Synthesis, thermal and photoluminescent properties of ZnSe-based oxyfluoride glasses doped with samarium

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Abstract. Rare earth (RE) doped glasses and glass ceramic materials have recently received considerable attention because of their potential or realized applications as X-ray intensifying screens, phosphors, detectors, waveguides, lasers etc. [1]. In this work, we present a new RE doped ZnO-ZnSe-SrF 2 -P 2 O 5 -B 2 O 3 -Sm 2 O 3 -SmF 3 (ZSPB) glass system synthesized by melt quenching technique. The resulting glasses were visually fully transparent and stable with glass transition temperatures around 530°C. The thermal properties of this glass system were characterized by Modulated Differential Scanning Calorimetry (MDSC) measurements before and after annealing at 650°C. We have characterized these glasses by Raman spectroscopy and photoluminescence (PL) measurements over the UV-VIS range using light emitting diodes (LED) and laser diodes (LD) excitation sources. We have also irradiated thermally treated and non-treated glass samples by X-rays and have studied the resulting PL. We discuss the results in terms of previously reported models for Sm-doped Zn-borophosphate oxide, oxyfluoride and oxyselenide glasses.

1. Introduction

Rare earth (RE) doped glasses and glass ceramic materials have recently received considerable attention because of their potential or realized applications as X-ray intensifying screens, phosphors, detectors, waveguides, lasers etc. [1]. We have been studying ZnO based material systems including Zn-phosphate glass-ceramics [2] and Zn-B-phosphate glasses and glass ceramics [3, 4]. Most recently we included other backbone elements as fluorine and other additional metals such as Sr to this material system [5].

In various applications, it is desirable to have a stable RE-doped material system that exhibits photo- and X-ray luminescent characteristics. In the present work, our primary interest is the induced conversion of RE ions from one valence state to another towards developing a sensing medium for the measurement of dose. If such a conversion is possible, this system can be applied for high dose X-ray synchrotron-based techniques for cancer treatment such as Microbiem Radiation Therapy (MRT) as discussed previously [6]. However, there may also be additional applications of these materials such as high resolution indirect X-ray imaging [7, 8], radiation sensing, optical filters etc.

This work attempts to convert the ZnO-based oxyfluoride glass and glass ceramic systems to oxyselenide systems by including selenium components. Ciceo-Lucacel at al. have already reported the synthesis of non-doped selenium containing borophosphate glasses with possible bioactivity [7].

2. Materials and methods
2.1. Synthesis
The following reagents were used for the preparation of glass compositions: ZnO (Alfa Aesar, 99.9%), ZnSe (Alfa Aesar, 99%), SrF\textsubscript{2} (Alfa Aesar, 99%), P\textsubscript{2}O\textsubscript{5} (Alfa Aesar, 98%), B\textsubscript{2}O\textsubscript{3} (Alfa Aesar, 99.98%), Sm\textsubscript{2}O\textsubscript{3} (Alfa Aesar, 99.99%), SmF\textsubscript{3} (Alfa Aesar, 99.99%). The synthesis was performed in a zirconia furnace Zircar 110 (with a temperature range 0 – 1750 °C) at a temperature of 1350 °C for 1 h.
Seven samples of ZnO-ZnSe-SrF\textsubscript{2}-P\textsubscript{2}O\textsubscript{5}-B\textsubscript{2}O\textsubscript{3}-Sm\textsubscript{2}O\textsubscript{3}-SmF\textsubscript{3} (ZSPBS) glass system were synthesised by conventional melt quenching technique. We varied the ZnSe content from 6.5 to 66.5 mol %.

2.2. Differential Scanning Calorimetric characterization
Differential Scanning Calorimetric (DSC) and Temperature Modulated DSC (TMDSC) experiments were performed using the TA Instruments DSC Q100 with an attached Fast Air Cooling System (FACS) at heating rates of 2 K/min, a period of 60 s and amplitude of ±1 K.

2.3. Photoluminescent Experiments
The photoluminescence (PL) spectra of synthesized glasses were measured by a fibre optic coupled CCD Aventes spectrometer AveSpec-2048 with a grating in the range 250-1100 nm. Laser diodes (LD) and Light Emitting Diodes (LED) from UV to NIR range were used as excitation sources. 3D graphs were generated using a MatLab software.

2.4. X-Ray Glass Samples Treatment
We exposed as-prepared and heat treated samples to x-rays under an x-ray tube (43855D, Faxitron) set to 110 kVp with a filament current of 3 mA. PL before and after X-ray irradiation was recorded by a spectrometer EPP2000.

2.5. Raman Spectroscopy
The Raman analysis was performed on RAM II (Bruker Optics) apparatus with a focused laser beam Nd: YAG laser (wavelength 1054 nm). Glass bulk samples were placed and scanned from 4000 cm\textsuperscript{-1} to 400 cm\textsuperscript{-1} with a resolution of 2 cm\textsuperscript{-1}.

3. Result and Discussion
The compositions of synthesized glasses are shown in table 1. The fabricated new glass compositions are fully transparent and visually homogenous as can be seen in figure 1.

The thermal characteristics were measured by MDSC measurements. The evaluation of heat flow and heat capacity results was performed using TA Instruments Universal Analysis (UA) software. Figure 2 shows the T\textsubscript{g} of composition 1 and the T\textsubscript{g} of composition without any ZnSe, base sample (ZnO(71.4) – SrF\textsubscript{2}(0.72) – P\textsubscript{2}O\textsubscript{5}(9.69) – B\textsubscript{2}O\textsubscript{3}(18) – Sm\textsubscript{2}O\textsubscript{3}(0.12) – SmF\textsubscript{3}(0.12)) with the same glass matrix. The addition of ZnSe leads to an increase in the T\textsubscript{g} of the glass matrix of about 20°C.

| Sample № | Component content (mol %) | ZnO | ZnSe | SrF\textsubscript{2} | P\textsubscript{2}O\textsubscript{5} | B\textsubscript{2}O\textsubscript{3} | Sm\textsubscript{2}O\textsubscript{3} | SmF\textsubscript{3} |
|----------|---------------------------|-----|------|--------------------|------------------------|---------------------|-----------------------|-------------------|
| 1        | 64.9                      | 6.5 | 0.72 | 9.69               | 18                     | 0.12                 | 0.12                  |
| 2        | 54.9                      | 16.5| 0.72 | 9.69               | 18                     | 0.12                 | 0.12                  |
| 3        | 44.9                      | 26.5| 0.72 | 9.69               | 18                     | 0.12                 | 0.12                  |
| 4        | 34.9                      | 36.5| 0.72 | 9.69               | 18                     | 0.12                 | 0.12                  |
| 5        | 24.9                      | 46.5| 0.72 | 9.69               | 18                     | 0.12                 | 0.12                  |
| 6        | 14.9                      | 56.5| 0.72 | 9.69               | 18                     | 0.12                 | 0.12                  |
| 7        | 4.9                       | 66.5| 0.72 | 9.69               | 18                     | 0.12                 | 0.12                  |
The glass transition temperatures of synthesized samples (numbers 1 to 7) are shown in figure 3. Obviously increasing the ZnSe content in the glass matrix do not significantly change the glass transition temperatures. It possibly means that oxygen and selenium are replaceable in this oxyselenide glass structure. Once selenium is included in the oxide glass system it makes the system more stable.
(higher $T_g$). Samples 1, 2, 3 and 4 were annealed at 650 °C (close to the glass crystallization temperature) for 3 hours. The MDSC data of the thermally treated samples are shown in figure 4. The results reveal a small change in $T_g$ (about 2 °C) due to annealing. There are also some minor visual changes, e.g. samples are less transparent but are not fully crystalized with the thermal treatment process. The upper curve in figure 4 shows the $T_g$ data of non-annealed samples for comparison.

![Figure 4](image)

**Figure 4.** Glass transition temperature of samples 1, 2, 3 and 4 before and after annealing at 650 °C. The upper curve is for the non-annealed sample.

The Raman spectra of these samples are shown in figure 5. There is one strong peak at 961 cm$^{-1}$ and two less intensive peaks at 576 and 430 cm$^{-1}$ for all samples including those without ZnSe content. The Raman bands for Zn-phosphate glasses are 961 cm$^{-1}$ (PO$_4$) stretch (non-bridging oxygen/selenium), 576 cm$^{-1}$ is a bend mode related to the zinc-phosphate network or ZnO$_4$/ZnSe$_4$, and 430 cm$^{-1}$ is a bend mode of phosphate polyhedral with a zinc modifier according to the Sandia national laboratories (USA) report [9]. The present Raman spectroscopy results are in agreement with the above findings from the MDSC analysis (figure 3) which suggest that ZnO and ZnSe based glasses are structurally identical.

![Figure 5](image)

**Figure 5.** a/ Raman spectra of ZnSe based samples (1, 2, 5, 6 and 7) and sample without ZnSe content b/ Raman spectra of sample 5 (a typical example).
Photoluminescence experiments were performed by various LEDs with emission wavelengths of 370, 395, 405, 410, 415, 425, 435, 450, 470, 490, 505, 515, 565, 572, 590, 605, 615, and 632 nm. The results are shown in figure 6. This figure shows a 3D graph of excitation wavelengths from LEDs together with PL emission spectra for sample 1. All samples demonstrated strong photoluminescence peaks in the visible range (650 – 710 nm) due to the PL emission from Sm$^{3+}$ ions in the glass matrix. Figure 7 presents the PL spectra before and after 60 minutes of X-ray irradiation of sample 1. The PL signal, as expected, is a typical Sm$^{3+}$ emission spectrum. However, no conversion from Sm$^{3+}$ to Sm$^{2+}$ is observed after 60 min of X-ray irradiation. It can be seen from figures 8 and 9 that the PL generated by using two excitation sources (460 and 535 nm) has no PL signature from Sm$^{2+}$ ions; even after annealing at 650 °C for 3 hours, there is no evidence of x-ray induced Sm$^{3+}$ to Sm$^{2+}$ conversion. Glass samples are stable under X-ray irradiation; the only effect is a minor transparent darkening.

A typical fluorescence of Sm$^{3+}$ ions is observed with four strong peaks corresponding to transitions for all samples:

\[
\begin{align*}
564 \text{ nm} & \leftrightarrow 4G_{5/2} \rightarrow 6H_{5/2} \\
600 \text{ nm} & \leftrightarrow 4G_{5/2} \rightarrow 6H_{7/2} \\
645 \text{ nm} & \leftrightarrow 4G_{5/2} \rightarrow 6H_{9/2} \\
710 \text{ nm} & \leftrightarrow 4G_{5/2} \rightarrow 6H_{11/2}
\end{align*}
\]

Figure 6. Excitation and emission wavelength vs. PL intensity of sample 1.

Figure 7. Photoluminescence (460 nm excitation) of sample 1 before and after 60 min X-ray irradiation. The PL arises from Sm$^{3+}$ ions in the glass matrix.

Figure 8. PL (535 nm excitation) of glass samples after 60 min X-ray irradiation.

Figure 9. PL (460 nm excitation) of annealed glass samples (650 °C) after 60 min X-ray irradiation.
4. Conclusions
4.1. ZSPB glasses doped with Sm with a gradual increasing of ZnSe content from 6.5 to 66.5 mol% to replace ZnO were synthesized. These glasses are transparent, homogeneous, non-hydroscopic and nontoxic with high glass transition temperatures above 500°C.
4.2. ZnSe addition to ZnO based borophosphate glasses leads to an increase of the glass transition temperature by approximately 20°C.
4.3. Glass transition temperatures do not significantly change with the variation of ZnSe to replace ZnO in the oxyselenide glass matrix (backbone structures are identical).
4.4. The similarity of ZnO and ZnSe borophosphate glass structures is confirmed by Raman spectroscopy.
4.5. ZnSe based glasses demonstrate strong photoluminescence in the visible wavelength range due to Sm³⁺ ions in the glass matrix.
4.6. After 60 min of X-ray irradiation of annealed and non-annealed samples, the PL signal generated by using two excitation sources (460, 535 nm) shows only the Sm³⁺ spectra (no conversion of Sm³⁺ to Sm²⁺) with some minor transparent darkening.

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References
[1] Edgar A 2006 Springer Handbook of Electronic and Photonic Materials eds S.O.Kasap, P.Capper (New York, NY, USA: Springer Science) chapter 40 pp 983
[2] Stoeva Z, Patronov G, Kostova I, Chrysanthou A, Tonchev D and Kasap S 2013 Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B 54 121
[3] Kostova I, Pashova T, Patronov G, Tonchev D and Eftimov T 2013 Scientific research of the Union of Scientists in Bulgaria-Plovdiv: series C. Natural Sciences and Humanities ed S. Vasilev vol XVI (Plovdiv, BG: House of Scientist) pp 231
[4] Patronov G, Kostova I and Tonchev D 2013 Bulgarian Chemical Communications 45 536
[5] Tonchev D at al. 2014 Nanoscience advances in CBRN agents detection, information and energy security eds P. Petkov, W. Kulish, D. Tsiliyanu (Dordrecht, NL: Springer the NATO-ASI Science for peace and security series: A – Chemistry and Biology) (accepted for publication)
[6] Belev G, Okada G, Tonchev D, Koughia C, Varoy C, Edgar A, Wysokinski T, Chapman D and Kasap S 2011 Phys. Status Solidi C 8 2822
[7] Ciceo-Lucacel R, Radu T, Ponta O, Simon V 2014 Materials Science and Engineering C 39 61
[8] Edgar A, Varoy C, Koughia C, Okada G, Belev G and Kasap S 2013 Journal of Non-Crystalline Solids 377 124
[9] Brow R, Bencoe D, Tallant D and Kovacic L 1997 United States Department of Energy Sandia Corporation SAND97-2391 UC-704 8