Structure and optical properties of nobium-sodium borophosphate glasses.

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We report the characterization of (100-x)$NaPO_3$-x$Na_2B_4O_7$, (100-x)$NaPO_3$-xNb_2O_5 and (100-x)[0.95$NaPO_3$-0.05$Na_2B_4O_7$]-x Nb_2O_5 glasses with ^{31}P and ^{93}Nb NMR. The introduction of nobium in phosphate and borophosphate networks leads to a depolymerization. There is evidence for two nobium environments in (100-x)$NaPO_3$-xNb_2O_5 glasses.

introduction

Borophosphate glasses have found many applications : solid state silver electrolytes[1], electrodes of lithium batteries[2], fuel cells[3], biomaterials[4], sealing glasses[5,6] and optical components[7]. In the latters, the introduction of nobium enables to obtain glasses with non-linear optical properties[7]. The non-linearity is due to the nobium polyhedra. EXAFS study[7] of sodium nobium borophosphates have shown that nobium polyhedra are isolated in the phosphate matrix at low nobium concentration, but become connected to each others at higher concentrations.

Our aim is to study the structure of sodium nobium borophosphates, and relate the structural data to optical properties. Solid state NMR is used to investigate the borophosphate glass structure. MAS-NMR is indeed a powerfull tool to characterize the phosphate glass networks. One dimensional NMR methods, mainly ^{31}P MAS-NMR, provide a short range description, limited to Q^n site distribution. The recently introduced two-dimensional NMR in solid state experiments has brought considerable improvement of the structure characterization, extending the description to medium range order by introducing arguments based on the connectivities between homo-[8] or heteronuclei[9].

Due to severe resonance overlapping which originate from chemical shift distribution, the investigation of complex glass systems is still difficult. This is why we decomposed the sodium-nobium borophosphate glasses in simpler pseudo-binary glasses : $NaPO_3$-Nb_2O_5, and $NaPO_3$-$Na_2B_4O_7$. These two systems were chosen because some data are already available on their structure and properties, as well as chemical shift references[10]. Then the more complex $NaPO_3$- $Na_2B_4O_7$-Nb_2O_5 system will be characterized.

We report here the investigation of (100-x)$NaPO_3$-x$Na_2B_4O_7$, (100-x)$NaPO_3$-xNb_2O_5 and (100-x)[0.95$NaPO_3$-0.05$Na_2B_4O_7$]-x Nb_2O_5 glasses using ^{31}P and ^{93}Nb NMR.

Experimental procedures

The glasses were prepared from $NaPO_3$, Nb_2O_5 and $Na_2B_4O_7$. They were melted in crucible under air atmosphere, with two hours melting time. The melt was then quenched on a steel plate.

The ^{31}P NMR experiments were carried out at Bo= 2.3 T using a Bruker ASX100 spectometer. The ^{31}P Larmor frequency is 40.53 MHz at this magnetic field. A 7 mm MAS probe was used at a MAS frequency of 7 kHz. All the glass samples were prepared with an addition of 0.2 wt% MnO to reduce the spin lattice relaxation time T_1. At this low magnetic field, the T_1 relaxation time is close to 1s (measured by inversion-recovery). Thus the repetition time could be limited to 5 s, and 32 scans have been accumulated. The pulse length for the 1D experiment was 1.5 μs ($\pi/4$).

The ^{93}Nb spectra were recorded on a Avance400 spectrometer operating at 97.9MHz. MAS spectra were recorded as echoes, with 0.1s repetition time.

Results and discussion

Fig. 1 shows the ^{31}P MAS-NMR spectra of (100-x)$NaPO_3$-x$Na_2B_4O_7$ glasses for x=0 and x=5. In $NaPO_3$ glass, only Q^2(Na) sites are observed at -20 ppm. In the sodium borophosphate glass, according to reference[10], two resonances are observed : middle phosphate groups bonded to sodium Q^2(Na) at - 20ppm, end-phosphate groups bonded to 1 borate group: Q^1(OB) at -10 ppm, and end-phosphate groups charge compensated by sodium (Q^1(Na)) at 2 ppm.

Figure 2 shows the ^{31}P spectra of (100-x)$NaPO_3$-xNb_2O_5 glasses. Despite that chemical shift references are not available for nobium phosphates, the depolymerisation of $NaPO_3$ chains into Q^1 sites (located at – 8 ppm) is clearly visible. When the Nb_2O_5 content is increased, the Q^1 resonance shifts to lower field (Fig. 2). It is attributed to the bonding of these end-groups to an increased number of Nb^{5+}, as observed in aluminophosphate[11], or to the apparition of Q^0 sites (isolated monomeric phosphate sites).

The ^{93}Nb spectra of (100-x)$NaPO_3$-xNb_2O_5 glasses (Figure 3) show two broad components at – 900 and -1700 ppm. The intensity of the low field resonance increases with x, and, for the highest Nb_2O_5 content (x=30), only one resonance appears on the spectrum. In crystalline nobiate compounds, the chemical shift of 93-nobium in corner shared nobium polyhedra like $Pb_2Nb_2O_7$ is ca. -1000 ppm[12]. In $PbNb_2O_6$, nobium polyhedra share both corners and edges, and the chemical shift is -1250 ppm[12]. This would indicate that the high field resonance in the glasses is due to edge and corner-shared polyhedra, and the low field one to corner-shared polyhedra. However, the relative intensity of the high field resonance decrease for increasing nobium contents. This interpretation would be then contradiction with EXAFS results[7]. Another hypothesis would be that the coordinence of nobium is different for the two resonances : the low field one could be attributed to nobium polyhedra bonded to a higher number of phosphate groups than the high field one. Further crystalline reference are needed for testing this hypothesis, in particular nobium phosphate salts will be investigated.

The ^{31}P MAS-NMR spectra (Figure 4) of (100-x)[0.95$NaPO_3$-0.05$Na_2B_4O_7$]-x Nb_2O_5 glasses are broad, owing to the multiple possibilities of nobium bonding to the borophosphate network. The shift of the spectra to lower field with increasing amounts of Nb_2O_5 indicates a depolymerization of the network, in accordance with the behavior in(100-x)$NaPO_3$-xNb_2O_5 glasses.

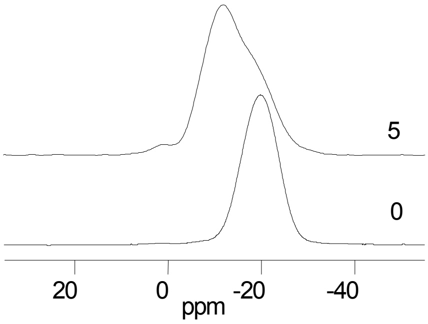

Figure 1 : ^{31}P MAS-NMR spectra of (100-x)$NaPO_3$-x$Na_2B_4O_7$ glasses.

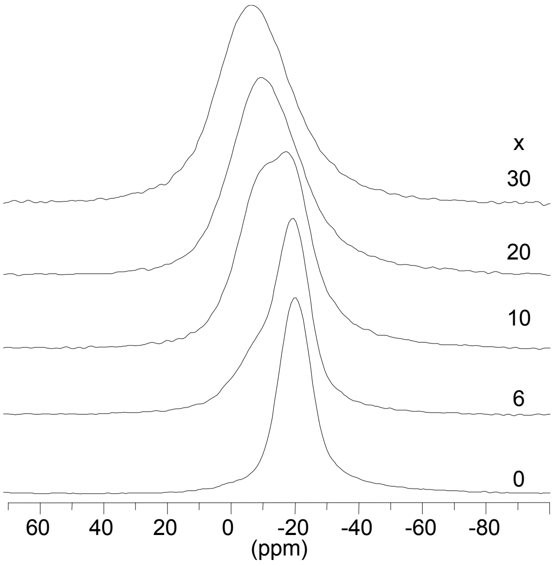

Figure 2 : ^{31}P MAS-NMR spectra of (100-x)$NaPO_3$-xNb_2O_5 glasses.

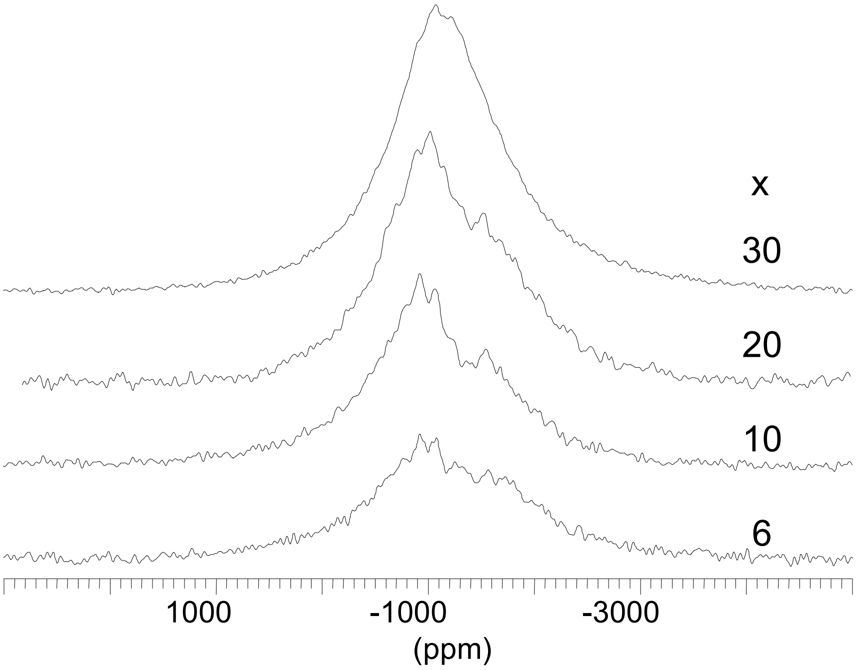

Figure 3 : ^{93}Nb NMR spectra of (100-x)$NaPO_3$-xNb_2O_5 glasses.

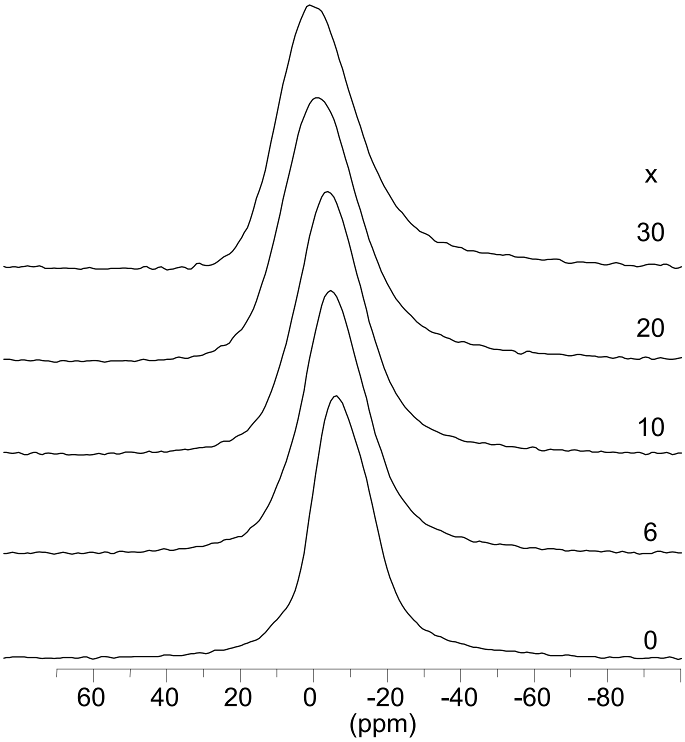

Figure 4 : ^{31}P MAS-NMR spectra of (100-x)[0.95$NaPO_3$-0.05$Na_2B_4O_7$]-x Nb_2O_5 glasses.

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[1] A. Magistris, G. Chiodelli, M. Duclot, Solid State Ionics **9&10**, p. 611 (1983).

[2] N.J. Dudney, B.J. Neudecker, Curr. Opinion Solid state Mater. Sc. **4**, p. 479 (1999).

[3] P.H. Larsen, P.F. James, J. Mater. Sc. **33**, p. 2507 (1998).

[4] J.F. Ducell, J.J. Videau, K.S. Suh, J. Senegas, Phys. Stat. Sol. **a 144**, p. 23 (1994).

[5] R.K. Brow, J. Non Cryst. Solids **194**, p. 267 (1996).

[6] L. Koudelka, P. Mosner, J. Non Cryst. Solids **293-295**, p. 625 (2001).

[7] T. cardinal, E. Fargin, G. Le Flem, S. Leboiteux, J. Non Cryst. Solids **22**, p. 228 (1997).

[8] C. Jäger, P. Hartmann, R. witter, M. Braun, J. Non Cryst. Solids **263-264**, p. 61 (2000).

[9] S. Prabakar, R.M. Wenslow, K.T. Mueller, J. Non Cryst. Solids **263-264**, p. 82 (2000).

[10] J.F. Ducell, J.J. Videau, K.S. Suh, J. Senegas, Phys. Chem. Glasses **35**, p. 10 (1994).

[11] R.K. Brow, R.J. Kirkpatrick, G.L. Turner, J. Am. Ceram. Soc. **76-4**, p. 919 (1993).

[12] S. Prasad, P. Zhao, J. huang, J.J. Fitzgerald, J.S. Shore, Solid State NMR **19**, p. 45 (2001).