Published in final edited form as:

Radiat Meas. 2010 ; 45(3-6): 485–489. doi:10.1016/j.radmeas.2009.11.029.

Multi-functionality of fluorescent nanocrystals in glass ceramics

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Abstract

Thermal processing of as-made fluorozirconate glasses, which were additionally doped with rare-earth and chlorine ions, results in the formation of fluorescent nanocrystals therein. For medical applications, the glasses were doped with divalent europium ions as the fluorescent rare-earth ion, while trivalent neodymium was used to develop up-conversion systems. The samples were annealed up to 290 °C to initiate the growth of hexagonal or orthorhombic phase BaCl₂ nanocrystals therein. Upon annealing some of the rare-earth ions were incorporated into the BaCl₂ nanocrystals leading to enhanced fluorescence properties. The particle diameters were in the range of a few nanometers to several tens of nanometers.

Keywords

Glass ceramics; Nanocrystals; Radiation detection; Up- and down-conversion

1. Introduction

A class of fluorozirconate (FZ) glass ceramics were developed for ionizing radiation detection and photon up- or down-conversion applications. In medical imaging the FZ glasses were doped with europium and bromine or chlorine ions. Appropriate annealing produced barium bromide/chloride nanocrystals in the glass. Depending on its phase the nanocrystalline materials behave either as scintillators (able to convert ionizing radiation to visible light) (Johnson et al., 2006), or as storage phosphors (able to convert the radiation into stable electron-hole pairs, which can be readout afterwards with a scanning laser beam) (Johnson et al., 2007).

The low-phonon energies of FZ-based glass ceramics are the main criteria to use these systems for photon up- and down-conversion (Schweizer et al., 2008). Up-conversion occurs when a high-energy photon is emitted after sequential absorption of two low-energy photons. Note that the up-conversion efficiency depends critically on the phonon energies of the host material; low-phonon energies reduce non-radiative losses and increase up-conversion efficiencies. A practical application is in bifacial solar cells where the efficiency

can be further improved by using a layer on the backside to up-convert the far-infrared photons to a more suitable wavelength (Trupke et al., 2002a). The glass ceramics can also be used for down-conversion (quantum cutting) applications. The solar cell efficiency in the ultraviolet spectral range can be significantly increased by applying a transparent glass-ceramic top layer, which down-converts the incident ultraviolet photons to photons of a wavelength more effectively absorbed by the solar cell (Trupke et al., 2002b).

2. Experimental

The Eu- or Nd-doped fluorochlorozirconate (FCZ) glasses presented in this work were based on the well-known ZBLAN composition (Aggarwal and Lu, 1991); they were comprised of $(53 - x)\text{ZrF}_4 - 10\text{BaF}_2 - 10\text{BaCl}_2 - 20\text{NaCl} - 3.5\text{LaF}_3 - 3\text{AlF}_3 - 0.5\text{InF}_3 - x\text{EuF}_2$ in the case of Eu-doping and $(53 - x)\text{ZrF}_4 - 10\text{BaF}_2 - 10\text{BaCl}_2 - (20 - x)\text{NaCl} - x\text{KCl} - 3.5\text{LaF}_3 - 3\text{AlF}_3 - 0.5\text{InF}_3 - x\text{NdF}_3$ for the Nd-doped FCZ glasses. All values are in mole percent. The constituent chemicals were melted in a glassy carbon crucible at 745 °C in an inert atmosphere of nitrogen and then poured into a brass mold that was at a temperature of 200 °C, i.e., below the glass transition temperature of 260 °C for an FZ-based glass (Aggarwal and Lu, 1991), before being slowly cooled to room temperature. Additional subsequent annealing steps were performed in an inert nitrogen atmosphere. The visible appearance of the initial FCZ glasses is transparent, but after annealing there was evidence of crystallization in all of them, ranging from a near-transparent glass, which was light yellow in transmitted light, to one which was opaque and milky-white.

In addition, Er-doped FZ glasses comprised of $(53 - x)\text{ZrF}_4 - 20\text{BaF}_2 - 20\text{NaF} - 3.5\text{LaF}_3 - 3\text{AlF}_3 - 0.5\text{InF}_3 - x\text{ErF}_3$ (values in mole percent) were prepared.

3. Results and discussion

3.1. Eu-doped FCZ glass ceramics for medical applications

Fig. 1 shows the X-ray diffraction (XRD) data for a Eu-doped FCZ glass first quenched to 200 °C and then held at the temperatures indicated for 20 min. The XRD data for a sample processed at 250 °C comprises very broad reflections from the glass matrix (Edgar et al., 2001) and sharper peaks that we identify as arising from hexagonal BaCl_2 (Liu and Eick, 1989). The XRD peaks are wider than the instrumental linewidth, suggesting size-broadening effects. Using the Scherrer formula (Scherrer, 1918) applied to the linewidths, the particle size was estimated to be approximately 9.0 nm. There was a systematic increase in the hexagonal crystallite size with increasing annealing temperature (Schweizer et al., 2005).

After annealing at 280 °C, the XRD data showed reflections associated with orthorhombic BaCl_2 (Brckett et al., 1963). There was a systematic decrease in the XRD linewidths of the orthorhombic BaCl_2 phase with increasing temperature. The orthorhombic BaCl_2 crystallite size was estimated to be 46 nm. There was no evidence of hexagonal BaCl_2 in the XRD data after annealing at and above 280 °C. However, additional reflections from unknown phases started to appear (Schweizer et al., 2005).

For medical applications, the FCZ glasses were doped with divalent europium. Surprisingly, in the FZ base glass as well as in the as-made FCZ glass Eu^{2+} did not luminesce although it was clear from electron paramagnetic resonance (EPR) (Furniss et al., 1987) and Mössbauer studies (MacFarlane et al., 1999) that it was in the glass.

After annealing, however, a significant Eu^{2+} photoluminescence (PL) was observed which was attributed to the typical 5d–4f transition of Eu^{2+} ions present in the above described hexagonal or orthorhombic phase BaCl_2 nanocrystals. The intensity of the Eu^{2+} emission

was increased significantly upon annealing. Fig. 2, open squares, shows that the PL intensity of the Eu^{2+} emission in glass ceramics containing predominantly orthorhombic phase nanocrystals was about one order of magnitude more intense than that found in samples containing predominantly hexagonal phase nanocrystals (Schweizer et al., 2005).

It can also be seen in Fig. 2, open circles, that the photo-stimulated luminescence (PSL) efficiency of the Eu-doped FCZ glass ceramics increases with increasing annealing temperature. Part of the initial increase in the PSL efficiency, with increasing annealing temperature from 260 °C to 290 °C, is due to an increasing volume fraction of orthorhombic BaCl_2 . This is based on the relative increase in the orthorhombic BaCl_2 volume fraction with respect to the hexagonal BaCl_2 volume fraction observed in the XRD data. After annealing at 280 °C for 20 min the relative PSL efficiency was about 40%, and there was no hexagonal BaCl_2 in the glass ceramic. However, the PSL efficiency continued to increase with increasing annealing temperature (Schweizer et al., 2005).

Fig. 3 shows a photostimulated luminescence image recorded on a 2 mol% Eu-doped ZBLAN glass-ceramic plate (top) and on a commercial Agfa MD30 storage phosphor screen (bottom) (Chen et al., 2005). The two sets of parallel grids shown in these images are part of a Huettner phantom. The numbers at the top of the image indicate their spatial frequency, i.e., the right parallel lines have a spatial frequency of 20 lp/mm (lp = line pairs), and the left ones are 19 lp/mm. These two images were taken under the same experimental conditions. As seen from Fig. 3, top, the ZBLAN-based storage phosphor plate has spatial resolution higher than 20 lp/mm. Further analysis showed that this imaging plate had a resolution of 28 lp/mm at the modulation transfer function (MTF) value equal to 0.2. In contrast, Fig. 3, bottom, demonstrates that the commercial storage phosphor did not have high enough resolution to resolve 19 lp/mm parallel gold line pairs.

The readout mechanism used in the above described experiment was, however, different to that generally used for commercial storage phosphors: commercially used readout systems are based on a laser point-scan method, i.e., a focused laser beam traverses the sample point by point, and the stimulated luminescence light at each point is collected so that a whole image can be mapped out. In contrast, we used an expanded laser beam to stimulate the x-ray irradiated area on the sample, and then directly collect the image through a CCD camera and an objective lens. As a result, the Agfa material used in our study was not measured under optimum conditions (the laser point-scan method) and was used only for comparison.

Reference data on an Agfa MD30 storage phosphor screen showed that it had spatial resolution of 2.5 lp/mm at square wave response (SWR) = 0.2. In other words, the resolution of the 2 mol% Eu-doped ZBLAN glass-ceramic plate could be one order of magnitude better than that of an Agfa MD30 storage phosphor screen. The study thus demonstrated that it is possible to use the glass-ceramic storage phosphors for high-resolution digital radiography. In addition, the use of a “grainless” glass based plate potentially enables instantaneous readout of the image rather than the slower point-by-point technique required for polycrystalline materials.

In the course of studying the storage phosphor properties of the FCZ glassceramics, it turned out that, under certain conditions instead of being good storage phosphors, they were good scintillators. By changing the sample annealing conditions (Fig. 2), we can change the X-ray imaging property of the ZBLAN-based glass ceramics.

To demonstrate the applicability of the glass ceramic for medical X-ray imaging, it was used as a micro-CT scintillator (Chen et al., 2006). Fig. 4 is the transmission X-ray image of a mouse joint taken from an Eu-doped glass-ceramic plate, showing fine features such as nail, skin, bone, and hair. Apparently, the glass-ceramic scintillator has both high imaging

resolution and large dynamic range to resolve fine features as well as low contrast objects. Therefore, these glass ceramics show excellent potential for applications in high-resolution medical imaging.

3.2. Nd-doped FCZ glass ceramics for up-conversion applications

Fig. 5 shows the XRD data for the 5 mol% Nd-doped FCZ glass as-made and annealed for 20 min at the temperatures indicated. The data of the as-made sample consist of the very broad reflections at about 26° and 47° caused by the glass matrix (see above). However, in analogy to the results for the Eu-doped FCZ glasses, sharper peaks arise upon increasing the annealing temperature from 250 to 290 °C. These reflections derive from hexagonal BaCl_2 (Liu and Eick, 1989). There was no phase transition from the hexagonal to orthorhombic phase BaCl_2 as was found in Eu-doped FCZ glass ceramics. For the 290 °C annealed sample, there were reflections from phases which have not yet been identified; they are marked with asterisks in Fig. 5.

Again, the XRD peaks were wider than the instrumental resolution, suggesting size-broadening effects. The Scherrer formula is applied to the (201) reflection of hexagonal phase BaCl_2 at about 32° ; the line profile was fitted by a Lorentzian. Stress and strain effects, which may lead to additional line broadening, were not considered. The particle diameters, after annealing at 250, 260, and 270 °C, were between 20 and 60 nm; for annealing temperatures of 280 °C and above, the particles grew rapidly and their sizes become >100 nm (Fig. 6, open squares). The XRD linewidth of the (201) reflection for 280 and 290 °C annealing was too close to the instrumental resolution to allow a precise estimate of the particle size (see error bars in Fig. 6, open squares). However, the Scherrer analysis of the X-ray diffraction pattern provides a first estimate of the particle size; there was a trend to bigger particles for longer annealing. In addition, Fig. 6, full squares, shows that for annealing above 270 °C, the hexagonal phase BaCl_2 nanocrystals start to dissolve, i.e., the hexagonal phase BaCl_2 volume fraction in the glass decreases.

For up-conversion applications the FCZ glass ceramics were doped with trivalent Nd ions. Fig. 7 shows the energy level diagram of Nd^{3+} : infrared and up-conversion emissions (solid arrows) and possible up-conversion routes (dashed arrows) for an excitation at 800 nm are indicated (Dieke and Crosswhite, 1963; Stanley et al., 1993).

Up-conversion in the visible range was observed at room temperature under continuous wave infrared laser excitation at about 800 nm. The most intense up-converted fluorescence bands were located in the green (530 nm), yellow (590 nm), and red (660 nm) region. They arise from the ^4G multiplets (Stanley et al., 1993). The ^4G multiplets, comprised of the $^4\text{G}_{9/2}$, $^4\text{G}_{7/2}$, and $^4\text{G}_{5/2}$ states, produce overlapping emission bands, and are therefore the strongest in the spectrum. The ^4G multiplets are energetically accessible with two 800 nm photons.

Of particular importance to the up-conversion efficiency is the intermediate energy level lifetime, specifically for the 2-photon up-conversion processes the energy level lifetime of the $^4\text{F}_{3/2}$ level is important (Fig. 7). Fig. 8, full squares, shows that the lifetime of the $^4\text{F}_{3/2}$ to $^4\text{I}_{9/2}$ transition (880 nm) depends significantly on the annealing temperature: the longest lifetime was found for the 270 °C sample. This was in good agreement with the observation that the best up-conversion efficiency was also found for the 270 °C FCZ sample (Fig. 8, open squares).

As stated in the Introduction, a practical application of up-conversion FZ glasses could be in bifacial solar cells where the efficiency can be further improved by using an up-converting layer on the backside. Nd-doped systems are, however, not applicable for silicon solar cells,

for example, since the 800 nm excitation light of the Nd^{3+} up-conversion can be absorbed by a silicon solar cell directly. For photovoltaic applications a more suitable dopant like Er^{3+} has to be chosen. Initial tests with Er-doped FZ glasses showed huge potential of these systems as up-converters (Fig. 9).

4. Outlook

FZ-based glass ceramics present diverse properties and potential for applications due to the numerous options for processing in combination with doping of both rare-earths and halides. Challenges remain in these materials in preserving the valency of elements in these materials with multiple valence states in the desired form. For example, in the case of Eu-doping, which is desired for medical imaging, the preference is for Eu^{2+} and for Zr, the preference is for Zr^{4+} . However, a redox reaction can take place that renders both to the 3+ state. The answer to this problem may lie in a two-step synthesis process, where the glass matrix is formed in an oxidising atmosphere and the dopants are added later in a second melting step.

Unexplored territory includes two or more dopants, which may enhance both PSL and up-conversion due to increased defects and possible absorption routes, respectively. Overall, interesting challenges remain but applications are on the horizon.

Acknowledgments

This work was supported by the FhG Internal Programs under Grant No. Attract 692 034. In addition, the authors would like to thank the Federal Ministry for Education and Research for their financial support (BMBF Verbundvorhaben: NanoVolt – Optische Nanostrukturen für die Photovoltaik).

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Fig. 1. Plot of the XRD data for Eu-doped FCZ glasses held for 20 min at 250 °C and 280 °C. The XRD patterns of hexagonal BaCl₂ (PDF #45-1313) and orthorhombic BaCl₂ (PDF #24-0094) are also shown (Schweizer et al., 2005).

Fig. 2. Plot of the relative PL (squares) and PSL (circles) efficiencies vs. annealing temperature for an Eu-doped FCZ glass held for 20 min at the annealing temperature and normalized to the values obtained after annealing at 290 °C (Schweizer et al., 2005).

Fig. 3. (top) Photostimulated luminescence (PSL) image of a Huettner phantom recorded on a 2 mol% Eu^{2+} -doped ZBLAN glass ceramic plate (1 mm in thickness). (bottom) PSL image of the same Huettner phantom recorded on a commercial storage phosphor screen (Agfa MD30). Note that the measurements were made by illuminating the whole surface of the sample with 660 nm laser light and imaging the blue PSL emission. Scattering by grains in the MD30 resulted in image degradation compared to the “grainless” glass plate (Chen et al., 2005).

Fig. 4. Transmission X-ray image of a mouse joint recorded on a 2 mol% Eu-doped FCZ glass–ceramic plate (approximately 0.5 mm in thickness) (Chen et al., 2006).

Fig. 5. XRD data for 5 mol% Nd-doped FCZ glass ceramics, as made and annealed for 20 min at 250, 270, and 290 °C. The curves are vertically displaced for clarity; the line pattern of hexagonal phase BaCl₂ (PDF #45-1313) is shown for comparison (Ahrens et al., 2008).

Fig. 6.
(a) Particle size of the (201) reflection and (b) integrated intensity vs. annealing temperature (Ahrens et al., 2008).

Fig. 7.

Energy level diagram of Nd^{3+} : the infrared and up-conversion emissions (solid arrows) and possible up-conversion routes (dashed arrows) are indicated (Dieke and Crosswhite, 1963; Stanley et al., 1993).

Fig. 8.

(a) Decay time of the 880 nm Nd^{3+} emission in 5 mol% Nd-doped FCZ glass ceramics. The fluorescence was excited at 803 nm with an infrared laser diode. (b) Up-converted fluorescence intensity vs. annealing temperature normalized to as-made FCZ. The line is a guide to the eye (Schweizer et al., 2008).

Fig. 9. Digital photo of a commercial monocrystalline silicon solar cell with an up-converting Er-doped FZ glass sample on top. Excitation is carried out from the top with a CW laser diode operating at 1540 nm (not shown). The incident light is perpendicular to the solar cell and the glass sample. The dimensions of the solar cell are $2\text{ cm} \times 2\text{ cm}$ and those of the glass sample are $7\text{ mm} \times 7\text{ mm} \times 2\text{ mm}$ (Henke et al., 2009).