Materials Research. 2015; 18(Suppl 2): 13-16
DOI: http://dx.doi.org/10.1590/1516-1439.333814

Thermal, Structural and Crystallization Study of Niobium Potassium Phosphate Glasses

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Received: September 26, 2014; Revised: April 4, 2015

New glass compositions were investigated in the binary system KPO_3-Nb_2O_5. The glass forming domain was determined by melt-quenching of the starting nominal compositions and it has been experimentally observed that glass samples can be obtained between the molar compositions 95KPO_3-5Nb_2O_5 and 50KPO_3-50Nb_2O_5. Chemically stable compositions from 80KPO_3-20Nb_2O_5 to 50KPO_3-50Nb_2O_5 were characterized by DSC for determination of characteristic temperatures Tg, Tx, Tp and Tf. Glass transition temperatures strongly increase with Nb_2O_5 content whereas thermal stability against devitrification progressively decreases. Thermal data were used to suggest a structural model in which NbO_x polyhedra are inserted inside the phosphate chains of PO_4 units. For higher Nb_2O_5 contents, NbO_x units progressively link together to form amorphous NbO_x clusters, responsible for the yellow color and lower thermal stability against devitrification. For the composition 50KPO_3-50Nb_2O_5, it has been found that the first crystallization peak is related with precipitation of hexagonal Nb_2O_5 in the glass matrix whereas the high temperature exothermic peak is due to both phase transition of hexagonal niobium oxide to monoclinic niobium oxide and precipitation of niobium potassium phosphate $K_2Nb_6P_4O_{26}$.

Keywords: *glasses, phosphate, niobium, crystallization*

1. Introduction

Phosphate glasses are extensively studied and used for several technological applications because of specific physical and chemical properties when compared to other classical glass formers such as silicate, germanate or borate glasses. Phosphate glasses exhibit small liquidus viscosity, softening temperatures, large UV transparency and high solubility for other glass modifiers or intermediaries such as alcaline, rare earth or transition metal compounds[1-5]. Particularly, metaphosphate formers such as sodium polyphosphate $NaPO_3$ are known to be able to dissolve very large amounts of transition metal oxides because of the insertion of MO_x polyhedra inside the linear phosphate chains, resulting in higher network connectivities and thus higher viscosities and thermal stabilities against devitrification[6,7]. On the other hand, amorphous materials containing high contents of transition metal oxides are of great interest because of the improvement of rare earth ions luminescence when compared to the transition metal free material[8-10]. These properties are further enhanced when nanocrystals of the metal oxide are precipitated in the amorphous host since rare earth ions tend to migrate to the crystalline phase of higher refractive index and lower phonon energy. Such materials were largely investigated in silica prepared by sol-gel and containing transition metal oxide such as TiO_2, ZrO_2, HfO_2, Nb_2O_5 or Ta_2O_5[11-15]. However, the sol-gel methodology also presents some intrinsic limitations related with the drying process. For example, complete elimination of OH groups and obtaining of large pieces are hardly achieved. For this reason, incorporation of large amounts of transition metal oxide in other glass formers obtained by melt-quenching and preparation of glass-ceramics from these precursor glasses is of great interest to overcome the sol-gel difficulties.

In this work, we investigated the glass formation in the binary system KPO_3-Nb_2O_5 with increasing niobium oxide contents. Thermal characterizations were performed by DSC to determine characteristic temperatures and thermal stability against devitrification as a function of composition. The most Nb_2O_5-concentrated glass sample was annealed at the crystallization temperatures Tc_1 and Tc_2 observed from thermal analysis and the resulting crystalline phases were identified by X-ray diffraction. These results allowed identifying this glass composition as a good candidate for transition metal oxide precipitation and preparation of optical glass-ceramics.

2. Experimental Part

Investigated compositions were prepared from the starting compounds KH_2PO_4 99% from Aldrich and Nb_2O_5 99.9% from Aldrich. The starting powders were weighted using an analytical balance and grinded in an agate

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mortar before melting in a platinum crucible at 1100°C for 1 hour. The melts were poured in a steel mold preheated around 500°C and annealed at this temperature for 4 hour before cooling to room temperature inside the furnace. These glass samples were then cut and polished. DSC curves were obtained on bulk glass samples of 50mg in Pt/Rh covered crucibles between 200°C and 1100ºC at 10°C/min under N_2 atmosphere. These thermal analyzes were obtained using a DSC/TG calorimeter STA 449 F3 Jupiter 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)[16].

3. Results and Discussion

Binary compositions were melted and quenched in the binary system KPO_3-Nb_2O_5 in order to determine the glass forming domain for this system. Potassium metaphosphate doesn´t vitrify alone but forms a white non-transparent ceramic under melt quenching. Adding 5% of Nb_2O_5 is enough for sample vitrification. Transparent glass samples could be prepared for Nb_2O_5 contents ranging from 5 mol% to 50 mol%, which correspond to a P/Nb ratio from 9.5 to 0.5. However, KPO_3 rich samples (95% and 90%) are extremely hygroscopic and not stable under room atmosphere for more than a few minutes. For this reason, these glass compositions were not used for further characterizations.

The glass compositions selected for thermal characterizations are resumed in Table 1 and presented in Figure 1. Transparent, homogeneous and chemically stable glasses were obtained from 20 mol% to 50 mol% of Nb_2O_5 and a progressive yellowish-orange color appears for the most niobium oxide concentrated samples KNb40 and KNb50. For these compositions, the P/Nb ratio is 0.75 and 0.5 respectively, which means that the glass network is built up with more niobium than phosphorus atoms. Then, it should be expected that niobium oxide rich domains are formed in the glass from clustering of NbO_x units (probably NbO_6). It is known that several transition metal oxides tend to form non-stoichiometric oxygen-deficient compounds to reach a lower free energy. The charge balance is maintained by reduction of some transition metal ions[17,18]. In our case, It is expected that these niobium rich glass samples contain some reduced Nb^{4+} in amorphous NbO_x clusters, resulting in visible absorption from internal electronic d-d transitions.

DSC curves presented in Figure 2 for samples KNb20, KNb30, KNb40 and KNb50 were analyzed to extract characteristic temperatures and thermal stability against devitrification in function of the composition (Table 1). The first important result obtained from these curves is the clear increase of glass transition temperatures with increasing Nb_2O_5 content. High Tg values are commonly related with high vitreous network connectivities and strong chemical bonds. For our niobium potassium phosphate samples, increasing Nb_2O_5 contents result in a progressive phosphorus substitution with niobium ions in the glass network. Phosphorus atoms are four-fold coordinated in phosphate compounds with one of the P-O bonds being a double terminal bond. At the best, only three P-O bonds are able to connect phosphate tetrahedra through P-O-P bridging bonds[19]. In metaphosphate structures, linear phosphate chains are formed since only two P-O bonds are connecting the phosphate units. On the other hand, niobium ions usually exhibit high coordination number in oxide compounds, being the octahedral coordination the most common one[20]. Then, niobium oxide polyhedra inserted inside the linear metaphosphate structures cross-link the covalent chains to form a three-dimensional network with a much higher connectivity and a resulting higher viscosity.

Another structural information extracted from the DSC analysis is related with the thermal stability against devitrification estimated using the parameter Tx-Tg. In fact, sample KNb20 doesn´t suffer any devitrification between

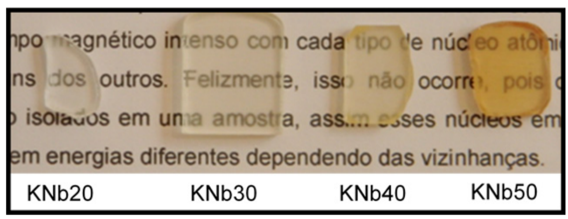

Figure 1. Glass samples prepared in the binary system KPO_3-Nb_2O_5. (Source: authors)

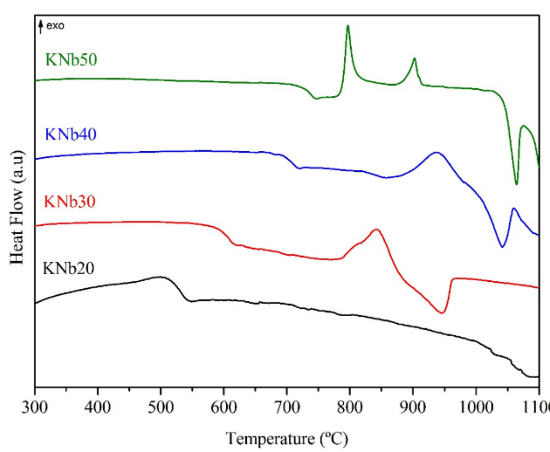

Figure 2. DSC curves of the glass samples KNb20, KNb30, KNb40 and KNb50. (Source: authors)

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

Sample	Molar composition (%)	Tg (°C)	Tx (°C)	Tp (°C)	Tf (°C)	Tx-Tg (°C)
KNb20	$80KPO_3$-$20Nb_2O_5$	500	-	-	-	-
KNb30	$70KPO_3$-$30Nb_2O_5$	580	780	840	940	200
KNb40	$60KPO_3$-$40Nb_2O_5$	690	870	930	1040	180
KNb50	$50KPO_3$-$50Nb_2O_5$	710	780	790	1060	60

Tg at 508°C and 1100°C suggesting a very stable glass network. For this composition, the P/Nb ratio is 2 and the glass network is built up with two phosphorus atoms for one niobium atom. Considering that all niobium ions are inserted inside the phosphate chains through P-O-Nb bridging bonds and that the niobium distribution is homogeneous along the covalent network, this P/Nb ratio is consistent with the formation of a three-dimensional network in which one NbO_x polyhedron is present between two PO_4 tetrahedra (PO_4-PO_4-NbO_x-PO_4-PO_4). Then, it can be understood that all PO_4 tetrahedra are bonded to another phosphate unit and a niobium oxide unit, promoting a very high thermal stability against devitrification.

Particularly, sample KNb50 presents two distinct crystallization peaks centered at 796°C and 900°C and a low thermal stability with Tx-Tg=62°C. For compositions containing more than 20 mol% of Nb_2O_5, the P/Nb ratio is lower than 2, suggesting that some PO_4 tetrahedra should be bonded to more than one NbO_x polyhedron. Since the thermal stability of phosphate glasses is strongly related with the presence of P-O-P bonds, i.e. bridging bonds between PO_4 tetrahedra, it can be understood that these Nb_2O_5 concentrated glass samples are less thermally stable and have a higher tendency for devitrification. In addition, the structural model proposed earlier in this work allows to suggest precipitation of a niobium phosphate crystalline phase since niobium oxide structural units are randomly inserted in the phosphate network. For P/Nb ratio lower than 1 (Nb_2O_5 contents higher than 33 mol%), it is also assumed that NbO_x units link together through Nb-O-Nb bridging bonds and form niobium oxide rich domains in the glass network. These clusters should induce Nb_2O_5 precipitation since only limited atomic diffusion is required for crystallization of these amorphous niobium oxide domains. Particularly, it is suspected that niobium oxide precipitation could be responsible for the first crystallization event detected in sample KNb50.

For these reasons, a careful crystallization study was performed on this sample. Heat-treatments were applied at the first crystallization temperature (800°C) for a short time (5min) in order to induce precipitation of the first phase without the second one. Another heat-treatment was also performed at the second crystallization temperature of 900°C for 1 hour to ensure complete precipitation of both phases. X-ray diffraction pattern of sample KNb50 heat-treated at 800°C is shown in Figure 3 and the diffraction peaks identified for this sample were attributed to hexagonal niobium oxide (PDF n°28-317) with cell parameters a=3.607Å and c=3.925Å. No other diffraction peaks are present but a residual diffraction halo is also identified, suggesting that this sample is a glass-ceramic containing hexagonal niobium oxide. Diffraction pattern of sample KNb50 heat-treated at 900°C is presented in Figure 4 and exhibit a large number of diffraction peaks between 10° and 70°. The first non-expected result is that diffraction peaks related with hexagonal Nb_2O_5 are not observed for this sample. Diffraction peaks identification performed using Crystallographica Search Match attributed better this pattern to the presence of both monoclinic Nb_2O_5 with cell parameters a=7.348Å, b=8.962Å, c=13.65Å and β=115.5° (PDF n° 19-864) and orthorhombic niobium potassium phosphate $K_3Nb_6P_4O_{26}$ with cell parameters a=14.748Å, b=31.58Å and c=9.386Å. Then, it must be assumed that hexagonal niobium oxide experiments a crystalline phase transformation to the monoclinic phase and that the overall remaining glass composition also precipitates as $K_3Nb_6P_4O_{26}$. It is acceptable to suggest that both events (phase transformation and crystallization) take place around 900°C since the exothermic peak identified at this temperature is asymmetric and is probably built up from several distinct events. This crystallization study performed on sample KNb50 supports previous assumptions that NbO_x clusters are formed inside the glass network and decrease the glass stability against devitrification, acting as crystallization nuclei for hexagonal niobium oxide precipitation. Only NbO_x units forming these clusters precipitate at 800°C whereas other NbO_x inserted inside the phosphate network remain in the vitreous phase. For that reason, at higher temperatures this remaining amorphous phase also crystallizes, forming niobium potassium phosphate $K_3Nb_6P_4O_{26}$.

These results obtained on sample KNb50 are very promising for transparent glass-ceramics containing the

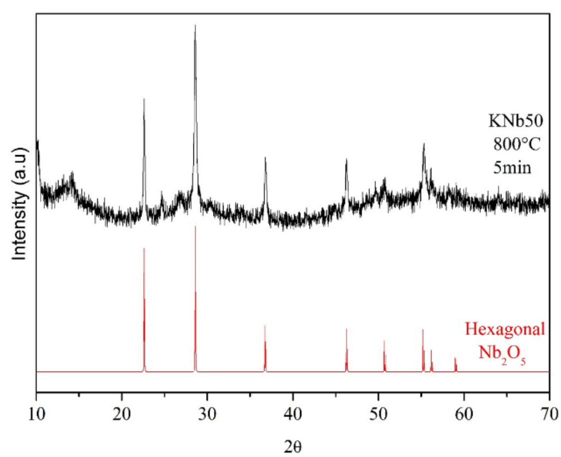

Figure 3. X-ray diffraction patterns of sample KNb50 heat-treated at 800°C for 5min and hexagonal Nb_2O_5. (Source: authors)

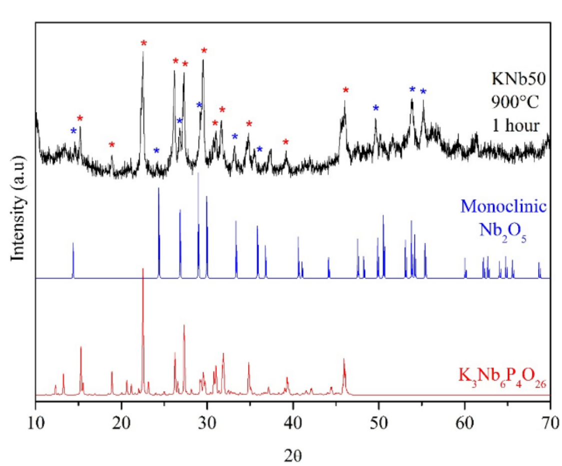

Figure 4. X-ray diffraction patterns of sample KNb50 heat-treated at 900°C for 1 hour, monoclinic Nb_2O_5 and orthorhombic $K_3Nb_6P_4O_{26}$. (Source: authors)

Nb_2O_5 crystalline phase since it has been shown that hexagonal Nb_2O_5 can be precipitated in the glassy matrix under suitable heat-treatments. These glass-ceramics can find interesting optical applications when doped with rare-earth luminescent trivalent ions.

4. Conclusion

The glass forming region has been investigated for the first time in the binary system KPO_3-Nb_2O_5 and transparent glasses can be obtained by melt-quenching for Nb_2O_5 contents ranging from 5 mol% to 50 mol%. DSC measurements of the chemically stable compositions against moisture ranging from 20 mol% to 50 mol% pointed out that the glass composition containing 20 mol% of Nb_2O_5 is the most stable against devitrification.. High niobium oxide contents induce lower thermal stabilities and appearance of crystallization events above Tg. Heat-treatment of sample KNb50 at the first crystallization temperature of 800°C for 5min induces the precipitation of hexagonal Nb_2O_5 in the vitreous material whereas heat-treatment at the second crystallization temperature of 900°C for 1 hour results in a crystalline phase transformation of hexagonal niobium oxide to monoclinic niobium oxide together with precipitation of the whole remaining vitreous phase to form niobium potassium phosphate $K_3Nb_6P_4O_{26}$. The ability of the glass KNb50 to precipitate hexagonal niobium oxide in the glass matrix opens interesting potential applications for luminescent materials since transparent rare-earth doped glass-ceramics could be prepared from this composition. Such results, already reported in silica-based materials obtained by sol-gel were identified for the first time in melt-quenched glass samples.

Acknowledgements

The authors would like to thank brazilian funding agencies FAPEMIG, FINEP, CNPq and CAPES for financial support and UNIFAL-MG for the laboratory structure.

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