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Review

New tungstate fluorophosphate glasses

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Abstract

A new class of tungstate fluorophosphate glasses was identified in the $NaPO_3$–BaF_2–WO_3 ternary system. The variation of several physical properties was determined with respect to chemical composition. Characteristic temperatures, density and refractive index increase as tungsten oxide content increases. The optical transmission range and specially the energy bandgap depend of the WO_3 amount. No crystallization could be observed for the most WO_3 concentrated vitreous samples ($\geqslant$20% molar). Color and optical properties of the glasses depend of the melting time because of the presence of reduced tungsten species like W^{5+} and W^{4+}. In addition, photodarkening is observed in tungsten rich glass samples under UV laser illumination and this phenomenon can be reversible by heat treatment near the glass transition temperature.

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1. Introduction

Phosphate and fluorophosphate glasses make a special group of optical glasses of technological interest. Their specific properties include larger thermal expansion coefficient, smaller liquidus viscosity and softening temperatures than silicate glasses. They have been developed for UV transmission and also as laser hosts with reduced non-linear refractive index. Other non-optical fields of interest include ionic conductivity and sealing [1]. Another interesting feature of these glasses is their ability to incorporate large amounts of transition metal, alkali and rare earth oxides without reduction of glass forming ability. Spectroscopic studies of doped glasses have been implemented in the scope of active applications while the ability of tungsten to have several oxidation states opens possibilities for electro-optical applications [2–5].

Numerous fluorophosphate glasses based on the association of sodium polyphosphate and divalent fluorides have already been reported [6,7]. This work intents to define a new group of fluorophosphate glasses, tungstate fluorophosphate glasses based on the ternary $NaPO_3$–BaF_2–WO_3 association. It was expected that tungsten oxide content would influence significantly thermal and optical properties [8–10]. Especially, large WO_3 concentrated vitreous samples would be very stable against devitrification [11–15] and would present special properties observed in crystalline WO_3 such as thermochromism, photochromism [16,17] or non-linear optical properties [18–23]. The aim of this study is to determine the effect of WO_3 incorporation on the

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thermal, physical and optical properties of a fluorophosphate-based glass and determine the influence of synthesis conditions on the oxidation state of tungsten atoms in the glass.

2. Experimental

2.1. Glass preparation

These glasses were synthesized by conventional method. Powdered starting materials were:

- Tungsten oxide WO_3 (99.8% pure).
- Sodium polyphosphate $NaPO_3$ (99+% pure).
- Barium fluoride BaF_2 (99.8% pure).

In a first step, powders were mixed and heated at 400 °C for 1 h to remove water and adsorbed gases. Then, the batch was melted at a temperature ranging from 800 °C to 1100 °C, depending on WO_3 content. Liquid was kept at this temperature for 15–75 min to ensure homogenization and fining. In practice, the melting time must be longer for higher WO_3 concentrations to remove the blue coloration of the vitreous samples expected to be due to tungsten reduction processes. The influence of the melting time on physical and optical properties is reported in this work. Finally the melt was cooled in a brass mold preheated below the glass transition temperature T_g (T_g – 20 °C). Annealing was implemented at this temperature for several hours in order to minimize mechanical stress resulting from thermal gradients upon cooling. Bulk samples were cut and polished before performing optical measurements.

2.2. Physical measurements

Characteristic temperatures (T_g for glass transition, T_x for onset of crystallization and T_p for maximum of crystallization peak) were determined by differential scanning calorimeter (DSC). The estimated error on the temperature is 2 K for glass transition and onset of crystallization witch are obtained from tangents intersection and 1 K for the position of the crystallization peak. Powdered samples were set in aluminum pans under N_2 atmosphere at 10 K/min heating rate. Infrared transmission spectra were recorded with a BOMEM Michelson Spectrophotometer in the 5000–2000 cm^{-1} range. Ultraviolet transmission between 300 and 500 nm was studied using a Varian spectrophotometer Cary 5. The densities were determined by pycnometry under He pressure (Micromeritics Accupyc), which allows a precision of about 10^{-4}. The refractive index was measured at 633 nm (He–Ne laser) using a Metricon prism coupler and the estimated error on these measurements is ±0.001.

3. Results

3.1. Vitreous domain

Glass forming area in the $NaPO_3$–BaF_2–WO_3 ternary system is drawn in Fig. 1. Limiting compositions correspond to quenched glasses. Sodium polyphosphate $(NaPO_3)_n$ which exists as a glass forms binary glasses with BaF_2 and WO_3. Up to 80 mol% of WO_3 could results in vitreous phases, even in the $NaPO_3$–WO_3 binary system. Only ceramics were obtained in the WO_3–BaF_2 system. However vitrification could occur with the addition of 10 mol% $NaPO_3$ or less. This suggests that rare earth alkali fluorotungstate glasses could be synthesized.

A set of samples with increasing WO_3 content were prepared according to the following composition rule: $(80–0.8x)NaPO_3$–$(20–0.2x)BaF_2$–xWO_3, x varying between 0 and 60 mol%. These compositions contain a constant $[NaPO_3]/[BaF_2]$ ratio in order to study the effect of WO_3 incorporation. As tungsten concentration increases, samples appear yellowish.

3.2. Thermal analysis

Characteristic temperatures were recorded using the DSC technique up to 600 °C. They are reported in Table 1 which also gives the value of the thermal stability range T_x–T_g as an estimate of glass stability. This value is not reported when crystallization peak is not observed at the applied heating rate (10 K min^{-1}).

As shown in Fig. 2, glass transition temperature increases from 240 °C to 524 °C as the amount of WO_3 rises from 0% to 60%. This increase of T_g with respect to the WO_3 concentration was already described for several glass matrix [9–11,24,25].

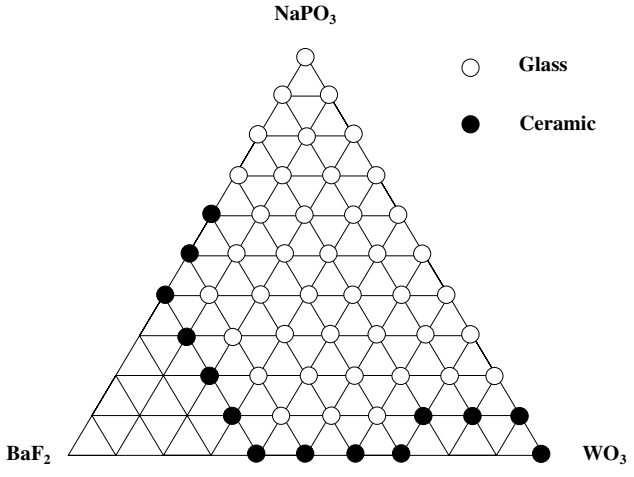

Fig. 1. Phase diagram in the $NAPO_3$–BaF_2–WO_3 ternary system.