

# <sup>31</sup>P MAS NMR Investigations of Crystalline and Glassy NASICON-Type Phosphates

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<sup>31</sup>P MAS NMR investigations of crystalline and glassy NASICON-type phosphates have been carried out. The origin for the two signals in the case of the crystalline compounds is discussed. The spectra show the presence of pyrophosphate units in all glasses studied along with various other phosphate species resulting from structural disproportionation. © 1996 Academic Press, Inc.

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## INTRODUCTION

Phosphates of the general formula  $A_m B_n (PO_4)_3$  where  $A$  is one of the alkali ions, often possess  $R3c$  and related structures (1–4), in which  $PO_4$  tetrahedra and  $BO_6$  octahedra are present in corner sharing arrangements. Alkali ions occupy octahedral interstitial positions formed in such a network. Some of the crystalline sodium salts of this family exhibit very high ionic conductivity (5, 6) and hence the popular name “NASICON”—an acronym for sodium super ionic conductors—for these materials (we use the name in this paper to indicate only their general chemical formula).  $B$  ions are tri-, tetra-, or pentavalent ions of either transition or nontransition elements. These phosphates can be melted and quite simply quenched into glasses. Properties of the glasses can be understood consistently by assuming that  $B$  atoms form  $[BO_{l/2}]^{n-}$  polyhedra (commonly either tetrahedra or octahedra) with  $l$  number of covalent  $B-O$  bonds. Structural differences between glasses and crystalline materials are due to the fact that in glasses  $[BO_{l/2}]^{n-}$  polyhedra and  $[POO_{m/2}O_k]^{k-}$  tetrahedra ( $l$ ,  $n$ , and  $k$  are integers) need not to exhibit any chemical or topological ordering as they would be required to do in crystalline phosphates.

Several reports in the literature (7–9) and our own vibrational spectroscopic investigations (10) suggest that some of the crystalline and glassy NASICONs consist of pyrophosphate units while the chemical formulation suggests that only metaphosphate units should be present in them. In an earlier study of  $Na_4NbP_3O_{12}$  both in crystalline and glassy forms using <sup>31</sup>P magic angle spinning nuclear mag-

netic resonance (MAS NMR) it was suggested that the structures of crystal and glass could be very different (11). The two <sup>31</sup>P resonances observed in the MAS NMR of the crystals were assigned to two crystallographically different phosphorus sites. Using high performance liquid chromatographic (HPLC) studies, Sales and Chakoumakos (7) have suggested that pyrophosphate units (and niobyl ions) are present in crystalline  $Na_4NbP_3O_{12}$ . It would be difficult to understand why two <sup>31</sup>P resonances are observed in crystalline  $Na_4NbP_3O_{12}$  unless there are two crystallographically different  $[P_2O_7]^{4-}$  sites. Lack of complete X-ray diffraction work makes the situation even more intractable. Therefore, we felt it necessary to study the <sup>31</sup>P MAS NMR of a number of NASICON-type phosphates, both in crystalline and glassy states, in order to gain further insight on structures of NASICONs.

In this communication we report <sup>31</sup>P MAS NMR studies of crystalline NASICONs containing Ti and Zr with the general formulas  $NaM_2(PO_4)_3$  or  $Na_5M(PO_4)_3$  and a number of glasses with the general formulas  $A_m B_n (PO_4)_3$  ( $A = Li, Na, \text{ or } K$  and  $B = Ga, Ti, Ge, V, \text{ or } Nb$ ). We find evidence to support formation of dimerized pyrophosphate units, which are due to the tendency of phosphates to undergo chemical and structural disproportionations.

## EXPERIMENTAL

The crystalline compounds were prepared by solid-state reaction. Alkali metal carbonates, oxides of the metal  $B$ , and diammonium hydrogen phosphate were the starting materials. The stoichiometric mixtures were heated first to 573 K to decompose diammonium hydrogen phosphate, again ground, and heated at higher temperatures (1173 K for  $Na_5Zr(PO_4)_3$  and 1023 K for  $Na_5Ti(PO_4)_3$  for 12 to 15 hr, or at two steps of 1273 K and 1423 K for 12–15 hr each for  $NaZr_2(PO_4)_3$  and  $NaTi_2(PO_4)_3$  with intermittent grinding). The products were examined using X-ray diffraction for phase purity and only monophasic products were used in the experiments. Glasses have been made by the conventional melt quenching method. The details of

glass preparation have been given elsewhere (12). The glass pieces were annealed at 20 K below their glass transition temperatures. The glasses were powdered just before the NMR experiment.  $^{31}\text{P}$  NMR spectra were recorded with a Bruker MSL-300 solid-state high resolution spectrometer operating at 121.494 MHz (magnetic field 7.05 T). Pulses ( $90^\circ$ ) of 5  $\mu\text{sec}$  duration were employed with a delay of 5 sec between pulses in all the experiments. A cylindrical zirconia rotor was used and spinning rates of 2.7–4.2 kHz were employed. All the spectra have been recorded at room temperature. The chemical shift values are given with respect to 85%  $\text{H}_3\text{PO}_4$ .

## RESULTS AND DISCUSSION

The  $^{31}\text{P}$  MAS NMR spectra of the crystalline compounds examined in this study are shown in Fig. 1 and the corresponding chemical shifts are listed in Table 1. (Negative chemical shifts are toward higher fields in all our spectra).

In crystalline  $\text{NaZr}_2(\text{PO}_4)_3$ , Zr atoms are present in octa-

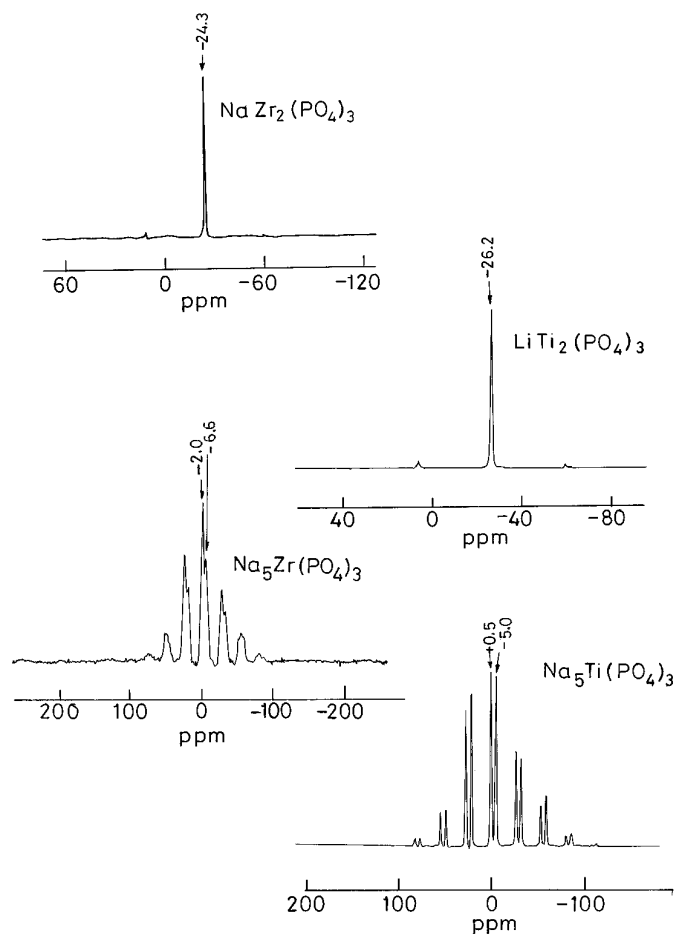


FIG. 1.  $^{31}\text{P}$  MAS NMR spectra of the NASICON-type crystalline compounds.

TABLE 1  
Isotropic Chemical Shifts  
for the Crystalline Compounds

Composition	Chemical shift (ppm)
$\text{NaZr}_2(\text{PO}_4)_3$	-24.3
$\text{LiTi}_2(\text{PO}_4)_3$	-26.2
$\text{Na}_5\text{Zr}(\text{PO}_4)_3$	-2.0, -6.6
$\text{Na}_5\text{Ti}(\text{PO}_4)_3$	0.5, -5.0

hedral positions and in view of the covalent bonding to oxygen, the structural units in which Zr atoms are present can be written as  $[\text{ZrO}_{6/2}]^{2-}$ . Thus  $\text{NaZr}_2(\text{PO}_4)_3$  itself is equivalently described as  $\text{Na}^+ \cdot 2[\text{ZrO}_{6/2}]^{2-} \cdot 3[\text{PO}_{4/2}]^+$ . Phosphorus is thus present in  $[\text{PO}_{4/2}]^+$  units as a result of which electron density is shifted away from phosphorus atom. Correspondingly,  $^{31}\text{P}$  resonances are observed at values as high as -24.3 ppm. Due to the high symmetry of  $[\text{PO}_{4/2}]^+$ , all types of anisotropies are effectively removed and a near ideal, sharp, essentially side band free  $^{31}\text{P}$  MAS NMR signal is observed in  $\text{NaZr}_2(\text{PO}_4)_3$  (Fig. 1). The situation is almost identical with  $\text{LiTi}_2(\text{PO}_4)_3$  in which the  $^{31}\text{P}$  chemical shift is again a high -26.2 ppm. The chemical shift is slightly higher than that in the Zr compound because Ti has a slightly higher electronegativity (1.5) than Zr (1.4) and therefore more effectively pulls away the electron density from phosphorus atom.  $\text{Li}^+$  ion, by virtue of its small size, is likely to be present in an off-center position in the octahedral voids of the crystal structure and causes a slight anisotropy of the chemical shifts as a result of which tiny side bands appear in the spectrum of  $\text{LiTi}_2(\text{PO}_4)_3$ .

The spectra of  $\text{Na}_5\text{Zr}(\text{PO}_4)_3$  and  $\text{Na}_5\text{Ti}(\text{PO}_4)_3$  shown in Fig. 1 are significantly different. First, there is substantial anisotropy as seen from side bands. Second, substitution of one atom of either Zr or Ti by an equivalent number of alkali ions decreases the demand on covalently bonded oxygens in the structural units. Therefore, in terms of structural units,  $\text{Na}_5\text{Zr}(\text{PO}_4)_3$  is  $5\text{Na}^+ [\text{ZrO}_{6/2}]^{2-} 3[\text{POO}_{2/2}\text{O}]^-$  suggesting that the phosphorus atom is now present in metaphosphate units of lower symmetry.  $^{31}\text{P}$  resonance is therefore characterized by higher anisotropy. Association of a nonbridging and double-bonded oxygen with phosphorus results in a higher electron density around it, which pushes the chemical shift values strongly in the positive direction and to values typical of meta- or pyrophosphates. The resonance peaks suggest the presence of two chemical shift values in both the crystalline compounds  $\text{Na}_5\text{Ti}(\text{PO}_4)_3$  and  $\text{Na}_5\text{Zr}(\text{PO}_4)_3$ . We had earlier associated two similar chemical shift values in the spectrum of crystalline  $\text{Na}_4\text{NbP}_3\text{O}_{12}$  to the presence of two phosphorus sites (11). The presence of two inequivalent phosphorus sites in

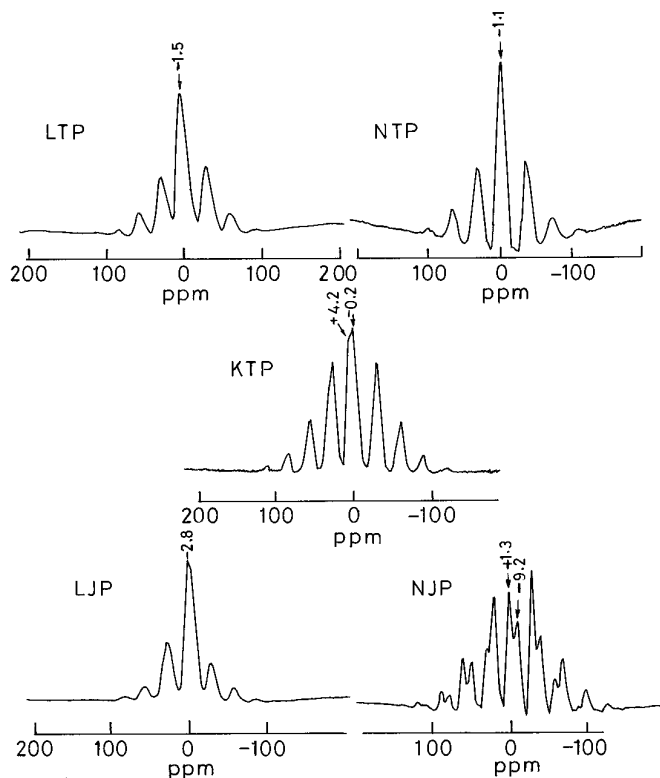
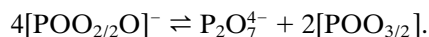


FIG. 2.  $^{31}\text{P}$  MAS NMR spectra of the NASICON-type glasses, for  $B = \text{Ti}$  or  $\text{Ge}$ .

$\text{Na}_5\text{Zr}(\text{PO}_4)_3$  was suggested in the crystallographic work of Boilot *et al.* (4). But in view of the work of Sales and Chakoumakos (7), we now feel that the origin of the two chemical shift values can be traced to a different origin and we will discuss this later. The character of the resonance peaks and the magnitudes of chemical shifts in the above compounds are consistent with the assumption that  $B$  atoms are present in  $[\text{BO}_{l/2}]^{n-}$  polyhedra in which the  $B\text{-O}$  bonds are quite covalent in nature. We now examine the MAS NMR spectra of  $^{31}\text{P}$  in glasses with the assumption that  $[\text{BO}_{l/2}]^{n-}$  polyhedra of similar type are present in glasses.

MAS NMR spectra of  $^{31}\text{P}$  for the various glasses are shown in Figs. 2 and 3. The glass compositions and observed chemical shifts are given in Table 2, and the structural units expected to be present in each glass are also listed in Table 2. In general, the spectra of glasses reveal the inherent anisotropy of the phosphate tetrahedra. Chemical shifts are all negative but close to zero, with a maximum value of about 6.1 (excluding the two cases where two signals are observed). Since the glasses are obtained through the melt route, the  $[\text{POO}_{m/2}\text{O}_k]^{k-}$  and  $[\text{BO}_{l/2}]^{n-}$  polyhedra establish a high temperature equilibrium in which formation of  $B\text{-O-B}$  and  $\text{P-O-P}$  bonds normally absent in the crystalline compounds can be expected to

form. Further, in phosphate metals several types of chemical and structural disproportionation reactions can occur quite generally (13, 14), for example,



Structurally this amounts to the isolation of one ditetrahedral unit from a chain of four metaphosphate units with simultaneous formation of two 3-connected neutral phosphate units. The required bond switching can be visualized as very facile because the  $\text{P}=\text{O}$  itself is known to resonate with  $\text{P-O}^-$  within the structure (13, 15).  $B$  atoms like  $\text{Ti}$  can form tetrahedral  $[\text{TiO}_{4/2}]$ , square pyramidal  $[\text{TiO}_{5/2}]^-$ , or octahedral  $[\text{TiO}_{6/2}]^{2-}$  units as well (9).  $\text{Ga}$  (16) and  $\text{Ge}$  (17) have known propensity to form tetrahedra while  $\text{Nb}$  can be expected to form  $[\text{NbO}_{6/2}]^-$  octahedra. Vanadium behaves like phosphorus and forms tetrahedral  $[\text{VOO}_{3/2}]$  units (18). Thus, a variety of structural entities are expected to be present and they are listed in Table 2.

Only the  $\text{Ga}$  containing glass has a formula similar to  $\text{NaZr}_2(\text{PO}_4)_3$  although its crystalline form does not show a NASICON structure. However,  $\text{Ga}$  like  $\text{Al}$  can be present in both six and four coordinations. Vibrational spectroscopic evidence (10, 16) is in favor of the presence of

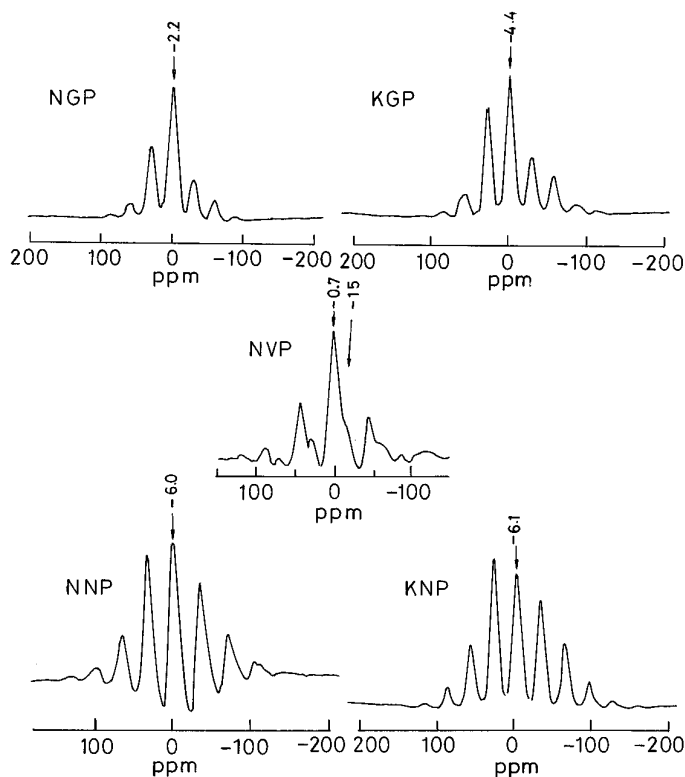


FIG. 3.  $^{31}\text{P}$  MAS NMR spectra of the NASICON-type glasses, for  $B = \text{Ga}$ ,  $\text{V}$ , or  $\text{Nb}$ .

TABLE 2  
Glass Composition, Designation, Chemical Shifts, and the  
Structural Units Expected to be Found in the Glasses

Composition and designation	Chemical shift (ppm)	Possible structural units $A = \text{Li, Na, or K}$
$\text{Na}_3\text{Ga}_2\text{P}_3\text{O}_{12}$ (NGP)	-2.2	$3A^+ + 2[\text{GaO}_{4/2}]^- + 2[\text{POO}_{3/2}] + 1[\text{POO}_{2/2}\text{O}]^-$
$\text{K}_3\text{Ga}_2\text{P}_3\text{O}_{12}$ (KGP)	-4.4	
$\text{Li}_5\text{TiP}_3\text{O}_{12}$ (LTP)	-1.5	
$\text{Na}_5\text{TiP}_3\text{O}_{12}$ (NTP)	-1.1	$5A^+ + [\text{TiO}_{4/2}]^0 + 2[\text{POO}_{1/2}\text{O}_2]^{2-} + 1[\text{POO}_{2/2}\text{O}]^-$ $5A^+ + [\text{TiO}_{5/2}]^- + [\text{POO}_{1/2}\text{O}_2]^{2-} + 2[\text{POO}_{2/2}\text{O}]^-$ $5A^+ + [\text{TiO}_{6/2}]^{2-} + 3[\text{POO}_{2/2}\text{O}]^-$
$\text{K}_5\text{TiP}_3\text{O}_{12}$ (KTP)	4.2, -0.2	
$\text{Li}_5\text{GeP}_3\text{O}_{12}$ (LJP)	-2.8	
$\text{Na}_5\text{GeP}_3\text{O}_{12}$ (NJP)	1.3, -9.2	$5A^+ + [\text{GeO}_{4/2}]^0 + 2[\text{POO}_{1/2}\text{O}_2]^{2-} + [\text{POO}_{2/2}\text{O}]^-$
$\text{Na}_4\text{VP}_3\text{O}_{12}$ (NVP)	-0.7, -15.0	$4A^+ + [\text{VOO}_{3/2}]^0 + 2[\text{POO}_{2/2}\text{O}]^- + [\text{POO}_{1/2}\text{O}_2]^{2-}$
$\text{Na}_4\text{NbP}_3\text{O}_{12}$ (NNP)	-6.0	
$\text{K}_4\text{NbP}_3\text{O}_{12}$ (KNP)	-6.1	$4A^+ + [\text{NbO}_{6/2}]^- + 3[\text{POO}_{2/2}\text{O}]^-$

isolated  $[\text{GaO}_{4/2}]^-$  units in glass. We would therefore expect formation of  $[\text{POO}_{2/2}\text{O}]^-$  and  $[\text{POO}_{3/2}]$  units in the glass. In fact the presence of these two types of units can lead to the formation of pyrophosphate units as mentioned earlier. However, only a single resonance is observed with an averaged chemical shift value (averaged over all the three different possible species). Similarly in Ti and Ge glasses also, one should expect the presence of meta- and pyrophosphate units assuming that  $[\text{TiO}_{4/2}]$  and  $[\text{GeO}_{4/2}]$  units are formed in the glass. But it was shown in the literature (9) and also observed in our earlier IR studies (10) that Ti could be present as square pyramidal  $[\text{TiO}_{5/2}]^-$  units. We do observe both in KTP and NJP a splitting of the resonance peaks, which can be associated with meta- (KTP: -0.2 ppm and NJP: -9.2 ppm) and pyro- (KTP: 4.2 ppm and NJP: 1.3 ppm) phosphate units. The Li salts, LTP and LJP, each seem to give only a single resonance and we suspect that this could be due to the motion of Li ions which averages out small chemical shift differences arising from direct Coulombic interactions with phosphate groups. In the case of NNP and KNP glasses, although there is much evidence for anisotropy, single averaged resonances are seen at -6.1 ppm. However, for vanadium containing glasses in which V is present in  $[\text{VOO}_{3/2}]$  tetrahedra, there is clear evidence of two different  $^{31}\text{P}$  resonances which is as expected (Table 2) and attributed to chemical shifts of meta- (-15.0 ppm) and pyro- (-0.7 ppm) phosphate units.

The structural and chemical disproportionation of phosphate units assumed above can be easily considered as a number of studies reported in the literature (7, 14, 19, 20) suggest that in glasses several types of phosphate units are present quite generally. However, the observed  $^{31}\text{P}$

chemical shifts assigned to meta- and pyrophosphates are very close. In order to understand this further we have examined the chemical shifts together with the corresponding values of  $Z_{\text{eff}} \cdot q/r$  for these glasses, where  $Z_{\text{eff}}$  is the partial charge on the B ion,  $q$  the partial charge on P, and  $r$  the radius of the B ion corresponding to its formal valence. We have shown earlier that a plot of chemical shift vs.  $Z_{\text{eff}} \cdot q/r$  differentiates regions of meta-, pyro-, and orthophosphates very well (21). We have reproduced in Fig. 4 the boundaries of the regions corresponding to various types of phosphate units from our earlier work (21) and plotted the points corresponding to the observed chemical

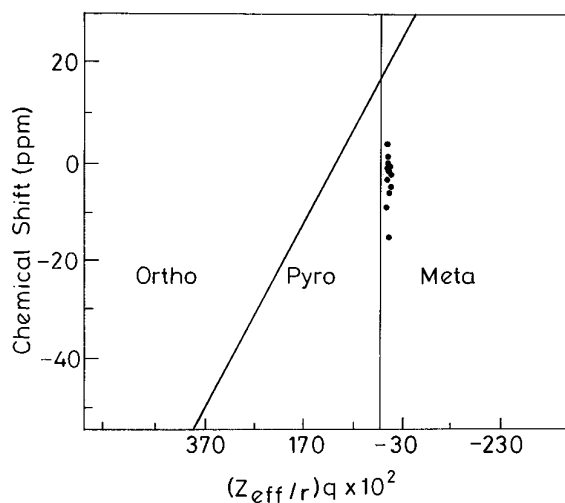


FIG. 4. Points of this study (for the glasses) mapped onto the  $(Z_{\text{eff}}/r)q$  versus chemical shift plot for the phosphate glasses of Ref. (21).

shifts in the present work. It is interesting to see that indeed these glasses are located close to the border of pyro- and meta-phosphates, on the metaphosphate side. The closeness to the meta-pyro boundary is perhaps related to the close and often undifferentiated  $^{31}\text{P}$  resonances of meta- and pyrophosphates observed in the present glasses.

An important observation to which a reference was made earlier relates to the origin of two closely located  $^{31}\text{P}$  resonances in crystalline NNP (11) which were also seen in the spectra of crystalline  $\text{Na}_5\text{Zr}(\text{PO}_4)_3$  and  $\text{Na}_5\text{Ti}(\text{PO}_4)_3$  in the present work. It was suggested that the structures of crystal and glass are very similar on the basis of Raman spectra (22). Unfortunately there are no unique features in the vibrational spectra that allow one to distinguish different types of phosphate units. Vibrational spectroscopic evidence suggests that pyrophosphate units are present even in the crystalline phases (8, 10). These observations could be reconciled if there were a dynamic (resonating) structural and chemical disproportionation operating in the crystalline phase also. We may consider four closely located  $[\text{POO}_{2/2}\text{O}]^-$  tetrahedra in crystalline NNP which are not connected among themselves (no P–O–P linkage); they can switch bonds in such a way that any two of the tetrahedra establish a P–O–P connection and snap other connections so as to form  $[\text{P}_2\text{O}_7]^{4-}$ . The snapped P–O–M connections are reestablished by conversion of the other two tetrahedra into  $[\text{POO}_{3/2}]$  units. In a crystal lattice this would require no more than slight rotations of phosphate tetrahedra without modification of the position of phosphorus or of the center of mass of the phosphate units. This “bond-breaking” and “bond-making” process can happen quickly and reversibly. If the time scales of equilibrations are typically on the order of 10 nsec or slower, both NMR and vibrational spectroscopy can distinguish the pyro- and metaphosphate units. This possibility rationalizes the results of NMR (11), Raman (22), and IR (8) investigations reported in the literature on NNP systems. Preparation of aqueous extracts of phosphates for chromatographic studies (7) containing highly charged ions like  $\text{Nb}^{5+}$  may not allow phosphate species to remain unaffected since  $\text{Nb}^{5+}$  has a tendency to bond to oxygen in order to reduce niobium charge.

The NMR studies reported here have established two important aspects related to the structural model for the NASICON glasses: (i) the presence of  $[\text{BO}_{1/2}]^n-$  polyhedra with strong B–O covalent bonds in random connection to similar polyhedra and phosphate tetrahedra and (ii) the essential equilibration of phosphate species leading to structural and chemical disproportionation.

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#### REFERENCES

1. J. Alamo and R. Roy, *J. Mater. Sci.* **21**, 444 (1986).
2. L. Hagman and P. Kierkegaard, *Acta Chem. Scand.* **22**, 1822 (1968).
3. M. Pintard-Scrépel, F. d'Yvoire, and F. Rémy, *C.R. Acad. Sci. Paris C* **286**, 381 (1978).
4. J. P. Boilot, G. Collin, and R. Comes, *J. Solid State Chem.* **50**, 91 (1983).
5. J. B. Goodenough, H. Y-P. Hong, and J. A. Kafalas, *Mater. Res. Bull.* **11**, 203 (1976).
6. H. Y-P. Hong, *Mater. Res. Bull.* **11**, 173 (1976).
7. B. C. Sales and B. C. Chakoumakos, *J. Solid State Chem.* **105**, 406 (1993).
8. B. Wang, M. Greenblatt, and J. Yan, *Solid State Ionics* **69**, 85 (1994).
9. S. Krimi, A. El Jazouli, L. Rabardel, M. Couzi, I. Mansouri, and G. L. Flem, *J. Solid State Chem.* **102**, 400 (1993).
10. K. C. Sobha and K. J. Rao, submitted for publication.
11. S. Prabakar and K. J. Rao, *J. Solid State Chem.* **91**, 186 (1991).
12. K. C. Sobha and K. J. Rao, submitted for publication.
13. J. R. Van Wazer, “Phosphorus and Its Compounds,” Vol. 1 and 2. Interscience, New York, 1951.
14. S. Anantharaj, K. B. R. Varma, and K. J. Rao, *Solid State Ionics* **27**, 5 (1988).
15. A. Osaka, K. Takahashi, and M. Ikeda, *J. Mater. Sci. Lett.* **3**, 36 (1984).
16. S. Sakka, H. Kozuka, K. Fukumi, and F. Miyaji, *J. Non-Cryst. Solids* **123**, 176 (1990).
17. H. Verweij and J. H. J. M. Buster, *J. Non-Cryst. Solids* **34**, 81 (1979).
18. S. Muthupari, S. Prabakar, and K. J. Rao, *J. Phys. Chem.* **98**, 2646 (1994).
19. B. C. Sales, J. O. Ramey, and L. A. Boatner, *Phys. Rev. Lett.* **59**, 1718 (1987).
20. B. C. Sales, J. O. Ramey, L. A. Boatner, and J. C. McCallum, *Phys. Rev. Lett.* **62**, 1138 (1989).
21. S. Prabakar, K. J. Rao, and C. N. R. Rao, *Chem. Phys. Lett.* **139**, 96 (1987).
22. A. El Jazouli, C. Parent, J. M. Dance, G. Le Flem, P. Hagenmuller, and J. C. Viala, *J. Solid State Chem.* **74**, 377 (1988).