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The effect of trivalent iron on the properties of fluorochlorozirconate glass ceramics

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ABSTRACT

Heat treating fluorochlorozirconate (FCZ) glasses precipitates nanocrystals in the glass matrix, resulting in glass ceramics that have storage phosphor properties suitable for use as a medical imaging plate. As the temperature of heat treatment rises, the resulting FCZ glass ceramic becomes more turbid as the size of the orthorhombic phase $BaCl_2$ nanocrystals grow. This cloudiness results in scattering of the stimulating laser light, negatively affecting spatial resolution in computed radiography applications. The effect of Fe^{3+} on the valence state of zirconium and overall glass quality was investigated. The addition of small amounts of $FeCl_3$ (1–2% on a molecular weight basis) to a ZBLAN glass composition allows for the precipitation of orthorhombic phase $BaCl_2$ crystals while maintaining transparency of the glass ceramic.

1. Introduction

Fluorochlorozirconate (FCZ) glass ceramics have been shown to have potential in applications for medical imaging, radiation detection, non-destructive testing, and solar cells [1–5]. The function of the glass ceramic can be changed by tuning the phase of $BaCl_2$ nanocrystals within the glass matrix during heat treatment. The phase of $BaCl_2$ has a significant effect on the optical properties of the resultant glass ceramic: hexagonal phase $BaCl_2$ scintillates (converts ionizing radiation to visible light), while orthorhombic phase $BaCl_2$ exhibits storage phosphor characteristics when irradiated with X-rays (converts radiation into stable electron–hole pairs for later readout with a laser beam) [6,7]. FCZ scintillators have uses in X-ray detection systems and computed tomography systems for medical applications. FCZ storage phosphors, on the other hand, are employed as reusable imaging plates for X-ray medical imaging in a technique known as computed radiography (CR).

FCZ glass ceramics containing orthorhombic phase $BaCl_2$:Eu^{2+} nanocrystals have shown the potential for greatly improved resolution when compared to traditional storage phosphor materials [8,9]. With nanocrystals much smaller in diameter (~50–100 nm) than the wavelength of the stimulating light, scattering is greatly reduced and resolution is improved [7,10–12]. For these reasons, FCZ glass ceramics are an attractive option to replace current X-ray storage phosphor technology (BaBrF:Eu^{2+}) [8,11,13–15].

FCZ glasses, however, are difficult to produce. Zirconium fluoride is a volatile compound above 450 °C in ZrF_4-based glasses [16]. ZBLAN glasses can experience evaporation losses as high as ~15% weight during the high temperature melting process. Some of this weight loss is attributed to the sublimation of ZrF_4 during synthesis [16]. A greater loss of anions causes a portion of the Zr^{4+} in the glass matrix to reduce to Zr^{3+}, contributing to the formation of black inclusions within the glass [16]. These inclusions can cause artifacts in computed radiography images.

In order to help stabilize the valence state of zirconium within the glass matrix, small amounts (0–4%) of $FeCl_3$ were added to the glass composition. Iron can exist in many oxidation states, most commonly as Fe^{2+} and Fe^{3+}. We speculated the versatility of the iron valence state will help stabilize zirconium from reducing during synthesis, resulting in a final product with better optical properties. To the authors' knowledge, this is the first time $FeCl_3$ has been added to a ZBLAN composition to improve its quality for imaging applications.

The purpose of this work is to evaluate the effect that the addition of $FeCl_3$ has on the crystallization and optical properties of fluorochlorozirconate glass ceramics containing orthorhombic $BaCl_2$:Eu^{2+} crystals for use as a storage phosphor. FCZ glass samples doped with $FeCl_3$ and either Eu^{2+} or Eu^{3+} were produced and then heat-treated to precipitate orthorhombic $BaCl_2$ crystals within the glass matrix, subsequently creating glass ceramics capable of performing as a storage phosphor. The approximate temperature of the $BaCl_2$ hexagonal-to-orthorhombic phase transformation was estimated using differential scanning calorimetry (DSC) [17–19]. After heat treatment, X-ray

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diffraction (XRD), phosphorimetry, and spectrometry measurements were used to identify the crystalline phases present in the glass ceramics [8]. Samples were then exposed to 70 kV X-rays to determine photostimulated emission characteristics.

2. Materials and methods

Ten FCZ glass samples, split into two groups of five, were synthesized for research. Five were doped with $EuCl_2$ and contained the following composition in mole percentage: 51.0 ZrF_4 − (20.0 − x) $BaCl_2$ − 20.0 NaF − 3.0 AlF_3 − 3.5 LaF_3 − 0.5 InF_3 − 2.0 $EuCl_2$ − x $FeCl_3$, where 0 ≤ x ≤4 in whole number increments. The other five samples were doped with $EuCl_3$ and followed a similar composition: 51.0 ZrF_4 − (20.0 − x) $BaCl_2$ − 20.0 NaF − 3.0 AlF_3 − 3.5 LaF_3 − 0.5 InF_3 − 2.0 $EuCl_3$ − x $FeCl_3$, where 0 ≤ x ≤ 4 in whole number increments.

Synthesis of samples was conducted in a glovebox (MBRAUN Labmaster SP) with an argon atmosphere to prevent contamination from water vapor and oxygen. All raw materials (fluoride and chloride powders) were procured from Sigma-Aldrich. Synthesis followed a two-step process. First, fluoride powders (ZrF_4, LaF_3, AlF_3, NaF, and InF_3) were placed in a platinum crucible and weighed. The mixture was then heated in a programmable tube furnace (MTI Corporation OTF-1200X) to 800 °C. The furnace was connected through a doorway that also contained an argon atmosphere. After 50 min, the crucible was removed from the tube furnace for the addition of the remaining chloride powders ($BaCl_2$, $EuCl_2$ or $EuCl_3$) and returned to the tube furnace at 750 °C for 50 min. Upon completion of the melt cycle, the glass was poured into a brass mold preheated to a temperature of 200 °C. Heating of the brass mold was controlled through a cartridge heater connected to a proportional-integral-derivative (PID) controller, allowing for the gradual cooling of the glass to room temperature over a 4-hour period. Samples with 3% and 4% $FeCl_3$ were too opaque to be effective as storage phosphor imaging plates; these samples were removed from consideration and were not heat treated or characterized.

Differential scanning calorimetry (Netzsch DSC 200F3) scans were made from 100 °C to 400 °C at a rate of 10 K/min with nitrogen purge gas. Sample mass for each scan was 20 ± 10 mg. The results of these scans determined the temperatures for heat treating the glass samples to precipitate orthorhombic phase $BaCl_2$ nanocrystals, converting the samples into glass ceramics.

A portion of approximately 1 cm × 1 cm was taken from each glass sample for subsequent heat treatment in a tube furnace in ambient air. To monitor temperature during the heat treatment process, the samples were held in an aluminum compartment that had an embedded thermocouple. Prior to heat treatment, the samples were preheated in a stainless steel boat on a hotplate to 200 °C to prevent thermal shock; once the sample was preheated and the aluminum compartment was at the desired heat treatment temperature, the sample was transferred directly into the compartment. The temperature for each sample's heat treatment corresponded to the precipitation of orthorhombic phase $BaCl_2$ nanocrystals as determined from the DSC measurements. Samples were heat treated at this temperature for 5 min. Following heat treatment, samples were returned to the 200 °C hot plate to prevent thermal shock before being allowed to cool in ambient conditions.

The resulting heat treated samples underwent X-ray diffraction measurements on a Phillips X'Pert MRD X-ray Diffractometer (PANalytical Inc.) with a Cu anode X-ray source in the 2θ range from 20° to 80°. Scanning rate step size was 0.05° with a time step of 5 s. MDI Jade 9 analytical software (Materials Data, Inc.) was employed to identify crystal phases.

Emission spectra were measured using a QM-3-PH phosphorescence/fluorescence spectrofluorometer (Photon Technology International, Inc.) with Czerny-Turner monochromators at the source and detector. The system was equipped with a Type L4633 Xenon Flash Lamp (Hamamatsu Photonics K.K.) and an R1527P Photomultiplier tube (Hamamatsu Photonics K.K.). The computer interface was a PC equipped with FeliX32 software for data analysis. Measurements were made using the following parameters: excitation wavelength (emission spectra) = 360 nm, emission wavelength (excitation spectra) = 410 nm, step size = 1 nm, integration time = 50 μs, averages (number of repeated scans for which results are averaged) = 3, shots (lamp pulses per each individual scan with results averaged) = 50, lamp frequency = 100 Hz. Additional emission spectra between wavelengths 550 and 650 nm were measured using an HR4000CG-UV-NIR spectrometer (Ocean Optics, Inc.). Measurements were made with an integration time of 2 s and an average of 3 spectra. Samples were excited with a UV-A lamp at 365 nm. The computer interface was a PC equipped with SpectraSuite software for data analysis.

Photostimulated emission characteristics were measured using a custom system consisting of a 4″ integrating sphere (Labsphere, Inc.), a photosensor module and power supply (Hamamatsu HC124–06 and C7169), a data acquisition card (National Instruments NIUSB-6215), and a 532 nm pumped diode Nd/YAG laser operating at 60 mW. To measure the emission, the material was exposed to 70 kVX-rays at a distance of 45 cm for 1.6 s. The estimated dose at the sample was 8 R. A 2.3 mm^2 portion of the sample was stimulated diffusely from within the integrating sphere; the laser power at the sample was 31 μW. Matlab software operating on a personal computer was used to collect the data generated.

3. Results and discussion

3.1. Differential scanning calorimetry

DSC scans were performed on each transparent as-made glass sample as shown in Fig. 1. The first exothermal peak indicates the formation of hexagonal phase $BaCl_2$ and generally occurs around 240–250 °C [20]. This peak is consistent amongst 0–1% $FeCl_3$ samples and occurs at 243 °C (± 3 °C).

The second, smaller exothermal peak indicates the transformation of $BaCl_2$ nanocrystallites into the orthorhombic phase, the desired phase for application as a storage phosphor. This transformation generally occurs at 300 °C (± 5 °C) [20]. The 0% and 2% $FeCl_3$ samples have similar orthorhombic transformations at 300 °C (± 8 °C). The 1% $FeCl_3$ samples, however, experience phase transformations at much cooler temperatures (278 °C for $EuCl_2$, 283 °C for $EuCl_3$).

It is evident from the DSC curve that as $FeCl_3$ is integrated into the sample, the temperature for the hexagonal-to-orthorhombic phase transformation is lowered significantly (up to 27 °C). The authors hypothesize that increased chlorine content from the addition of $FeCl_3$

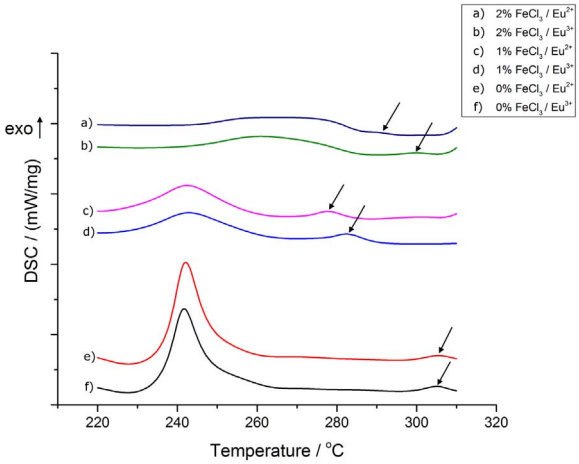

Fig. 1. DSC scans for each as-made, amorphous glass sample. The results are stacked for easier comparison. Arrows indicate the exothermic peak corresponding to the orthorhombic phase transformation of $BaCl_2$.