CRYSTALLIZATION OF Na₄Nb₈P₄O₃₂ IN BOROPHOSPHATE GLASSES

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Abstract Samples with chemical composition (1-x) [0.95NaPO₃ - 0.05Na₂B₄O₇] - x Nb₂O₅ have been annealed at T ≥ 750°C. For x ≥ 0.3, the presence of Na₄Nb₈P₄O₃₂ crystalline phase were detected by X ray diffraction. The size and the distribution of micro - crystallites in the bulk glass samples were determined in relation to the thermal treatment. The crystallized glasses were studied by Raman micro probe and ³¹P MAS NMR and discussed in comparison with the glassy samples.

INTRODUCTION

Transition metal ions with empty d⁰ shell, such as Nb⁵⁺, contribute strongly to increase the optical nonlinearity in oxide glasses. Recently, a structural investigation has shown that the high third-order optical nonlinear response in transparent borophosphate glasses containing large amount Nb₂O₅ might be correlated to the tridimensional Nb-O framework. Nevertheless, the nature of this niobate groups could not be clearly identified. Vitreous materials annealing allows to obtain the crystalline phases giving data about the structure of the glass forming network and possibly the formation of a transparent glass ceramic with potential electrooptical properties. This paper presents the result of crystallization of rich-niobium sodoborophosphate glasses as function of the temperature and the duration of thermal treatment. The various phases have been characterized by Raman microprobe and ³¹P MAS NMR.

EXPERIMENTAL PROCEDURE
The glass preparations with chemical composition (1-x) \[0.95\text{NaPO}_3 - 0.05\text{Na}_2\text{B}_4\text{O}_7\] \(x\) \(\text{Nb}_2\text{O}_5\) (0 \(< x < 0.40\)) have been described elsewhere. The resultant glasses (powder or bulk) were annealed at 750°C during 1, 2, 7, 9, 19, or 55 hours.

\(\text{Na}_4\text{Nb}_8\text{P}_4\text{O}_{32}\) crystallized phase (\(\text{NaNbP}\)) have been synthesized from \(\text{Na}_2\text{CO}_3\), \((\text{NH}_4)_2\text{HPO}_4\) and \(\text{Nb}_2\text{O}_5\) starting compounds. The appropriate mixture was heating in an electric furnace under oxygen flow at 200, 400 and 1000°C during 1, 2 and 24 hours, respectively, then quenched at room temperature.

The crystallized phases in glasses (CG) and \(\text{NaNbP}\) compound powder were identified by X-ray diffraction analysis (CuK\(\alpha\) radiation).

The Raman spectra were recorded with a Labram confocal micro - Raman instrument from Dilor instrument (typical resolution of 2 cm\(^{-1}\)), in backscattering geometry at room temperature. The system consist of an holographic notch filter for Rayleigh rejection, a microscope equipped with 10x, 50x and 100x objectives (the latter allowing a spatial resolution of less than 2\(\mu\)m) and CCD detection. The source was 632.8nm line of a He - Ne laser with an output power of 10mW.

NMR spectra were recorded on a Bruker MSL 200 spectrometer (4.7 T magnet). MAS at 12 KHz was used for \(^{31}\text{P}\) (80.96 MHz), with a single-pulse (3.5 \(\mu\)s) sequence and phase cycling with a 60 S repetition time. The spectral width was 20 KHz. The reference used was \(\text{H}_3\text{PO}_4\) (85%). Decomposition of the experimental signal was performed using the WinFit program, with a Gaussian lineshape.

RESULTS AND DISCUSSION

In the glass series, only the vitreous compositions with \(x\geq0.35\) easily recrystallize. As a matter of fact, the crystallization temperature is undetectable for \(x<0.35\). The glass powder with \(x=0.35\) with glass transition and crystallization temperatures of 600 and 810°C respectively, has been heated at 750°C during 2 hours. The resulting product consist of the glass - ceramic with the presence of only one crystalline phase which have been identified to \(\text{Na}_4\text{Nb}_8\text{P}_4\text{O}_{32}\) prepared and studied previously by G. Costentin et al.

From optical microscopic observations, the bulk glasses heat treated during at least 2 hours shows the crystallites presence in needle form with 5-6\(\mu\)m of length, as illustrated.
in Figure 1. For longer duration, the number of crystallites growths without size increasing perceptibly. For 55 hours of treatment, the X-ray diffractogram reveals always the mixture of glassy and NaNbP phases.

FIGURE 1. Optical microscopic photographs Na₄Nb₈P₄O₃₂ crystallites in the needle form obtained by heat treatment during 7 h with x260 objective enlargement.

FIGURE 2. Raman spectra (VV) of Na₄Nb₈P₄O₃₂ phase, crystalline phase in glass ceramic (x = 0.35, thermal treatment 7 h) and x = 0.35 glass.
The comparison of the Raman spectra (VV) of the bulk CG (heat - treatment during 7 h) with NaNbP powder and x = 0.35 bulk glass are reported in Figure 2. The CG and NaNbP spectra are similar with a predominance of strong asymmetric band between 600 and 750 cm\(^{-1}\) including NbO\(_6\) octahedra (650 cm\(^{-1}\)) and Nb-O-Nb (680 cm\(^{-1}\)) vibrational modes as found, for example, in the tungsten bronze type niobiate NaBa\(_2\)Nb\(_3\)O\(_{15}\)\(^5\) and in LiNbO\(_3\)\(^6\) respectively, in agreement with the NaNbP structure \(^4\). On the contrary, the comparison between glass and CG shows additional large bands above 750 cm\(^{-1}\) typical of stretching modes of two distorted NbO\(_6\) octahedral types previously assigned \(^3\).

The comparison of the \(^{31}\)P MAS NMR lines of the bulk CG (heat - treatment during 7 h) with NaNbP powder and x = 0.35 bulk glass are presented in Figure 3. The decomposition results of the experimental signals are reported in Table 1.

**FIGURE 3.** \(^{31}\)P MAS NMR of Na\(_4\)Nb\(_8\)P\(_4\)O\(_{32}\) phase, crystalline phase in glass ceramic (x = 0.35, thermal treatment 7 h) and x = 0.35 glass Arrows correspond to the maximum of the component obtained by decomposition of the experimental signal.

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In NaNbP 31P MAS NMR spectra, the only one experimental signal with a Gaussian shape peaking at -11.1 ppm may be assigned to the phosphorus of monophosphate group in a same environment. Actually, the structure of NaNbP was solved assuming two closely types of PO4 tetrahedra which are sharing its four corners 4. Such similar structural arrangement can explain the simple line of the NMR spectra. In the CG spectrum, the same component observed well confirms the presence of NaNbP crystallites as in glass where this one shows the existence PO4 tetrahedra connected with NbO₆ octahedra. The two others components in the CG spectra may be due to different environments around the PO4 tetrahedra in the matrix glass which the composition 0.808 NaPO₃ - 0.076 Na₂B₄O₇ - 0.184 Nb₂O₅ can be deduced from the area percentage. The component at -5.5 ppm in glass could be assigned to PO₄ tetrahedra bonded to one phosphorus and one boron atoms or two boron atoms as in borophosphate glasses published elsewhere 7. Structural study is in progress to clarify these assumptions.

**SUMMARY**

In this work, glass ceramics containing Na₄Nb₈P₆O₃₅ crystallites (needle form, length 5-6mm) have been obtained by thermal treatment (750°C, 2h) from glasses with chemical composition 0.6175NaPO₃ - 0.0325Na₂B₄O₇ - 0.35 Nb₂O₅. In the bulk glass samples, the micro - crystallite number increases as the annealing duration without apparent change of size. The analysis of the Raman micro probe and 31P MAS NMR spectra show that the existence of PO₄ tetrahedron shared its four corners with NbO₆.

<table>
<thead>
<tr>
<th>NaNbP powder</th>
<th>CG (7 h)</th>
<th>Glass (x = 0.35)</th>
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</thead>
<tbody>
<tr>
<td>-11.1 ppm (100%)</td>
<td>-13.8 ppm (53%)</td>
<td>-11.1 ppm (53%)</td>
</tr>
<tr>
<td></td>
<td>-11.1 ppm (44%)</td>
<td>-11.1 ppm (53%)</td>
</tr>
<tr>
<td></td>
<td>-0.4 ppm (3%)</td>
<td>-5.5 ppm (47%)</td>
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**TABLE 1.** Isotropic chemical 31P shifts and percentage of area (in brackets) of components determined by decomposition of experimental signals.
octahedra-in glass is originally due to the Na₄Nb₆P₄O₃₂ crystallite formation. Electrooptical investigations are in progress.

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REFERENCES


