

Synthesis and properties of Er-doped $\text{KPO}_3\text{-Ca}(\text{PO}_3)_2$ glass and glass-ceramic

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ABSTRACT

In the present work, we studied Er-doped $\text{KPO}_3\text{-Ca}(\text{PO}_3)_2$ metaphosphate glass and its devitrification behavior. It is shown that two concurrent crystallization processes (surface and bulk crystallization) are observed in this glass with the precipitation of two different phases of $\text{KCa}(\text{PO}_3)_3$: the hexagonal phase is mostly formed at the surface, whereas the orthorhombic isomorph is found in the bulk. The possibility of synthesizing a transparent glass-ceramic is demonstrated. From the changes in the spectroscopic properties of the obtained glass-ceramic materials, Er^{3+} ions are suspected to enter into the lattice of the $\text{KCa}(\text{PO}_3)_3$ crystal.

Keywords: phosphate glasses, glass-ceramic, erbium.

1. INTRODUCTION

Phosphate glasses are of great technological interest due to their specific thermal properties like low thermal glass transition and melting temperatures. In comparison to silicate glasses, the solubility of the rare-earth elements (REE) is higher and the REE-optical centers typically exhibit higher absorption/emission cross sections in phosphate glasses. For these reasons, REE-doped phosphate glasses have been used for many years as active media for lasers and optical amplifiers[1].

To the moment it became clear that transparent ceramic materials have a great potential as a host medium for optical applications, special attention has been paid to the glass-ceramic (GC) materials. Such materials allow to combine the flexibility and scalability of the glass fabrication process with the good thermal and optical properties of the crystalline materials [2]. In this context, the fabrication of transparent REE-doped GCs starting from phosphate glasses should be the next step in the development of the active optical media for laser applications. However, despite the significant progress in the development of oxyfluoride glass-ceramics, studies on phosphate based GC are still limited.

According to the phase diagram of the $\text{KPO}_3\text{-Ca}(\text{PO}_3)_2$ system[3], devitrification of the glass with $\text{K/Ca}=1$ should result in a single crystalline phase, namely $\text{KCa}(\text{PO}_3)_3$ compound. Due to the similarity of the ionic radii of Ca^{2+} and Er^{3+} , it should be possible to incorporate Er^{3+} ions in the lattice of the $\text{KCa}(\text{PO}_3)_3$ crystal.

In this work, we present our recent results on the development of a Er^{3+} doped phosphate GC with the composition $50\text{KPO}_3\text{-}50\text{Ca}(\text{PO}_3)_2$. We report the thermal, optical as well as structural properties of the synthesized glass and glass-ceramic materials.

2. MATERIALS AND METHODS

2.1 Glass preparation

The glass with the composition of $49\text{KPO}_3\text{-}49\text{Ca}(\text{PO}_3)_2\text{-}2\text{Er}_2\text{O}_3$ (in mol.) was prepared by conventional melt-quenching approach. KPO_3 and $\text{Ca}(\text{PO}_3)_2$ precursors were independently prepared from mixtures of the K_2CO_3 and H_3PO_4 (85 wt. % in H_2O) and of the CaCO_3 and $(\text{NH}_4)_2\text{HPO}_4$, respectively. The synthesis of the precursors was confirmed using XRD. The batch was melted at 1100°C for 30 minutes in a Pt-crucible, quenched by pouring the melt on a brass plate and annealed for 10 minutes at T_g and slowly cooled to release the stress induced during the quench.

2.2 Glass characterization

The thermal properties were measured using a Netzsch F1 instrument. Bulk glasses were used for the experiment and the heating rate was $10^\circ\text{C}/\text{min}$.

The Raman spectra were measured using an inVia™ Qontor® Renishaw confocal Raman microscope using a 405 nm laser.

The absorption spectra were measured using Lambda 1050 UV-VIS-NIR spectrophotometer (PerkinElmer, USA).

The Panalytical EMPYREAN multipurpose X-Ray Diffractometer with a nickel filtered copper $K\alpha$ radiation was used to measure the XRD pattern of the glasses. The samples were crushed into fine powder and spread over a “zero-background holder” Si-plate. The spectra were obtained using the Bragg-Brentano geometry and by rotating the sample holder around the Phi-axis at a constant speed of 16 revolutions per minute.

The emission spectra of the investigated glasses were measured using Spectro 320-131 Vis-NIR emission spectrometer (Instrument Systems, Germany). A monochromatic single-mode fiber pigtailed laser diode (CM962UF76P-10R, Oclaro) emitting at 965 nm was used for the excitation.

3. RESULTS AND DISCUSSION

3.1 Thermal properties

The DTA curve of the as-prepared glass is shown in Figure 1a. Besides the endothermic glass-liquid transition peak with inflection point at $T_g=433$ °C (onset at 425 °C) and, two exothermic peak are observed at $T_{p1}=587$ and $T_{p2}=646$ °C, evidencing about two crystallization processes happening in the glass, the onset of the first crystallization peak is at $T_x=558$ °C indicating that the glass is stable against crystallization ($T_x-T_g > 100$ °C)

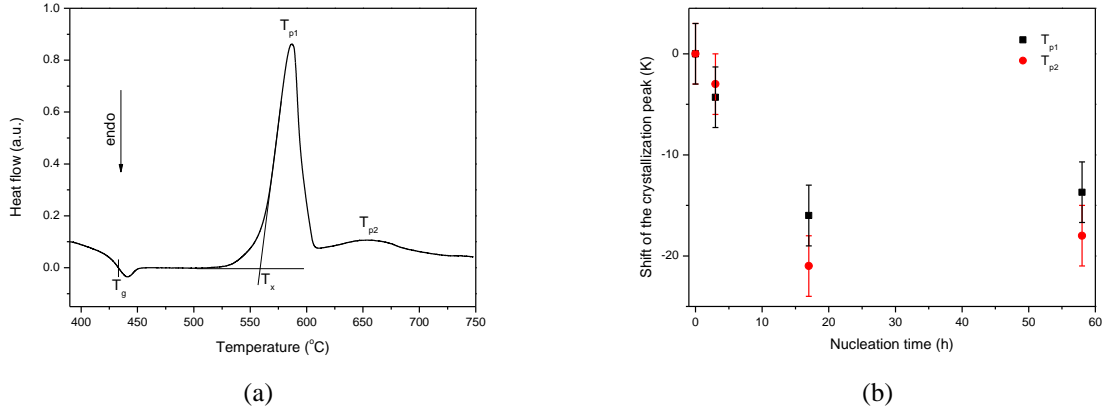


Figure 1. (a) DTA curve of the as-prepared glass. (b) Shift of the crystallization peaks position relative to the ones observed for the as-prepared glass.

Following Marotta et al.[4], to determine the temperatures and times for controlled devitrification of the glass, the glass was nucleated at 425, 435, 445 and 455 °C for 3 h and the DTA curve was recorded for each of the nucleated glasses to measure the crystallization peaks. The T_{p1} was found to shift to 582.5°C (-4.5 °C), independently of the nucleation temperature. This allows to conclude that the nucleation rate does not change significantly within this temperature range. The glass was, then, nucleated at 425 °C for 1, 3, 17 and 58 hours. As seen in Figure 1b, a systematic shift of the two crystallization peaks can be observed. The degree of nucleation approaches the saturation already after 17 h treatment.

3.2 Glass-ceramics preparation

A two-step heat-treatment procedure was used to produce the glass-ceramics and the details are given in Table 1.

Table 1. The heat treatment parameters

ID	Nucleation		Growth	
	Temp.(°C)	Time(h)	Temp.(°C)	Time(min)
GC-A1	425	17	595	5
GC-A2	425	17	595	10
GC-B	425	58	595	5
GC-C	440	58	640	1

The pictures of the as-prepared glass prior to and after heat treatment are shown in Figure 2a.

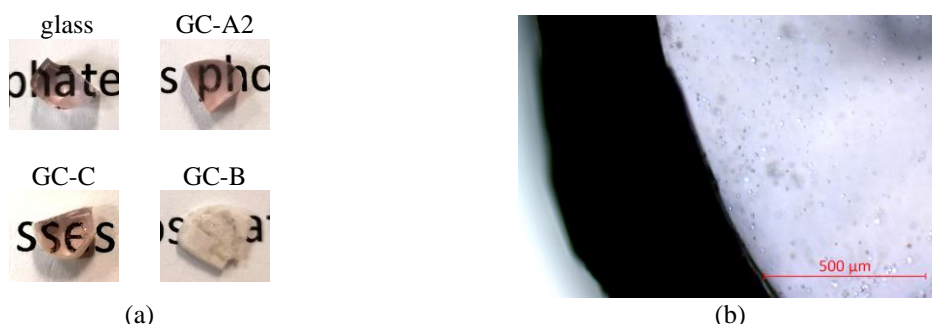


Figure 2. (a) Picture of the prepared glass and glass ceramic materials. (b) Optical microscope image of GC-A1 sample: both crystallized surface and internal crystallites are visible on the

For the samples GC-A1, GC-A2 and GC-C a crystalline layer was formed at the surface and crystals could also be seen in the volume of the glass (Figure 2b) whereas GC-B is almost completely crystallized. However, in all samples, including GC-B, it is possible to recognize relatively loose surface layer and dense internal part.

3.3 Structural characterization

The XRD pattern of the glass-ceramics were measured and are shown in Figures 3.

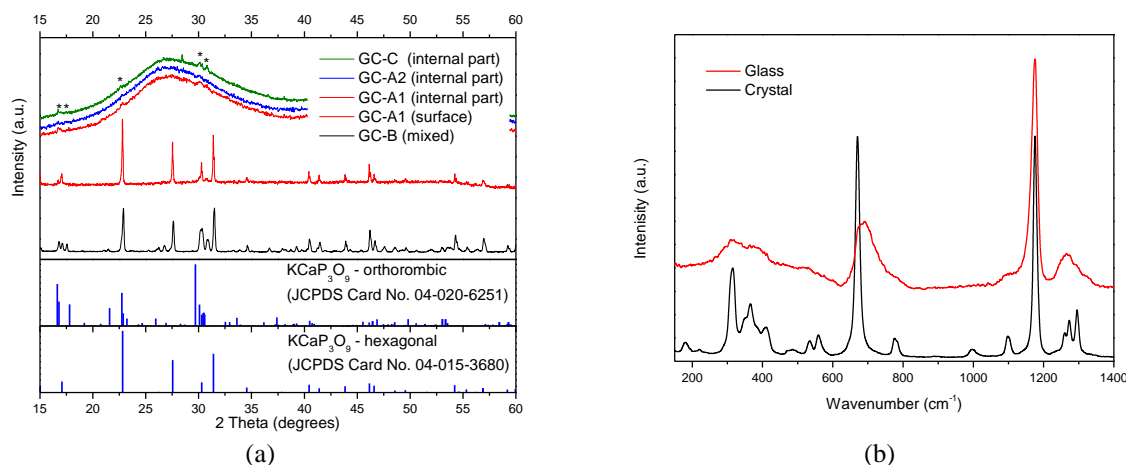


Figure 3. (a) XRD patterns of the GCs. The patterns of GC-C and GC-A2 were obtained from the internal part of the sample, after removal of the outer layer; both internal part and crystallized surface layer patterns are shown for GC-A1; GC-B sample is a mixture of both internal and outer parts. The peaks present inside the GC-A1, GC-A2 and GC-C samples are marked with * and correspond to orthorhombic $KCaP_3O_9$. (b) Raman spectra of the glass and of the GC-B sample measured in the inert part. The Raman spectrum of the glass is shifted vertically for clarity.

The XRD pattern of the GC-B sample shows that it is highly crystallized with two isomorphs of $KCaP_3O_9$ crystal: orthorhombic and hexagonal (Figure 3a). The latter one is a high-temperature isomorph of the calcium potassium cyclotriphosphate. At the same time, the surface layer of the GCs consists mostly of the hexagonal phase, as it can be seen from the XRD pattern of the GC-A1 outer layer (Figure 3a). Only orthorhombic $KCaP_3O_9$ phase can be in the internal transparent parts of the GC-A1, GC-A2 and GC-C (the outer layer was removed mechanically before the measurement).

According to the Raman scattering (Figure 3b) the structure of the glass is dominated by Q^2 structural units, which is typical for metaphosphate glasses. More detailed description of the vibrational bands can be found elsewhere[5]. Also shown is the Raman spectrum of the glass after heat treatment (GC-B), measured at the glassy spot. It is clearly shown that amorphous and crystalline phases of the compound consist of the same structural units at the short-range order although the width of the Raman bands decreases significantly upon the crystallization.

3.4 Emission and absorption properties

The absorption spectra of the as-prepared glass and glass-ceramic samples are shown in Figure 4.

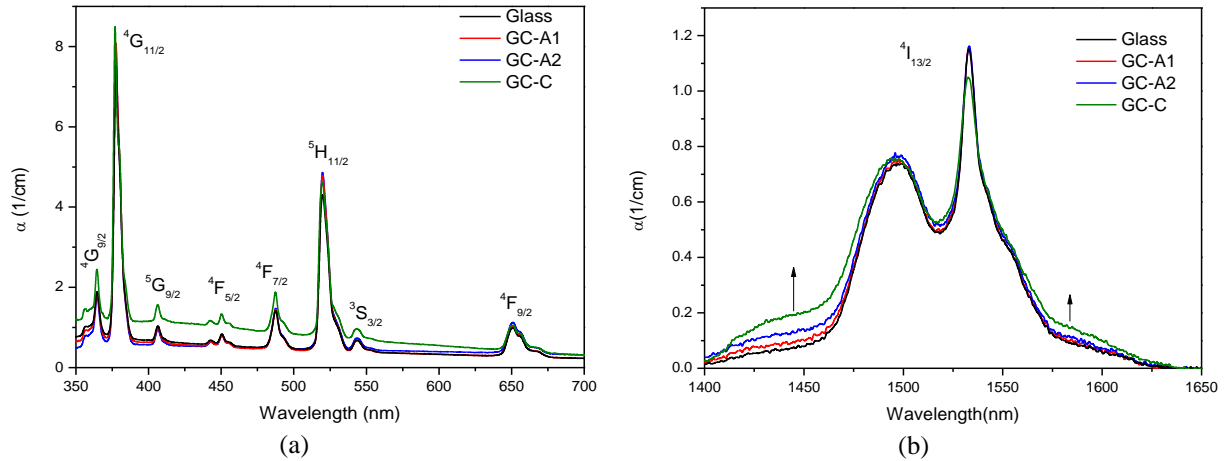


Figure 4. Visible (a) and NIR (b) absorption spectra of the glass and glass-ceramics. The optical transitions are observed from the $^4I_{15/2}$ ground state, whereas the labels at the top of each peak correspond to the final state.

The spectra exhibit absorption bands which are attributed to Er^{3+} 4f-4f transitions. It is well known that these transitions are well shielded from external fields of the Er^{3+} surrounding. It is found, that the absorption coefficient at 377 nm ($^4I_{15/2} \rightarrow ^4G_{11/2}$) for all the GCs and at 520 nm ($^4I_{15/2} \rightarrow ^5H_{11/2}$) for GC-A1 and GC-A2 increase after crystallization. The NIR absorption band at about 1530 nm ($^4I_{15/2} \rightarrow ^4I_{13/2}$) also becomes broader due to the increase of the absorption at 1450 and 1580 nm shoulders. The changes in the absorption spectra tend to indicate that the site of Er^{3+} ions is modified after heat treatment. One should remind that the $^4I_{15/2} \rightarrow ^4G_{11/2}$, $^4H_{11/2}$ optical transitions are hypersensitive, and the changes observed for this band confirms that part of the Er^{3+} ions is entering a new site after the crystallization, most probably incorporating into the crystalline lattice. At the same time, some increase of the baseline is observed in GC-C, due to higher scattering present in this sample. The crystallization also leads to changes in the shape of the Er^{3+} emission band centered at 1.5 μm (Figure 5).

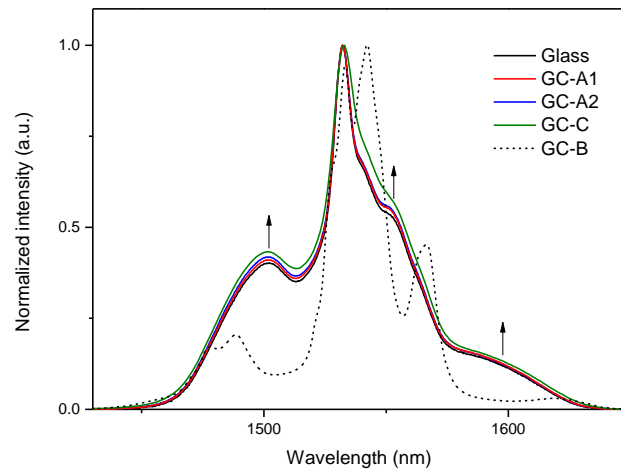


Figure 5. Normalized emission spectra of the glass prior to and after heat treatment under 965 nm excitation.

The partially crystallized glasses (GC-A1, A2 and C) exhibits a broader emission band due to an increase of the relative intensities at 1500, 1550 and 1600 nm. The crystallized GC-B sample exhibits an emission band with several well-resolved peaks as compared to the parent glasses. The intensity of GC-A2 sample emission is about 20% higher than the emission from the as-prepared glass while the intensity of GC-B sample emission increases twice when compared to the as-prepared glass confirming that the Er^{3+} ions are located in a more defined environment around Er^{3+} ions in this case.

4. CONCLUSIONS

Er -doped $KCa(PO_3)_3$ metaphosphate glass and especially its devitrification behavior have been studied. The heat treatment leads to surface and bulk crystallization with formation of two different phases of $KCa(PO_3)_3$: orthorhombic and hexagonal. The optimization of the heat-treatment procedure allowed us to prepare transparent Er -doped phosphate glass-ceramic. Small changes in the optical properties are observed for the transparent GCs, which can be explained by the similarity of the short-range order between the amorphous glass and the

crystalline $\text{KCa}(\text{PO}_3)_3$. Nevertheless, it is shown that the devitrification leads to a broadening of the Er^{3+} absorption and emission bands at $1.5 \mu\text{m}$, due to the incorporation of Er^{3+} ions in the crystalline lattice. It is shown, that changes in the shape and an increase in the intensity of the emission can be expected from the Er-doped $\text{KCa}(\text{PO}_3)_3$ GCs with higher degree of crystallinity.

ACKNOWLEDGEMENTS

Academy of Finland (Flagship Programme, Photonics Research and Innovation PREIN-320165 and Academy Project -326418) is greatly acknowledged for the financial support.

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