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Local Structures in $Na_4Nb(PO_4)_3$ Glass and Crystal: ^{31}P MAS NMR Studies*

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^{31}P NMR spectra of $Na_4Nb(PO_4)_3$ in both the crystalline and the glassy state have been examined. It was found that local structures are not comparable in the two states.

Introduction

El Jazouli *et al.* (*1*) have reported their investigation on a NASICON glass which they suggest undergoes a reversible crystal–glass transition. The system, indeed, is very unique since the formula suggests that it is a complex orthophosphate, which forms a glass, and that the glass crystallizes into a NASICON of the same composition. In orthophosphates glass formation is generally difficult, and therefore we expect bonding in this material to be highly covalent. We were surprised by two features in the reported work. First, the Raman spectrum of the glass does not appear to be a simple ("approximate") (*1*) envelope of the crystallized phosphate spectrum as described by the authors. The threshold energy in the reflectance spectra is somewhat different, which the authors suggest is due to the higher covalency of the Nb–O bonds in the glass. We believe the latter to be a general feature in all glasses (*2–4*).

The $R\bar{3}C$, hexagonal structure of NASICON may be described as $M_1^x M_2^{VI} A_2^{VI} B_3^{IV} O_{12}$ (*5*). On comparison with $Na_4Nb(PO_4)_3$, it is evident that one of the A sites is vacant (or perhaps occupied by a Na^+ ion). Three Na^+ ions are statistically distributed in M_2 sites. The PO_4 units in the crystal are, therefore, distorted as the authors suggest, due to the highly asymmetric potential exerted on them by Nb^{5+} and Na^+ ions.

We may note that the formulae of $Na_4Nb(PO_4)_3$ can be rewritten as $4Na_2O \cdot Nb_2O_5 \cdot 3P_2O_5 = 8\ Na^+ \cdot 2[NbO_{6/2}]^- \cdot 6[PO\,O_{2/2}O^-]$, which suggests that the tetrahedra are in reality metaphosphate units which, in the glassy state, condense into polymeric chains of different lengths as dictated by the chemistry and local structures. It would, therefore, be surprising if the NaNbP413 cyrstal and the glass were to possess similar local structures. We have examined this aspect using high-resolution magic-angle spinning (MAS) nuclear magnetic resonance (NMR) of ^{31}P.

Experimental

NaNbP413 glass was prepared by the method described in Ref. (*1*). Crystalline

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* Contribution 730.

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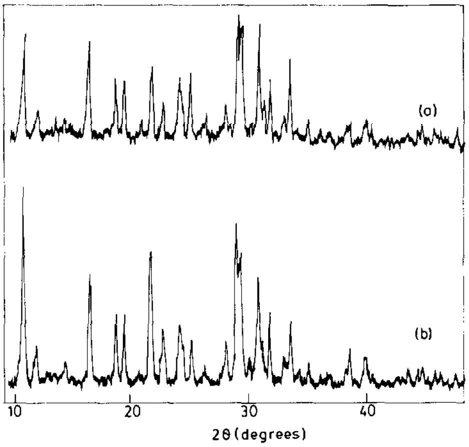

FIG. 1. Powder X-ray diffraction patterns of (a) crystalline $Na_4Nb(PO_4)_3$ and (b) $Na_4Nb(PO_4)_3$ crystallized glass.

NaNbP413 was obtained both by crystallization of the glass and by direct solid state reaction. This, we felt necessary to confirm that the glass was not phase-separated and gave rise to two different crystalline phases. ^{31}P NMR spectra were recorded with a Bruker MSL-300 solid state high-resolution spectrometer operating at 121.494 MHz (magnetic field 7.05 T). The duration of the 90° pulse was 5 μsec and the pulse delay was 5 sec. A cylindrical zirconia rotor, with a spinning rate of 3 kHz, was used in the MAS experiments. Chemical shift values are given with respect to 85% H_3PO_4.

Results and Discussion

In Fig. 1 we compare the X-ray diffraction patterns of crystalline NaNbP413 prepared directly from high temperature and that obtained from crystallization of glass; they are identical within experimental error.

High-resolution ^{31}P NMR spectra of the glass and the crystalline NaNbP413 are presented in Fig. 2. The glass shows only a single isotropic signal at -5.8 ppm, and both samples of crystalline NaNbP413 show clearly split peaks with chemical shift values of -4.5 and -12.9 ppm, respectively. The chemical shifts are in the range generally observed for metaphosphate units (6, 7). Since one of the Nb sites is vacant, [$PO\,O_{2/2}O^-$] units coordinated to the filled and vacant Nb sites in the NASICON structure are chemically different. Thus we have at least two types of metaphosphate units in the crystalline NaNbP413, which is confirmed by NMR spectra.

In the glass, however, an extensive network is formed with corner-shared [PO

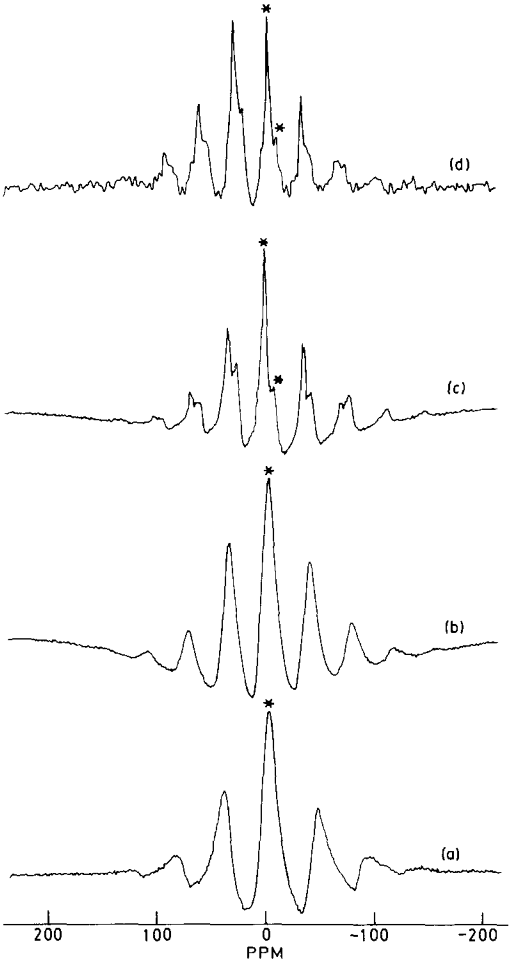

FIG. 2. ^{31}P MAS NMR spectra of $Na_4Nb(PO_4)_3$ (a) glass, (b) glass heated up to T_g, (c) crystallized glass, (d) crystalline compound. * indicates isotropic peaks; all other peaks are spinning sidebands.

$O_{2/2}O^-$] tetrahedra and $[NbO_6]^-$ octahedra like in phosphomolybdate glasses (*8*). The Na^+ ions occupy the available voids in the network. The ^{31}P NMR signal from such a network is both structurally and dynamically averaged and a signal at −5.8 ppm is observed. The FWHM of the peak in the glass registers little change up to T_g, indicating that the tetrahedra are bound in a strongly covalent network. The phosphorus environments in the crystal and the glass are indeed different. However, the high degree of covalency results in high deshielding of phosphorus in both crystal and glass, which is not so in an orthophosphate ion.

We conclude that the local structures in $Na_4Nb(PO_4)_3$ glasses and crystals are not strictly comparable and are not topologically related. The structures of glass and crystal are therefore quite different in details. Crystallization of glass involves substantial restructuring, which is why a strong exotherm of crystallization has been observed by El Jazouli *et al.* (*1*).

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