glass. Local compositional analyses were therefore carried out using electron-energy loss spectroscopy (EELS) analysis. Figure 4(a) shows the region of a TEM specimen prepared from an *ex situ* heat-treated piece of Sample 2. The sample was annealed at 300°C and the specimen was prepared by grinding in a mortar and pestle. FFT analysis of the region shows the presence of BaF₂ nanocrystals. Figure 4(b) shows a section of an EELS spectrum recorded from the same region. The EELS spectrum shows a clear Eu M_{4,5} edge, indicating that Eu is associated with the BaF₂ nanocrystals, which would therefore be expected to contribute to the optical storage and emission properties of the FCZ glass.

The photoluminescence spectra for the three *ex situ* heat-treated samples are shown in Fig. 5. The excitation wavelength was 325 nm. A strong emission peak centered on 402 nm is observed for all samples. The 402 nm peak is attributed to the 5*d*–5*f* transition of Eu (II) in orthorhombic BaCl₂ crystals, which was determined to be present in each of the samples.¹⁵ The only difference between the spectra is a small peak in the emission spectrum from Sample 2 at ~390 nm. This peak results from absorbance of the emission at this wavelength by Eu (III) in sample 2, which is expected as it contained the highest Eu (III) content. The PL data from these samples indicate that the orthorhombic BaCl₂ nanocrystals are optically active and correlated with some of the Eu (II), but there may also be a contribution to this luminescence from the BaF₂ nanocrystals. BaF₂ crystals and nanocrystals have been shown to luminesce, giving a broad peak centered around 400 nm.^{27,28} The hexagonal BaCl₂ nanocrystals in FCZ glass have been thought to dominate the scintillation behavior in samples heat-treated at 260°C.²⁹ Future testing of the scintillation behavior of samples heat-treated at 300°C, with no hexagonal BaCl₂ present, will help to explain the optical properties of the BaF₂: as BaF₂ crystals are the fastest known scintillation material.²⁴

The TEM investigation of the FCZ glass-ceramic during and after heat treatment has revealed the formation of BaF₂ nanocrystals. The nucleation of orthorhombic BaF₂ nanocrystals in the FCZ glass-ceramic may be similar to the formation of hexagonal BaCl₂: both are metastable phases under ambient conditions. The formation of metastable phases prior to stable phases is often seen in the devitrification of as-melt glasses.³⁰ The BaF₂

nanocrystals potentially act as nucleation sites in the early stages of the heat-treatment process for the formation of the known β -BaZrF₆ phase. This hypothesis would explain why the initial BaF₂ phase, present only in small amounts in the form of strained nanocrystals, would not be detected by XRD because the prominent large crystals in the matrix, such as BaCl₂ and β -BaZrF₆, would dominate the signal. The β -BaZrF₆ phase is known to form in ZBLAN glasses after heat treatment to >310°C, but the formation of the phase has never been investigated in detail.

The samples have a high heterogeneity after heat treatment as a result of the formation of the nanocrystals and the production of small amounts of gas. The production of gas pockets throughout the sample will increase scattering in the bulk samples and reduce the spatial resolution in X-ray imaging. Previous studies on the effect of heat-treatment time and temperature on the PSL signal from FCZ glass indicate that formation of larger crystals initially improves the PSL, but beyond 20 min of heat treatment, the PSL signal levels off.¹⁷ The PSL leveling off corresponds to the growth of the gas pockets in the sample, which increases the inhomogeneity in the material, and the nucleation of PSL-inactive BaZr₂F₁₀ or β -BaZrF₆ crystals.

V. Conclusion

In summary, analysis of the early stages of crystallization in FCZ glass-ceramics has shown the nucleation of the FCC and orthorhombic phases of BaF₂ in addition to nucleation of the expected BaCl₂ phases. The BaF₂ nanocrystals grow to ~30–80 nm in size. The BaF₂ phases are known to form during heat treatment, as they are not present in the as-melt glass. The BaF₂ nanocrystals are colocated with the optically active Eu dopant, suggesting that they contribute to formation of the desired optical behavior. The BaF₂ nanocrystals may also act as a potential nucleation site for the formation of the β -BaZrF₆ phase. The identification of the BaF₂ crystals is a step toward modeling the complex nucleation and growth of the nanocrystals in the glass matrix. The formation of nanocrystalline BaF₂ and BaCl₂ is not influenced by changes in the dopant oxidation state. A detailed understanding of the role of nucleation, growth, phase transitions, and in particular the Eu dopant distribution on the optical properties requires further microscopic examination.

Acknowledgments

The authors thank the National Science Foundation for their support under grant no. DMR-1001381. We acknowledge use of the Electron Microscopy Center for Materials Research and the Center for Nanoscale Materials at Argonne National Laboratory, a U.S. Department of Energy Office of Science Laboratory operated under contract no. DE-AC02-06CH11357 by UChicago Argonne, LLC. The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government. RL and JJ thank Ms. Sharon Gray for her assistance and the Center for Laser Applications (CLA) at the University of Tennessee Space Institute (UTSI) for its support and use of facilities.

References

1. Harrington JA. A Review of IR Transmitting, Hollow Waveguides. *Fiber Integr Opt.* 2000; 19:211–7.
2. Zhu X, Peyghambarian N. High-Power ZBLAN Glass Fiber Lasers: Review and Prospect. *Adv OptoElectron.* 2010; 2010:1–23.
3. Fuller KC, Robinson M, Pastor RC. The Origin of Optical Absorptions in Heavy-Metal Fluoride Glass: II. Surface-Layer and Bulk Absorptions. *J Non-Cryst Solids.* 1990; 116:277–81.

4. Weinberg M, Neilson G, Smith G. Crystallization of Barium Fluorozirconate Based Glasses. *J Non-Cryst Solids*. 1983; 56:45–50.
5. Moore L, MacFarlane D. Surface Crystallization of ZBLAN Glasses. *J Non-Cryst Solids*. 1992; 140:159–65.
6. Jha A. Kinetics of Glass Formation of Heavy Metal Fluoride Melts. *J Non-Cryst Solids*. 1991; 134:157–68.
7. Battezzati L, Baricco M. An Experimental Study of Thermodynamic Properties in a ZBLAN Glass-Forming System. *Mat Sci Eng A*. 1991; 133:584–7.
8. Sakaguchi S. Evaluation of Extrinsic Scattering Loss Due to Crystallization in Fluoride Optical Fibers. *J Lightwave Technol*. 1993; 11(2):187–91.
9. Leede G, Waal H, Hakkens F. Nucleation in ZBLAN Glasses. *J Am Ceram Soc*. 1989; 72(10):1991–2.
10. Baricco M, Battezzati L, Braglia M, Cocito G, Kraus J, Modone E. Crystallization Behaviour of Fluorozirconate Glasses. *J Non-Cryst Solids*. 1993; 161:60–5.
11. Rousset JL, Ferrari M, Duval E, Boukenter A, Mai C, Etienne S, Adam JL. First Stages of the Crystallization in Fluorozirconate Glasses. *J Non-Cryst Solids*. 1989; 111:238–44.
12. Dunkley IR, Smith RW, Varma S. The Study of Devitrification Processes in Heavy-Metal Fluoride Glasses. *Ann New York Acad Sci*. 2004; 1027:150–7. [PubMed: 15644353]
13. Edgar A, Spaeth JM, Schweizer S, Assmann S, Newman PJ, MacFarlane DR. Photostimulated Luminescence in a Rare Earth-Doped Fluorobromozirconate Glass Ceramic. *Appl Phys Lett*. 1999; 75(16):2386–8.
14. Chen G, Johnson JA, Weber R, Nishikawa R, Schweizer S, Newman P, MacFarlane D. Fluorozirconate-Based Nanophase Glass Ceramics for High- Resolution Medical X-Ray Imaging. *J Non-Cryst Solids*. 2006; 352:610–4.
15. Schweizer S, Hobbs LW, Secu M, Spaeth JM, Edgar A, Williams GVM. Photostimulated Luminescence in Eu-Doped Fluorochlorozirconate Glass Ceramics. *Appl Phys Lett*. 2003; 83(3):449–51.
16. Leonard RL, Gray SK, Albritton SD, Brothers LN, Cross RM, Eastes AN, Hah HY, James HS, King JE, Mishra SR, Johnson JA. Rare Earth Doped Downshifting Glass Ceramics for Photovoltaic Applications. *J Non-Cryst Solids*. 2013; 366:1–5.
17. Schweizer S, Hobbs LW, Secu M, Spaeth JM, Edgar A, Williams GVM, Hamlin J. Photostimulated Luminescence From Fluorochlorozirconate Glass Ceramics and the Effect of Crystallite Size. *J Appl Phys*. 2005; 97(8):083522, 8.
18. Ahrens B, Eisenschmidt C, Johnson JA, Miclea PT, Schweizer S. Structural and Optical Investigations of Nd-Doped Fluorozirconate-Based Glass Ceramics for Enhanced Upconverted Fluorescence. *Appl Phys Lett*. 2008; 92(6):061905, 3.
19. Schweizer S, Henke B, Miclea PT, Ahrens B, Johnson JA. Multi-Functionality of Fluorescent Nanocrystals in Glass Ceramics. *Rad Meas*. 2010; 45:485–9.
20. Parker JM. Fluoride Glasses. *Ann Rev Mat Sci*. 1989; 19(1):21–41.
21. Lu G, Bradley JP. Microstructure and Evolution of a Barium Fluorozirconate Crystal in a ZrF₄-BaF₂-LaF₃-AlF₃-NaF Glass. *J Am Ceram Soc*. 1986; 69(8):585–9.
22. Johnson JA, Weber J, Kolesnikov A, Schweizer S. Crystallization in Heat-Treated Fluorochlorozirconate Glasses. *J Phys Condens Matter*. 2009; 21(37):3751031–6. [PubMed: 19789720]
23. Henke B, Paßlick C, Keil P, Johnson JA, Schweizer S. Eu Oxidation State in Fluorozirconate-Based Glass Ceramics. *J Appl Phys*. 2009; 106(11):113501, 6. [PubMed: 20057931]
24. Derenzo S, Weber J. Measurements of the Intrinsic Rise Times of Common Inorganic Scintillators. *IEEE Trans Nucl Sci*. 1999; 44:2:860–4.
25. Laval M, Moszynski M, Allemand R, Cormoreche E, Guinet P, Odru R, Vacher J. Barium Fluoride — Inorganic Scintillator for Subnano-second Timing. *Nucl Instr Meth Phys Res*. 1983; 206:169–76.
26. Schlumberger CL, Melcher DR, Manente RA, Schweitzer JS. Applicability of Barium Fluoride and Cadmium Tungstate for Well Logging. *IEEE Trans Nucl Sci*. 1989; 36:1188–92.

27. Kobayasi T, Mroczkowski S, Owen JF, Brixner LH. Fluorescence Lifetime and Quantum Efficiency for 5d → 4f Transitions in Eu²⁺ Doped Chloride and Fluoride Crystals. *J Lumin.* 1980; 21(3):247–57.
28. Zhang X, Quan Z, Yang J, Yang P, Lian H, Lin J. Solvothermal Synthesis of Well-Dispersed MF(2) (M = Ca, Sr, Ba) Nanocrystals and Their Optical Properties. *Nanotechnology.* 2008; 19(7): 075603, 8. [PubMed: 21817640]
29. Johnson JA, Schweizer S, Lubinsky AR. A Glass-Ceramic Plate for Mammography. *J Am Ceram Soc.* 2007; 90(3):693–8.
30. Feltz, A. Amorphous Inorganic Materials and Glasses. VCH; New York: 1993. p. 60-72.

Fig. 1. Dark-field TEM images of Sample 2 (a) before, and (b) after *in situ* TEM heat treatment at 300°C for 20 min, together with the respective selected area diffraction patterns. Note: the two images are not from the same exact region in Sample 2.

Fig. 2. HREM images of Sample 2 with corresponding FFTs and simulated diffraction patterns, showing nanocrystals of (a) hexagonal BaCl_2 , (b) orthorhombic BaCl_2 , (c) orthorhombic BaF_2 , and (d) FCC BaF_2 . A twin plane is present in the FCC BaF_2 nanocrystal; the two sets of planes are indicated by white or black circles.

Fig. 3.

(a) Dark-field TEM image of nanocrystals in Sample 1. The circles indicate the locations at which the corresponding (b)–(d), respectively, nanobeam diffraction and (e) energy-dispersive X-ray spectra were recorded. No NBD pattern is shown for location 1 because the region is amorphous.

Fig. 4. Background-subtracted EELS spectrum from BaF₂ nanocrystal cluster of *ex situ* heat-treated sample 2. Region from which spectrum was recorded is inset (composition was determined by EDX). EELS spectrum displays a strong Eu M_{4,5} peak indicating that Eu is associated with the BaF₂ nanocrystals.

Fig. 5.
Photoluminescence spectra for the samples, recorded at an excitation wavelength of 325 nm.
The curves are vertically offset; samples are organized 3–1, top to bottom.

Table I

Ba and Eu Content of the Eu-Doped FCZ Glasses (mol%)

Sample	BaCl ₂	BaF ₂	EuF ₂	EuF ₃
1	20.0	0.0	2.0	0.0
2	20.0	0.0	0.0	2.0
3	20.0	0.0	1.2	0.8