Thermal, Structural and Crystallization Study of Niobium Potassium Phosphate Glasses

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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. Particularly, metaphosphate formers such as sodium polyphosphate NaPO₃ are known to be able to dissolve very large amounts of transition metal oxides because of the insertion of NbO₃ polyhedra inside the linear phosphate chains, resulting in higher network connectivities and thus higher viscosities and thermal stabilities against devitrification progressively decreases. Thermal data were used to suggest a structural model in which NbO₃ polyhedra are inserted inside the phosphate chains of PO₄ units. For higher NbO₃ contents, NbO₃ units progressively link together to form amorphous NbO₃ clusters, responsible for the yellow color and lower thermal stability against devitrification. For the composition 50KPO₃-50Nb₂O₅, it has been found that the first crystallization peak is related with precipitation of hexagonal NbO₃ in the glass matrix whereas the high temperature exothermic peak is due to both phase transition of hexagonal NbO₃-50Nb₂O₅ and 50KPO₃-20Nb₂O₅, it has been found that the first crystallization peak is related with precipitation of hexagonal NbO₃ in the glass matrix whereas the high temperature exothermic peak is due to both phase transition of hexagonal NbO₃-50Nb₂O₅ and 50KPO₃-20Nb₂O₅, it has been found that the first crystallization peak is related with precipitation of hexagonal NbO₃ in the glass matrix whereas the high temperature exothermic peak is due to both phase transition of hexagonal NbO₃-50Nb₂O₅ and 50KPO₃-20Nb₂O₅, it has been found that the first crystallization peak is related with precipitation of hexagonal NbO₃ in the glass matrix whereas the high temperature exothermic peak is due to both phase transition of hexagonal NbO₃-50Nb₂O₅ and 50KPO₃-20Nb₂O₅, it has been found that the first crystallization peak is related with precipitation of hexagonal NbO₃ in the glass matrix whereas the high temperature exothermic peak is due to both phase transition of hexagonal NbO₃-50Nb₂O₅ and 50KPO₃-20Nb₂O₅, it has been found that the first crystallization peak is related with precipitation of hexagonal NbO₃ in the glass matrix whereas the high temperature exothermic peak is due to both phase transition of hexagonal NbO₃-50Nb₂O₅ and 50KPO₃-20Nb₂O₅, it has been found that the first crystallization peak is related with precipitation of hexagonal NbO₃ in the glass matrix whereas the high temperature exothermic peak is due to both phase transition of hexagonal NbO₃-50Nb₂O₅ and 50KPO₃-20Nb₂O₅, it has been found that the first crystallization peak is related with precipitation of hexagonal NbO₃ in the glass matrix whereas the high temperature exothermic peak is due to both phase transition of hexagonal NbO₃-50Nb₂O₅ and 50KPO₃-20Nb₂O₅, it has been found that the first crystallization peak is related with precipitation of hexagonal NbO₃ in the glass matrix whereas the high temperature exothermic peak is due to both phase transition of hexagonal NbO₃-50Nb₂O₅ and 50KPO₃-20Nb₂O₅. 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 TiO₂, ZrO₂, HFO₂, Nb₂O₅, or Ta₂O₅. 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 KPO₃-Nb₂O₅ 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 NbO₃-concentrated glass sample was annealed at the crystallization temperatures Tc₁ and Tc₂ 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 KH₂PO₄ 99% from Aldrich and Nb₂O₅ 99.9% from Aldrich. The starting powders were weighted using an analytical balance and grinded in an agate
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 1100°C at 10°C/min under N2 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).

### 3. Results and Discussion

Binary compositions were melted and quenched in the binary system KPO3-NbO5 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% ofNb2O5 is enough for sample vitrification. Transparent glass samples could be prepared for Nb2O5 contents ranging from 5 mol% to 50 mol%, which correspond to a P/Nb ratio from 9.5 to 0.5. However, KPO3 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 Nb2O5 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, niobium oxide polyhedra inserted in 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 around 500°C and annealed at this temperature for 4 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 1100°C at 10°C/min under N2 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).

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar composition (%)</th>
<th>Tg (°C)</th>
<th>Tx (°C)</th>
<th>Tp (°C)</th>
<th>Tf (°C)</th>
<th>Tx-Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNb20</td>
<td>80KPO-20Nb2O5</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>KNb30</td>
<td>70KPO-30Nb2O5</td>
<td>580</td>
<td>780</td>
<td>840</td>
<td>940</td>
<td>200</td>
</tr>
<tr>
<td>KNb40</td>
<td>60KPO-40Nb2O5</td>
<td>690</td>
<td>870</td>
<td>930</td>
<td>1040</td>
<td>180</td>
</tr>
<tr>
<td>KNb50</td>
<td>50KPO-50Nb2O5</td>
<td>710</td>
<td>780</td>
<td>790</td>
<td>1060</td>
<td>60</td>
</tr>
</tbody>
</table>

For our niobium potassium phosphate samples, increasing Nb2O5 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. 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.

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.

### Figure 1. Glass samples prepared in the binary system KPO3-Nb2O5. (Source: authors)

### Figure 2. DSC curves of the glass samples KNb20, KNb30, KNb40 and KNb50. (Source: authors)
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 NbOx polyhedron is present between two PO4 tetrahedra (PO4-P-O-NbOx-P-O-P04). Then, it can be understood that all PO4 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 Nb2O5, the P/Nb ratio is lower than 2, suggesting that some PO4 tetrahedra should be bonded to more than one NbOx polyhedron. Since the thermal stability of phosphate glasses is strongly related with the presence of P-O-P bonds, i.e. bridging bonds between PO4 tetrahedra, it can be understood that these NbOx 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 (Nb2Ox contents higher than 33 mol%), it is also assumed that NbOx units link together through Nb-O-Nb bridging bonds and form niobium oxide rich domains in the glass network. These clusters should induce NbOx 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=7.348Å, b=8.962Å, c=13.65Å and β=115.5° (PDF n° 19-864) and orthorhombic niobium potassium phosphate K3Nb6P2O26 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 K3Nb6P2O26. 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 NbOx clusters are formed inside the glass network and decrease the glass stability against devitrification, acting as crystallization nuclei for hexagonal niobium oxide precipitation. Only NbOx units forming these clusters precipitate at 800°C whereas other NbOx 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 K3Nb6P2O26.

These results obtained on sample KNb50 are very promising for transparent glass-ceramics containing the
Nb$_2$O$_5$ crystalline phase since it has been shown that hexagonal Nb$_2$O$_5$ 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$_5$-Nb$_2$O$_5$ and transparent glasses can be obtained by melt-quenching for Nb$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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 $K_xNb_{y}P_{z}O_{5}$. 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.

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References