



Novel oxyfluorophosphate glasses and glass-ceramics



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ABSTRACT

Effect of CaF₂ addition at the expense of CaO on the thermal, physical, optical and structural properties of glasses in the NaPO₃-CaO system was studied. The glasses were prepared by the conventional melt quenching method. For each glass, the thermal properties were studied by differential thermal analysis (DTA) and the optical properties by UV-Vis-NIR spectroscopy. The changes in the glass structure induced by the progressive replacement of CaO by CaF₂ were investigated using IR and Raman spectroscopies. The glasses were heat treated at 20 °C above their respective glass transition temperature for 17 h to form nuclei and then at their peak crystallization temperature for 1 h to grow the nuclei into crystals. An increase in the CaF₂ content increased the polymerization of the phosphate network leading to shift of the band gap to lower wavelength and reduced the crystallization tendency of the glasses. At least two crystalline phases precipitated in all the investigated glasses, the composition of which depended on the CaF₂ content. Finally, bulk crystallization was suspected to occur in the oxyfluorophosphate glasses.

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1. Introduction

It is well known that fluoride glasses usually have lower phonon energy than oxide glasses, while oxide glasses usually have much better chemical durability, thermal stability and mechanical strength than the fluoride glasses. In that sense, the combination of oxides and fluorides, particularly to give so-called oxyfluorophosphate glasses, appears to be very interesting [1]. Fluorophosphate glasses have been studied for their use in high power and excimer lasers, microlithography, IR optical fibers and in UV-transmitting materials [2]. Depending on their composition, they can possess low refractive index and high transmittance in infrared and ultraviolet regions [3]. The most important technological advantage of fluorophosphate glasses is that they can more easily be prepared than their silica glass competitors.

Many investigators introduced fluorine in oxide based glasses and studied the nature of its bonding with the network forming cations [4–5]. Recently, the ternary phosphate glass series (50 – x)CaO–xCaF₂–50P₂O₅ (x = 0–20 mol%) was investigated [6]. It was found that increasing the CaF₂ content gives rise to an increase in both the density and the molar volume, and decreases the refractive index. The increase in the optical band gap energy and the decrease in the Urbach energy induced by the increase in CaF₂ content were related to the increase in the average number of the bridging oxygen atoms.

Over the years, glass-ceramics have turned out to be one of promising materials as they have found widespread use for various applications in the electro-optical, construction, dental, bioactive fields and so on [7]. In contrast with spontaneous surface crystallization, which is normally not wanted in glass manufacturing, these glass-ceramics are usually produced via controlled crystallization of the glass in a two stage heat treatment, namely a nucleation and a crystal growth stage. This procedure has some advantages in comparison with the ceramics that are produced via the powder metallurgy approach, e.g. minimal or even zero porosity, and homogeneous microstructure [8]. To the best of our knowledge, there have been only a few studies on the development of oxyfluorophosphate glass-ceramics.

In this study, we examine the impact of substituting fluorine for oxygen on the thermal, structural and optical properties of glasses with the composition 75NaPO₃–(25 – x)CaO–xCaF₂ (in mol%) when x = 0, 5, 10, 15 and 20. In addition, the influence of fluorine on the crystallization of the glasses is assessed with the aim to define a glass composition that can be processed into glass-ceramic.

2. Experimental

2.1. Glass preparation

Glasses with the composition 75NaPO₃–(25 – x)CaO–xCaF₂ (in mol%) with x = 0, 5, 10, 15 and 20 were prepared by the conventional melt quenching technique using analytical grade chemicals of NaPO₃, CaO, and CaF₂. The batches of 25 g were melted in a covered platinum

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crucible at 900 °C for 10 min. Then, the melt was casted in a graphite mold and annealed for 4 h at 40 °C below the glass transition temperature. X-ray diffraction analysis was performed to confirm the amorphous nature of the samples. No sharp diffraction peaks were observed in the diffraction patterns confirming that the as-prepared glasses are amorphous.

A Metrohm ion chromatography apparatus (Metrohm, Switzerland) was used to quantify the fluorine content in the glasses. Powdered glasses were dissolved in 50 ml of *nitric acid* (0.5 mol/L) at 50 °C for 10 min and then diluted 20 times for the measurement. Except for fluorine, the composition of the as-prepared glasses was found to be in accordance with the theoretical ones, within the accuracy of the measurement (~0.1 wt%). According to the IC analysis, about 10 at-% of fluorine had evaporated during the 10 min of melting.

2.2. Thermal and physical properties

Differential thermal analysis was carried out at a heating rate of 10 °C/min up to 600 °C on glass particles with the size ranging from 300 to 500 μm. The glass transition temperature (T_g) was taken at the inflection point of the endotherm peak. The onset (T_x) and peak (T_p) crystallization temperatures were taken at the inflection point and the highest point of the first exothermic peak, respectively. The accuracy of the measurement is ± 3 °C.

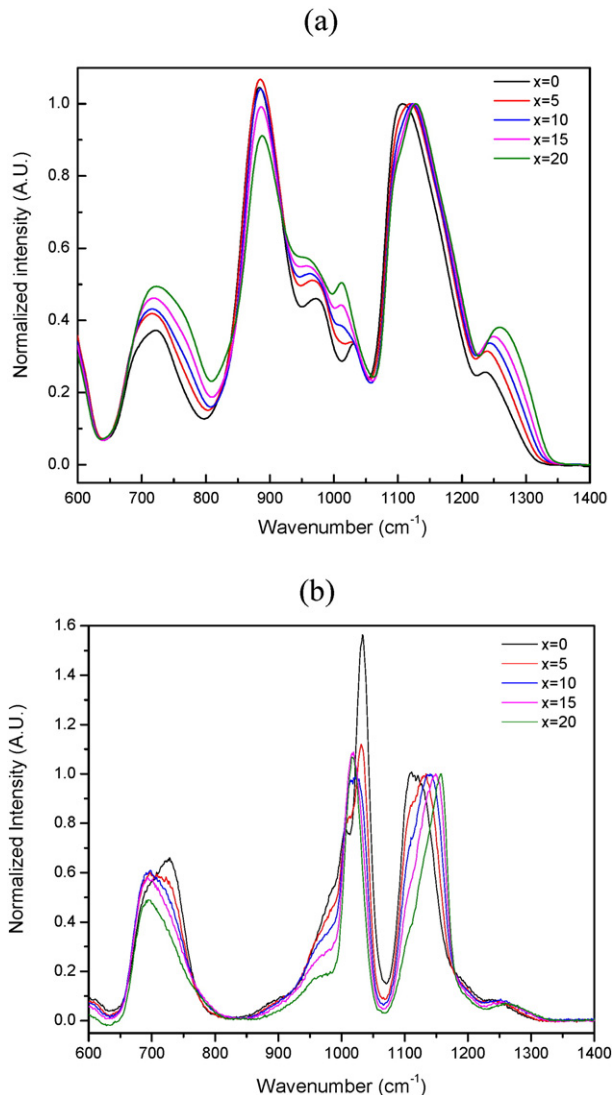


Fig. 1. IR (a) and Raman (b) spectra of the investigated glasses.

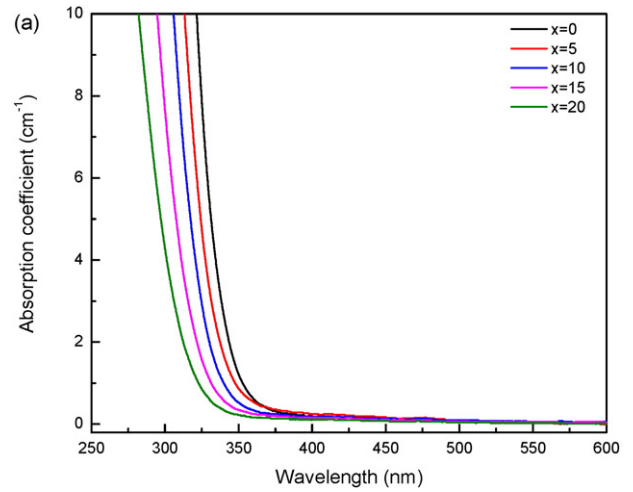


Fig. 2. Absorption spectra of the investigated glasses.

The density of the glass samples was determined using the standard Archimedes method at room temperature using ethanol as the immersion fluid. The accuracy of the measurement is ± 0.02 g/cm³.

2.3. Optical properties

The optical absorption spectra were recorded using a Shimadzu UV-3600 plus UV-Vis-NIR spectrophotometer in the spectral range from 200 nm to 700 nm. The spectra were corrected for Fresnel loss and sample thickness.

2.4. Structural properties

The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the glasses crushed into powder were recorded using a Perkin Elmer FTIR spectrometer equipped with a MIRacle single reflection ATR accessory (Pike Technologies). All spectra were measured within the range 600–1400 cm⁻¹ at room temperature and normalized to the absorption band at ~1100 cm⁻¹.

The Raman scattering measurements of polished glasses were measured from 600 to 1400 cm⁻¹ using a confocal micro-Raman microscopy (LabRam, Jobin-Yvon/Horiba) at room temperature. The excitation source was a 532 nm continuous wave laser. The applied power on the sample was 20 mW. The back-scattered light was collected through a Notch filter towards a cooled CCD detector. All spectra were normalized to the band at ~1100 cm⁻¹.

2.5. Glass crystallization

The investigated glasses were heat treated in a muffle furnace first at $T_g + 20$ °C for 17 h to form nuclei and then at T_p for 1 h to grow the nuclei into crystals. The polished glass pieces were placed on a platinum foil to prevent contamination from the sample holder. The heat treatments were performed in air.

Table 1

Glass transition temperature (T_g), temperature of crystallization onset (T_x), resistance to crystallization ($\Delta T = T_x - T_g$) and the density of the investigated glasses.

x	T_g [°C] (± 3 °C)	T_x [°C] (± 3 °C)	$\Delta T = T_x - T_g$ [°C] (± 6 °C)	T_p [°C] (± 3 °C)	Density [g/cm ³] (± 0.02 g/cm ³)
0	354	470	116	485	2.73
5	303	473	170	497	2.72
10	294	516	222	552	2.71
15	273	487	214	525	2.70
20	256	359	103	383	2.69

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