

CRYSTALLIZATION IN LEAD TUNGSTEN FLUOROPHOSPHATE GLASSES

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ABSTRACT

The glass forming ability was investigated in the ternary system $\text{NaPO}_3\text{-WO}_3\text{-PbF}_2$ with a constant $\text{NaPO}_3/\text{WO}_3$ ratio of 3/2 and increasing amounts of PbF_2 . It has been found that glass samples can be obtained from PbF_2 contents from 0 mole% to 60 mole%. The most lead fluoride concentrated samples (50% and 60%) were chosen for a crystallization study in order to investigate the possibility of obtaining glass-ceramics containing crystalline lead fluoride. DSC measurements allowed to determine the characteristic temperatures such as T_g , T_x , T_p and T_f . These glass samples were heat-treated near the crystallization peaks observed by thermal analysis. X-ray diffraction results of these heat-treated glasses pointed out that the dominant phase which precipitates from the glass sample containing 50% of PbF_2 is

the lead fluorophosphates phase $Pb_5F(PO_4)_3$ whereas the sample containing 60% of PbF_2 exhibits a preferential crystallization of cubic lead fluoride β - PbF_2 .

Key-words: glasses, phosphate, lead fluoride.

INTRODUCTION

Phosphate compounds are interesting glass formers and are largely investigated for their specific properties with respect to other classical glass formers such as silicate, borate or germanate glasses. Particularly, they are well known for their small liquidus viscosity, softening temperatures, large UV transparency and high solubility for other glass modifiers or intermediaries such as alkaline, rare earth or transition metal compounds⁽¹⁻³⁾. Another interesting behavior of phosphates glasses is their ability to incorporate fluoride compounds without reduction of the glass forming ability. These vitreous materials are known as fluorophosphate glasses and are of great interest for rare earth luminescence since the fluoride compounds strongly reduce the phonon energy of the glass host⁽²⁻³⁾. Heavy metal fluoride compound were also incorporated in several other glass formers and these materials were used to prepare the well-known ultratransparent glass ceramics⁽⁴⁻⁶⁾. These rare earth doped materials exhibit highly efficient luminescent properties since rare earth ions tend to migrate to the heavy metal fluoride crystalline phase during heat-treatment. On the other hand, tungsten phosphate glasses based on the binary system $NaPO_3$ - WO_3 are well-known for their great glass forming ability and very high thermal stability against devitrification due to the intermediary behavior of tungsten octahedra inside the metaphosphatene network⁽⁷⁻⁸⁾.

For these reasons, this work investigated the glass forming ability in the ternary system $NaPO_3$ - WO_3 - PbF_2 with a constant $NaPO_3/WO_3$ ratio of 3/2 and increasing amounts of PbF_2 . The thermal properties were investigated by DSC and the most PbF_2 concentrated samples were selected for investigation of the crystallization properties. These samples were heat-treated at specific temperatures determined

from the DSC curves and the resulting crystalline phases were identified by X-ray diffraction.

EXPERIMENTAL PART

Investigated compositions were prepared from the starting compounds $\text{NH}_4\text{H}_2\text{PO}_4$ 48% in P_2O_5 from Aldrich, Na_2CO_3 98% from Aldrich, WO_3 99,9% from Aldrich and PbF_2 99,9% from Aldrich. The starting powders were weighted using an analytical balance and grinded in an agate mortar. The resulting powder was transferred to a covered platinum crucible, heated at 400°C for 1 hour to remove residual moisture and adsorbed gases, at 600°C for 1 hour to promote $\text{NH}_4\text{H}_2\text{PO}_4$ and Na_2CO_3 decomposition and at 850°C for 10min for melting of these starting powders. The materials were kept at this temperature for only 10min to minimize fluoride losses and the melt was manually homogeneized after 5min and 10min. Finally, the melt was poured in a steel mold preheated 20°C below T_g and annealed at this temperature for 4 hour before cooling to room temperature inside the furnace. DSC curves were obtained on bulk glass samples of 10mg in aluminum pans between 160°C and 470°C at 10°C/min under N_2 atmosphere. These thermal analyzes were obtained using a DSC 200 F3 Maia calorimeter from Netzsch. X-ray diffraction measurements were performed on powder samples using a Rigaku Ultima IV diffractometer working at 40KV and 30mA between 10° and 70° in continuous mode of 0,02°/s. The crystalline phases were identified according to X-ray powder diffraction patterns (PDF file)⁽⁹⁾.

RESULTS AND DISCUSSION

The glass forming ability of compositions in the ternary system $(100-x)[0,6\text{NaPO}_3-0,4\text{WO}_3]-x\text{PbF}_2$ were investigated by melt-quenching and it was found that glasses can be obtained from $x=0$ to $x=60$. The most PbF_2 concentrated samples containing 50% and 60% of lead fluoride (labelled NaW50Pb and NaW60Pb) were selected for further characterizations since the main objective of this work is to

investigate the ability of these glass compositions to exhibit preferential PbF_2 crystallization. The molar compositions of these samples are summarized in Tab. 1.

Table 1: Molar compositions and characteristic temperatures of glass samples.

Sample	Molar composition	T _g	T _x	T _p	T _f	T _x -T _g
NaW50 Pb	30NaPO ₃ -20WO ₃ -50PbF ₂	237°C	312°C	325°C	-	75°C
NaW60 Pb	24NaPO ₃ -16WO ₃ -60PbF ₂	189°C	235°C	250°C	445°C	46°C

DSC curves of these samples are presented in Fig. 1 between 160°C and 470°C and allowed to determine the characteristic temperatures T_g, T_x, T_p and T_f as well as the thermal stability parameter T_x-T_g as presented in Tab. 1.

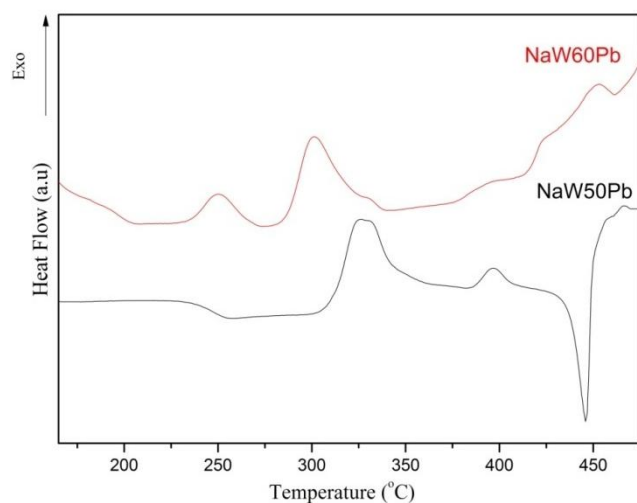


Figure 1. DSC curves of glass samples NaW50Pb and NaW60Pb.

It can be seen from these results that the thermal behavior of the glass samples is strongly dependent of the lead fluoride content. The glass transition temperature T_g decreases from 237°C to 189°C, which is in agreement with the expected modifier behavior of lead fluoride in the tungsten phosphate network. In fact, incorporation of fluoride compounds in covalent vitreous networks usually breaks the bridging bonds

by forming terminal bonds. In our case, it is assumed that terminal P-F and W-F bonds are formed and result in a strong decrease of the network connectivity. Thus, the glass transition temperature as well as thermal stabilities decrease since this less connected network is less viscous and tend to crystallize. Another important result extracted from the DSC curves is the identification of different crystallization peaks for each sample. Glass NaW50Pb exhibits to exothermic events centered at 312°C and 400°C whereas glass NaW60Pb presents two exothermic events at 235°C and 305°C. The melting event observed for sample NaW50Pb was not observed in the other sample, suggesting that at least one crystalline phase precipitated in this sample is not present in NaW60Pb. Since the main objective is to investigate eventual lead fluoride precipitation in these glasses, heat-treatments were performed to induce crystallization for further characterization. X-ray diffraction patterns of sample NaW50Pb heat-treated at 300°C (onset of the first crystallization event) for 2 hours and 390°C (onset of the second crystallization event) for 4 hours are presented in Fig. 2. The first heat-treated sample is mainly amorphous since the most intense event is the diffraction halo. A very weak diffraction peak centered at 30,5° is also observed. For the other sample heat-treated at higher temperature, intense diffraction peaks are observed without any residual diffraction halo, indicating the high crystallinity of this sample. Most of these diffraction peaks were attributed to the lead fluorophosphate phase $Pb_5F(PO_4)_3$, as illustrated in Fig. 2.

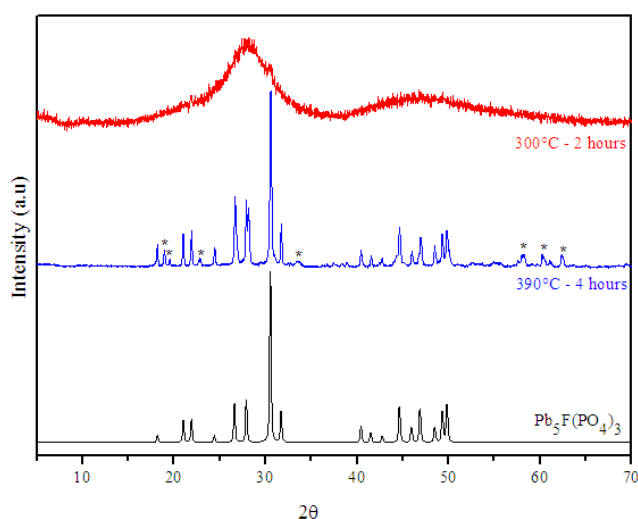


Figure 2. X-ray diffraction patterns of sample NaW50Pb heat-treated at 300°C for 2 hours, 390°C for 4 hours and crystalline $Pb_5F(PO_4)_3$.

Other weak diffraction peaks (identified by * in Fig. 2) were also observed but could not be attributed to any known phase containing the elements present in our sample and are not related with any lead fluoride crystalline phase. It can also be observed from Fig. 2 that the main diffraction peak of $\text{Pb}_5\text{F}(\text{PO}_4)_3$ is centered at $30,5^\circ$, suggesting that the weak diffraction peak observed for the sample annealed at 300°C is also due to a early stage of $\text{Pb}_5\text{F}(\text{PO}_4)_3$ crystallization. These results point out that this glass composition NaW50Pb is not promising for luminescent glass-ceramics since $\text{Pb}_5\text{F}(\text{PO}_4)_3$ is not a suitable crystalline host for rare earth ions due to high phonon energy of phosphate compounds. X-ray diffraction patterns of sample NaW60Pb heat-treated at 225°C (onset of the first crystallization event) for 1 hour and 300°C (onset of the second crystallization event) for 4 hours are presented in Fig. 3.

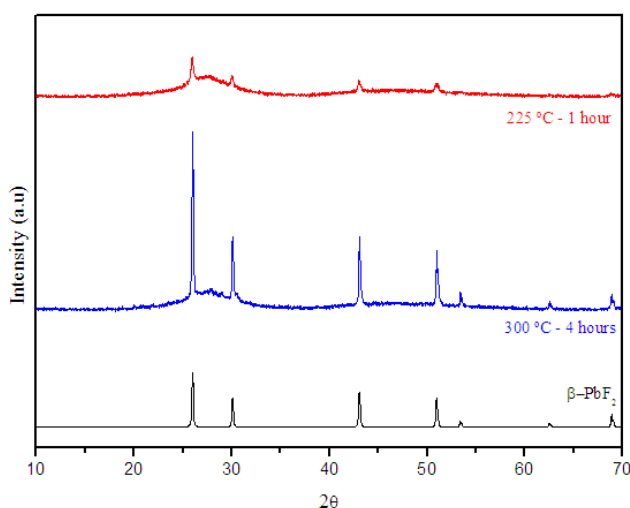


Figure 3. X-ray diffraction patterns of sample NaW60Pb heat-treated at 225°C for 1 hour, 300°C for 4 hours and crystalline $\beta\text{-PbF}_2$.

For this sample, it could be determined that cubic lead fluoride is precipitated under heat-treatment in both cases with a higher crystalline degree of the sample for higher heat-treatment temperature. In addition, results shown in Fig. 3 demonstrated that no other crystalline phase is precipitated under these conditions, suggesting that $\beta\text{-PbF}_2$ growth can be easily controlled in the glass sample in order to achieve the desired crystallite size and distribution. These results are promising and suggest that

this glass composition is suitable for preparation of transparent glass-ceramics containing β -PbF₂ for optical applications.

CONCLUSION

Glass samples could be obtained in the ternary system $(100-x)[0,6\text{NaPO}_3-0,4\text{WO}_3]-x\text{PbF}_2$ with x ranging from 0 to 60. The most PbF₂ concentrated samples ($x=50$ and $x=60$) were selected for thermal and crystallization characterizations. Thermal properties obtained by DSC for both samples pointed out a decrease of the glass transition temperature and glass thermal stability against devitrification related with the modifier behavior of lead fluoride. Heat-treatments performed near the crystallization peaks identified by DSC and X-ray diffraction measurements on the resulting samples indicated that the glass containing 50% of PbF₂ preferentially precipitates lead fluorophosphate Pb₅F(PO₄)₃ whereas the glass containing 60% of PbF₂ presents a first crystallization event due to β -PbF₂ without other undesirable crystalline phase. These results suggest that this later glass composition is promising for transparent glass-ceramics containing β -PbF₂ nanocrystals for optical applications.

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