

Infrared and Raman spectroscopic studies of glasses with NASICON-type chemistry

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Abstract. Structures of NASICON glasses of the general formula $AB_2(PO_4)_3$, where $A = Li, Na$ or K and $B = Fe, Ga, Ti, V$ or Nb , have been investigated using vibrational (IR and Raman) spectroscopies. Phosphate species appear to establish an equilibrium via a disproportionation reaction involving a dynamical bond-switching mechanism where both charge and bonds are conserved. B ions in the system acquire different coordinations to oxygens. Alkali ions cause absorptions due to cage vibrations. All the observed spectroscopic features are consistent with speciation involving disproportionation reactions.

Keywords. NASICON glasses; dynamical bond-switching mechanism; disproportionation reactions.

1. Introduction

NASICON is the acronym^{1,2} for ‘sodium super ionic conductors’ in the crystalline state with the general formula $AB_2(PO_4)_3$, where A is an alkali ion and B is generally a metal with a valency of 4 or more, but is also substitutable by trivalent elements. Crystalline NASICONs generally possess a rhombohedral $R\bar{3}c$ structure, in which BO_6 octahedra share corners with PO_4 tetrahedra. NASICONs possess ‘open’ structures in which alkali ions can move with significantly reduced activation barriers and hence the potential for applications as fast ion conductors. Since the B site can be substituted by a variety of transition and non-transition metals (and their combinations) with appropriate charge compensation in the structure by additional alkali ions, NASICONs constitute a very versatile class of materials^{3–5}.

NASICONs by virtue of their complex chemistry have a built-in propensity to form good glasses, (especially when the material is a phosphate). Higher valent elements such as vanadium (V) or niobium (Nb) increase the covalency of the B–O linkage and facilitate the formation of glasses. A number of NASICON glasses have been investigated^{6–9} in this laboratory. It has been found that contrary to expectations, the molar volumes of glasses with NASICON chemistry are sensitive to the size of the alkali ion to a much greater extent than their crystalline counterparts. Indeed, in the absence of the requirement of crystalline periodicity, the network structure collapses around the alkali ions, eliminating the ‘openness’ of the structure, and the observed conductivities are rather low. Additionally, the coordination numbers of the B ions also vary, facilitating the formation of different types of phosphate species, which have been identified¹⁰ by ^{31}P MAS NMR.

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Vibrational spectroscopic studies provide crucial structural information in glassy materials. In our earlier investigations⁶⁻¹⁰, we suggested that the structure of the NASICON glasses consists of a weak polymeric network of $[\text{POO}_{m/2}\text{O}_k]^{k-}$ and $[\text{BO}_{l/2}]^{n-}$ and A^+ ions where m is the number of bridging oxygens connected to phosphorus which is always four coordinated but $m (\leq 3)$ -connected, $k = 3 - m$, l is the coordination number of B and $n = l -$ valency of B. Molar volumes of these glasses change considerably upon interalkali substitution for the same B ion, suggesting that the A cations do not simply occupy designated spaces (like A sites in crystalline NASICON's^{1,11}) present in a structural framework, but are surrounded at close-packing distances by oxygens so as to optimize the volume. The glass transition temperatures (T_g) of the NASICON glasses occur within a narrow range of 30 K, when the B ion is fixed irrespective of the alkali ion. Therefore T_g is likely to be determined by the vibrational properties of alkali ions in these glasses unlike in the several systems we have examined¹². Therefore, the anion framework is likely to play an important role in determining the properties of the glasses with NASICON chemistry. It appears that the low dimensionality caused by the alkali modification and network flexibility enables the polymeric network to provide close coordinations to alkali ions, whereas the glass transition behaviour is determined by segmental motions of the anion framework which is constituted of $[\text{POO}_{m/2}\text{O}_k]^{k-}$ and $[\text{BO}_{l/2}]^{n-}$ units. These units possess characteristic vibrational features and infrared (IR) and Raman spectroscopies are particularly suited for their investigation. Very few reports have appeared in the literature on the vibrational spectra of this class of phosphate glasses. Some of the reported spectra refer to either a single glass composition or to the study of the systematic variation of composition with respect to one of the constituent oxides¹³⁻¹⁷.

We have therefore examined vibrational spectra of several glasses with NASICON chemistry. The spectra of a few crystalline NASICONs have also been studied in order to provide a comparison between the spectra of glasses and crystals of the same composition. Our findings are presented in this paper and discussed.

2. Experimental

Infrared transmission spectra of the glasses and crystals were recorded from 4000 to 200 cm^{-1} using a Perkin-Elmer 580 double beam IR spectrometer. IR spectra of the crystalline compounds and the glasses were recorded in KBr pellets. The Fourier transform IR (FTIR) spectra were recorded using a Bruker IFS 113 FTIR spectrometer. Mixtures of the glass powder and polyethylene were pelletized and used for recording the FTIR spectra. Unpolarized Raman spectra were recorded on a Spex 1403 Raman spectrometer making use of the excitation wavelength of 514.5 nm from an Argon ion laser (Spectra-Physics Series 2000). Polished faces of the pellets of the compounds and small rectangular, polished glass pieces or glass compacts (when large bits could not be obtained) were used for the Raman measurements. All the spectra have been recorded at room temperature (293 K).

3. Results and discussion

3.1 Crystalline NASICON compounds

The compounds whose vibrational spectra have been studied here are $\text{Na}_5\text{ZrP}_3\text{O}_{12}$, $\text{Na}_5\text{TiP}_3\text{O}_{12}$, $\text{Na}_3\text{Fe}_2\text{P}_3\text{O}_{12}$ and $\text{Na}_4\text{NbP}_3\text{O}_{12}$.

3.1a *Infrared studies:* IR spectra of crystalline $\text{Na}_3\text{Fe}_2\text{P}_3\text{O}_{12}$, $\text{Na}_5\text{ZrP}_3\text{O}_{12}$, $\text{Na}_5\text{TiP}_3\text{O}_{12}$ and $\text{Na}_4\text{NbP}_3\text{O}_{12}$ are given in figure 1. Spectra of these crystalline compounds have been examined for comparison with the spectra of glasses. IR spectra of $\text{Na}_5\text{ZrP}_3\text{O}_{12}$ or $\text{Na}_5\text{TiP}_3\text{O}_{12}$ both with $R\bar{3}2$ structure^{11,15} have more features than those of $\text{NaZr}_2\text{P}_3\text{O}_{12}$ and similar compounds with $R\bar{3}c$ structure¹⁸ (analysed in detail by Barj *et al*^{19,20} and Tarte *et al*²¹), particularly in the region above 900 cm^{-1} owing to greater distortion of PO_4 tetrahedra. In the compounds $\text{Na}_5\text{ZrP}_3\text{O}_{12}$ and $\text{Na}_5\text{TiP}_3\text{O}_{12}$, half of the B sites are occupied by Na (A) atoms, which lowers the symmetry of the PO_4 ion from T_d to C_2 . The internal modes of the PO_4 ion are obtained using factor group analysis (table 1): 5 asymmetric stretching, 1 symmetric stretching, 5 asymmetric bending and 2 symmetric

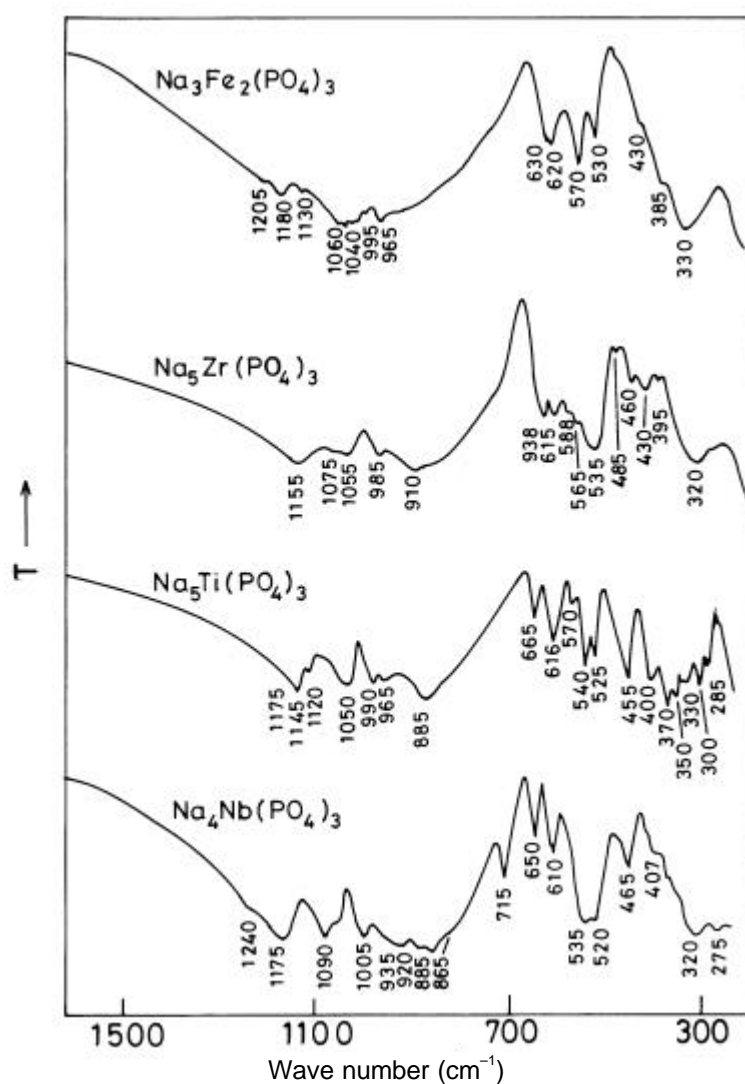


Figure 1. IR absorption spectra of crystalline NASICON compounds.

Table 1. Factor group analysis of the phosphate modes in Na₅TiP₃O₁₂.IR active modes: $E(\mathbf{n}_1)$, $2E(\mathbf{n}_2)$, $2A_2 + 3E(\mathbf{n}_3, \mathbf{n}_4)$ Raman active modes: $A_1(\mathbf{n}_1)$, $2A_1(\mathbf{n}_2)$, $2A_2 + 3E + A_1(\mathbf{n}_3, \mathbf{n}_4)$.

	Point group T_d	Site group C_2	Factor group D_3
\mathbf{n}_1	$A_1(\text{R})$	A	$A_1 + E$
\mathbf{n}_2	$E(\text{R})$	$2A$	$2A_1 + 2E$
$\mathbf{n}_3, \mathbf{n}_4$	$F_2(\text{IR, R})$	$A + 2B$	$A_1 + 3E + 2A_2$

bending modes of the PO₄ group to be infrared active. We may tentatively assign the infrared bands of Na₅TiP₃O₁₂ (figure 1) between 1175 and 885 cm⁻¹ to the asymmetric (5 bands) and symmetric (1 band) stretching, 655–525 cm⁻¹ to the asymmetric bending (5 bands) and 455–400 cm⁻¹ to the symmetric bending (2 bands) of the PO₄ unit. The bands below 370 cm⁻¹ probably involve modes of complex nature including external modes and cage vibrations of alkali ions. Similar assignments hold good for the IR spectrum of Na₅ZrP₃O₁₂.

3.1b *Raman spectrum:* Raman spectra of crystalline Na₃FeP₃O₁₂ and Na₅TiP₃O₁₂ are given in figure 2. The Raman bands between 1157–891 cm⁻¹ are assigned to the stretching modes (7 bands are expected), the 6 weak bands around 590 cm⁻¹ to the asymmetric bending and the 460 and 436 cm⁻¹ bands to the symmetric bending modes of PO₄ ion. But the 590 cm⁻¹ band could also arise from the vibrations of TiO₆ octahedra. The bands below 436 cm⁻¹ may again involve external modes of the PO₄ and modes arising from [FeO₆] and [TiO₆] groups.

Na₃Fe₂P₃O₁₂ has a structure similar to that of NaZr₂P₃O₁₂, except that two more A ion sites are occupied. The room temperature structure of Na₃Fe₂P₃O₁₂ (**a**NFP) is monoclinic and complex²² and has not been well-characterized. Therefore, spectroscopic assignments are even more difficult for this compound. However, it can be seen that the number of bands are few, though the bands are broad. The structure of Na₄NbP₃O₁₂ is also not known clearly. However, the bands at 1240 cm⁻¹ (generally considered as due to P=O stretching) and at 715 cm⁻¹ (which is usually assigned to P–O–P stretching)²³ found in the spectrum of Na₄NbP₃O₁₂, are absent in the crystalline Na₃Fe₂P₃O₁₂, Na₅ZrP₃O₁₂ or Na₅TiP₃O₁₂ which suggests that the structure of Na₄NbP₃O₁₂ is likely to be different from that of the other crystalline phases. Here again a number of studies^{19–21} suggest that the low frequency bands could be associated with external modes involving motions of octahedra centered around B ions. The somewhat prominent IR absorption band below 300 cm⁻¹, particularly in Na⁺ ion-rich compounds could be associated with vibrations of Na⁺ ions in oxygen cages²⁴.

3.2 Glasses

Spectroscopic investigations have been carried out on the various glass compositions. Since they are glasses, their compositions can be expressed in terms of the component oxides. This enables us to view glasses as BO_n–P₂O₅ networks modified by the alkali oxides and therefore identify the structural units expected to be present in each system. This information is summarized in table 2. There are three types of glass compositions: (1) 3A₂O–2B₂O₃–3P₂O₅, where B = Fe or Ga; (2) 5A₂O–2B₂O₃–3P₂O₅ where B = Ti or Ge

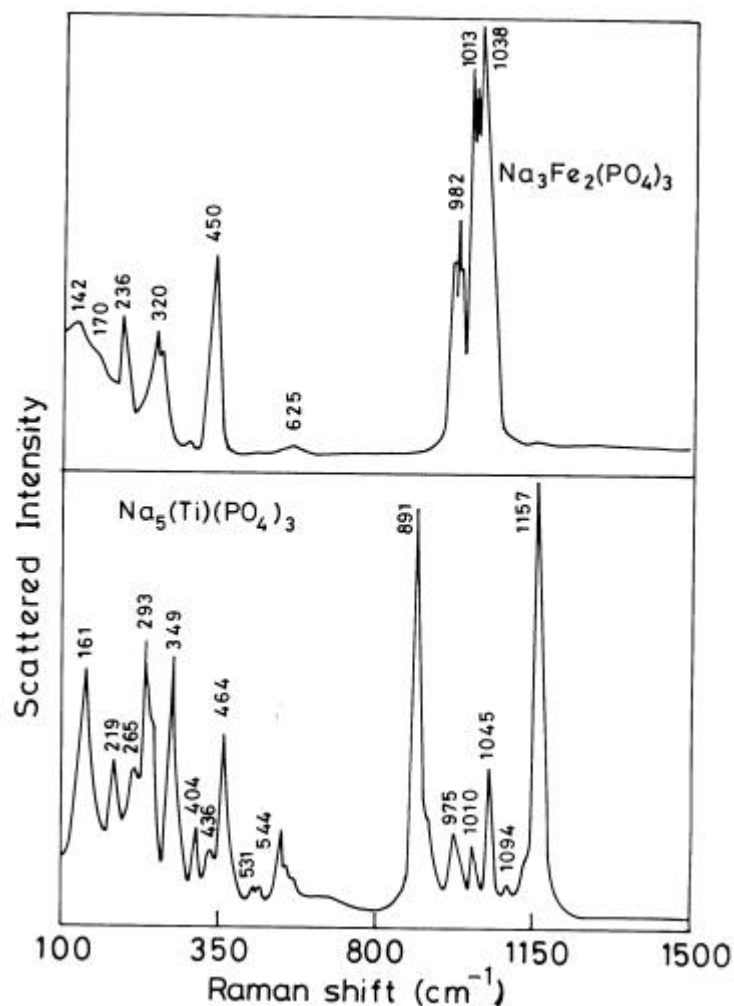


Figure 2. Raman spectra of crystalline $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ and $\text{Na}_5\text{Ti}(\text{PO}_4)_3$.

and (3) $4\text{A}_2\text{O}-\text{B}_2\text{O}_5-3\text{P}_2\text{O}_5$, where $\text{B} = \text{V}$ or Nb ; for $\text{A} = \text{Li}$, Na or K in all these glasses. Thus the three series are based on the (dominant) valency of the B ion. The spectra are discussed below keeping in view this chemical distinction.

3.2a Infrared spectra: The IR absorption spectra of three series of glasses from 1500 to 300 cm^{-1} are shown in figures 3–5. IR absorption bands of phosphates are not known to appear above 1300 cm^{-1} . The entire region down to 400 cm^{-1} is dominated by the vibrations of the PO_4 tetrahedra. Comparing with the band positions in the crystalline compounds discussed earlier, we can assign the broad band between 1200 cm^{-1} and 890 cm^{-1} to the asymmetric and symmetric stretching modes, the band centred at 600 cm^{-1} to the asymmetric bending modes and the weak band near 470 cm^{-1} to the symmetric bending modes of the PO_4 tetrahedra.

Table 2. Glass composition, spectroscopic investigation conducted and the structural units expected to be found in the glass.

Compd no.	Composition and designation	Spectroscopic investigation	Possible structural units, A=Li, Na or K
1	Li ₃ Fe ₂ P ₃ O ₁₂ (LFP)	IR, FTIR	
2	Na ₃ Fe ₂ P ₃ O ₁₂ (NFP)	IR, R, FTIR	3A ⁺ + 2[FeO _{4/2}] ⁻ + 2[POO _{3/2}] + 1[POO _{2/2} O] ⁻
3	K ₃ Fe ₂ P ₃ O ₁₂ (KFP)	IR, FTIR	3A ⁺ + 2Fe ³⁺ + 3[PO ₄] ³⁻
4	Na ₃ Ga ₂ P ₃ O ₁₂ (NGP)	IR, FTIR	
5	K ₃ Ga ₂ P ₃ O ₁₂ (KGP)	IR, R, FTIR	3A ⁺ + 2[GaO _{4/2}] ⁻ + 2[POO _{3/2}] + 1[POO _{2/2} O] ⁻
6	Li ₅ TiP ₃ O ₁₂ (LTP)	IR, R, FTIR	5A ⁺ + [TiO _{4/2}] ⁰ + 2[POO _{1/2} O ₂] ²⁻ + 1[POO _{2/2} O] ⁻
7	Na ₅ TiP ₃ O ₁₂ (NTP)	IR, R, FTIR	5A ⁺ + [TiO _{5/2}] ⁻ + 2[POO _{1/2} O ₂] ²⁻ + 2[POO _{2/2} O] ⁻
8	K ₅ TiP ₃ O ₁₂ (KTP)	IR, FTIR	5A ⁺ + [TiO _{6/2}] ²⁻ + 3[POO _{2/2} O] ⁻
9	Li ₅ GeP ₃ O ₁₂ (LJP)	IR, FTIR	
10	Na ₅ GeP ₃ O ₁₂ (NJP)	IR, R, FTIR	5A ⁺ + [GeO _{4/2}] ⁰ + 2[POO _{1/2} O ₂] ²⁻ + [POO _{2/2} O] ⁻
11	K ₅ GeP ₃ O ₁₂ (KJP)	IR, FTIR	
12	Na ₄ VP ₃ O ₁₂ (NVP)	IR, FTIR	
13	K ₄ VP ₃ O ₁₂ (KVP)	IR	4A ⁺ + [VOO _{3/2}] ⁰ + 2[POO _{2/2} O] ⁻ + [POO _{1/2} O ₂] ²⁻
14	Na ₄ NbP ₃ O ₁₂ (NNP)	IR, R, FTIR	
15	K ₄ NbP ₃ O ₁₂ (KNP)	IR, R, FTIR	4A ⁺ + [NbO _{6/2}] ⁻ + 3[POO _{2/2} O] ⁻

The spectra are very similar for the Li, Na and K members for a common B ion but less so for different B ions for the same alkali ion implying that B ions play a more significant role than alkali ions in the structure of the glass. It is known that variation of the alkali ion does not influence the higher energy side of the vibrational spectra of alkali metaphosphates²⁵. There is no absorption above 1200 cm⁻¹ (at least for glasses 1 to 8) (figures 3 and 4) which is the region of P=O stretch^{23,26}, indicating the absence of long phosphatic chains. However, presence of a band at 740 cm⁻¹ (which is absent in the crystalline NFP or NTP), which can be assigned to the P–O–P bonds²⁷, indicates the presence of interconnected [POO_{m/2}O_k]^{k-} tetrahedra in the glass. Several glasses possess bands either at 1027 cm⁻¹ or 1179 cm⁻¹ suggesting the presence of pyrophosphate [P₂O₇]⁴⁻ groups^{23,28,29}. The absorption at 1380 cm⁻¹, found only in hygroscopic glasses such as LJP (figure 4) can be due to P–O–H deformation²³ caused by water absorbed by the sample.

The band centred at 1030 cm⁻¹ (glasses 1–3 in figure 3) can be attributed to the stretching modes of the PO₄ by comparison with the spectra of crystalline compounds of the same composition. It can be seen that this band is significantly narrower in the spectra of the potassium-containing glasses compared to that of the lithium-containing glasses. The band centre frequency remains unaffected by variation of alkali ions for a given B ion. But the band centre shifts to higher energy for a heavier B ion (substitution of Ga for Fe in glasses 4 and 5 in figure 3) within a series. This peak is not so evident in other glasses. For example, in titanium-containing glasses this band appears split into two bands centred around 1130 cm⁻¹ and ~900 cm⁻¹ (figure 4). In germanium-containing glasses the resolution is even worse although the peak positions are identifiable. Vanadium-containing glasses (figure 5) are again resolved. However, niobium-containing

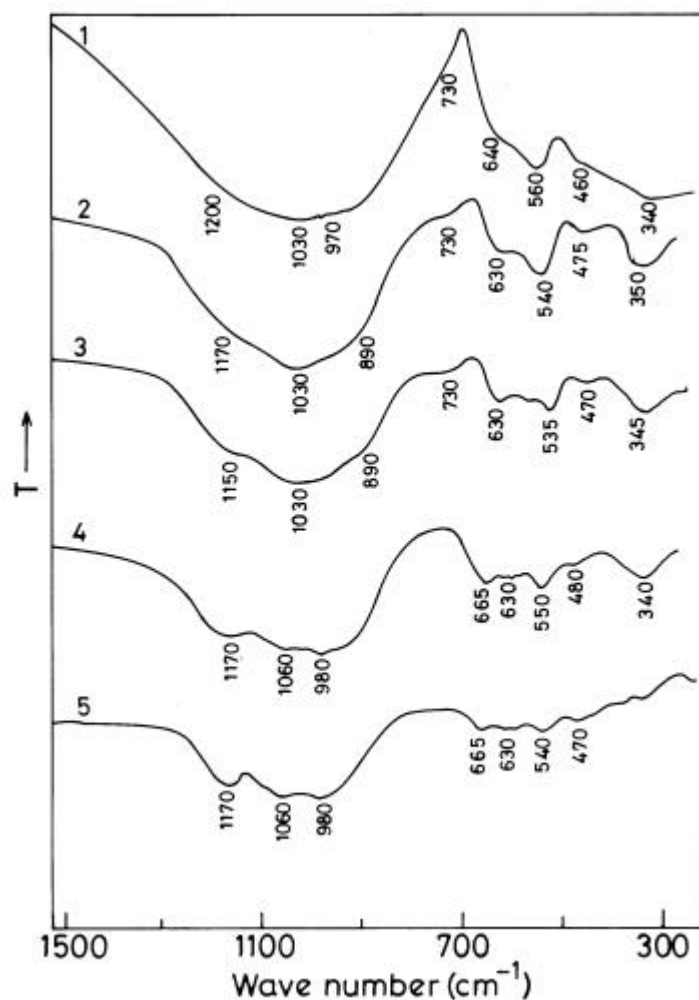


Figure 3. IR spectra of $A_3B_2P_3O_{12}$ glasses where $A = \text{Li, Na or K}$ and $B = \text{Fe or Ga}$ (the numbering of the glasses is the same as in table 2).

glasses have relatively better defined features. Thus the stretching modes in this region appear to arise from slight differences in structure (P–O bond lengths and O–P–O bond angles) and inequivalence of PO_4 groups (see later).

3.2b FTIR spectra: FTIR spectra of the glasses are given in figure 6. In glasses 1–3, the absorption peaks at 640 cm^{-1} and that at 540 cm^{-1} together appear to constitute a band. The position of this band corresponds to the asymmetric bending modes of the PO_4 ion in the spectra of its crystalline phases. An absorption band is present in this region ($500\text{--}650\text{ cm}^{-1}$) in all glasses and is attributable to O–P–O bending modes^{26,27}. This band is very sensitive to change of the alkali ion. The energy of this band is the highest for the Li member and lowest for the K member. As noted earlier, it is also affected, though to a

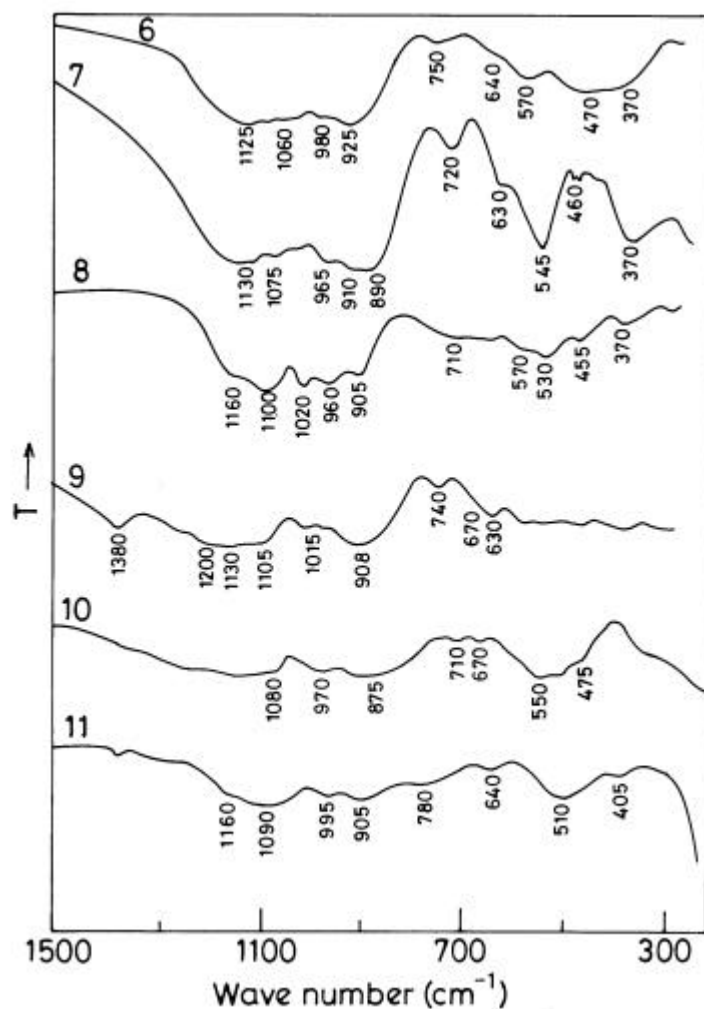


Figure 4. IR spectra of $A_3BP_3O_{12}$ glasses where $A = \text{Li, Na or K}$ and $B = \text{Ti or Ge}$ (the exact compositions of the glasses are given in table 2).

lesser extent, by the substitution of heavier B ions within a series (like Fe for Ga). The lighter B ion glass has this band at a lower energy than the heavier B ion member, for the same alkali ion.

The weak band at $\sim 460 \text{ cm}^{-1}$ (figure 6) is also assigned to bending mode of the PO_4 tetrahedra^{26,27,30}. This band appears very prominently in the infrared absorption spectrum of sodium metaphosphate glass (figure 7), but appears just as a weak band in higher alkali-containing glasses. The presence of this band strongly points towards the network features of phosphate species present in the glasses. The intensity of this band is notably high in the NJP glass.

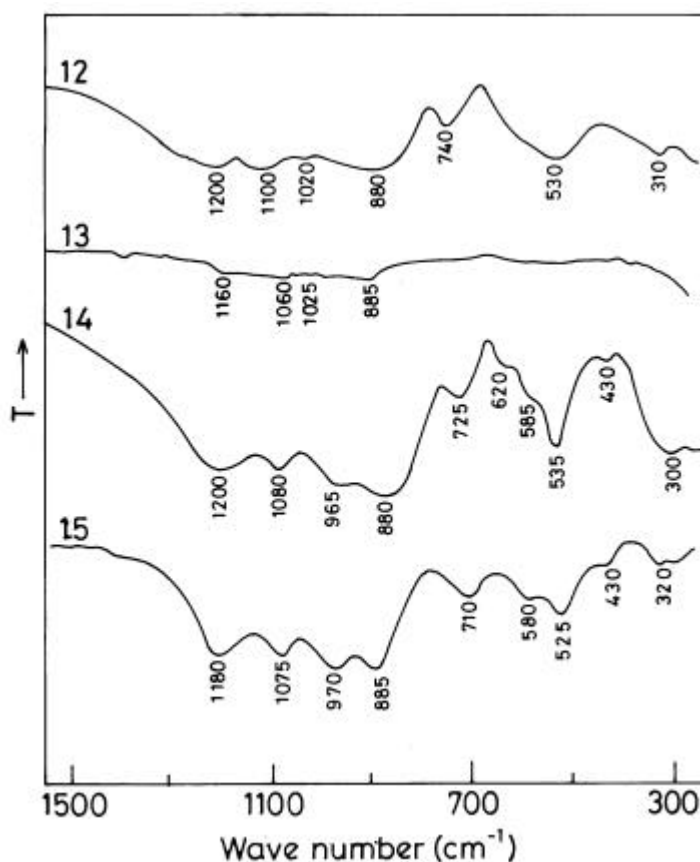


Figure 5. IR spectra of $A_4BP_3O_{12}$ glasses where $A = \text{Li, Na or K}$ and $B = \text{V or Nb}$ (see table 2 for the numbering of the glasses).

The other significant band which occurs below 400 cm^{-1} in FTIR spectra (figure 6) is attributed to the cage vibrations of the alkali ions. Positions of the alkali ion bands (marked by arrows for easy identification) are affected by the B ion, indicating that the charge on the oxygen ion around Na^+ is controlled by B atoms also which constitute part of the network. It is interesting to note that the energies of these bands ($\text{Li}^+ \sim 450\text{ cm}^{-1}$; $\text{Na}^+ \sim 245\text{ cm}^{-1}$; $\text{K}^+ \sim 160\text{ cm}^{-1}$) are higher than in alkali meta phosphate glasses, but more close to those observed in alkali metasilicate glasses²⁵. Since the alkali ions are present in cages surrounded by oxygens from both $[\text{POO}_{m/2}\text{O}_k]^{k-}$ and $[\text{BO}_{l/2}]^{l-}$ units, the average negative charge on the cage oxygen atoms is influenced by B atoms in the structure. In pure metaphosphate glass the average partial charge on oxygen in $[\text{POO}_{2/2}\text{O}]^-$ (-0.347) is low compared to the charges on the oxygens in $[\text{SiO}_{3/2}\text{O}]^-$ (-0.437) (these charges have been calculated using Sanderson's procedure³¹). Thus the charge on oxygen ions in $[\text{SiO}_{3/2}\text{O}]^-$ ions is higher in the metasilicate glass and this increases the force constant and thereby the cage vibrational frequencies. Charges on oxygens in most $[\text{BO}_{l/2}]^{l-}$ are also higher than those in $[\text{POO}_{2/2}\text{O}]^-$. Similar numbers of oxygen atoms from $[\text{BO}_{l/2}]^{l-}$ and

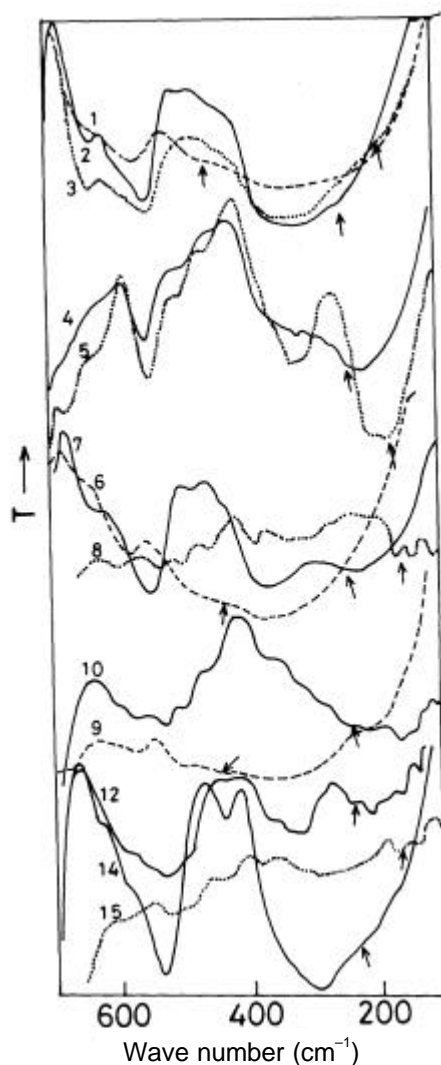


Figure 6. FTIR spectra of the glasses (see table 2 for the numbering of the glasses). The arrows denote the positions of the vibrations bands of the alkali ions' cage.

$[\text{POO}_{2/2}\text{O}]^-$ are present in the coordination sphere, because the ratio (B/P) is fixed in these glasses (glasses 6–15). Also the higher charge on the oxygen atoms attached to B increases the average partial charge on oxygens in the cage and renders the $\text{Na}^+ \dots \text{O}^-$ force constant higher. Thus the observed cage vibrational frequencies are also higher than in pure alkali metaphosphate glasses. As expected the intensity of the cage vibrational band increases as alkali ion concentration is increased.

The band at 340 cm^{-1} is very interesting (figure 6). This band appears broader due to overlap of the cage vibrational band of the alkali ions. The band appears split in the Ga glasses. This band appears at higher energy for the Ti and Ge glasses, but at lower energy

for the Nb and V glasses. The composition dependence of the band position could not be studied quantitatively. The band appears to be unaffected by the B ion mass, since in both Nb and V glasses this band appears at 310 cm^{-1} . Since this band is entirely absent in alkali phosphate glasses (figure 7), it is most likely to be related to the P–O–B bending vibrations. The frequency is low for Fe and Ga glasses because of the low force constants (low values of charges on Fe^{3+} and Ga^{3+}). But it is unclear as to why the frequency is again low in V and Nb glasses.

3.2c *Raman spectra:* The Raman spectra of the glasses are shown in figure 8. The Raman spectra could not be obtained for a number of samples because they are either deeply coloured (like the KFP or NVP glasses) or very hygroscopic like the KJP glass. The Raman spectra of the crystalline and glassy NNP¹³ are similar. The spectra are also in very good agreement with literature reports^{15,19,20}. The glass spectrum of NTP consists of all the important features present in the spectrum of the crystal. But in the case of NFP,

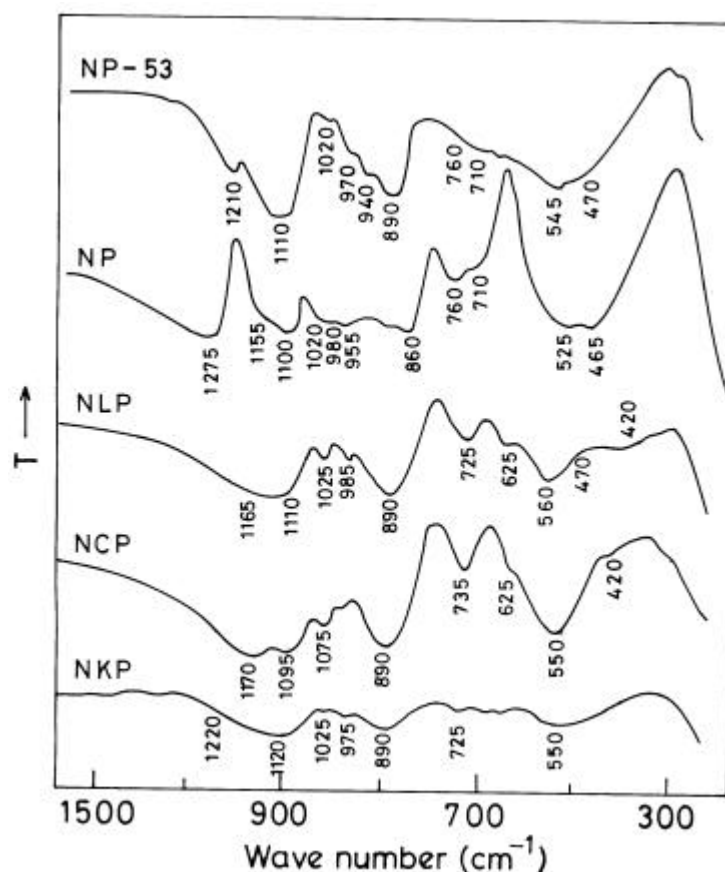


Figure 7. IR absorption spectra of some alkali phosphate glasses. The compositions are NP53 = $5\text{Na}_2\text{O}\cdot 3\text{P}_2\text{O}_5$, NP = NaPO_3 , NLP = $4\text{Na}_2\text{O}\cdot 1\text{Li}_2\text{O}\cdot 3\text{P}_2\text{O}_5$, NCP = $4\text{Na}_2\text{O}\cdot 1\text{CuO}\cdot 3\text{P}_2\text{O}_5$, NKP = $5\text{Na}_2\text{O}\cdot 1\text{K}_2\text{O}\cdot 3\text{P}_2\text{O}_5$.

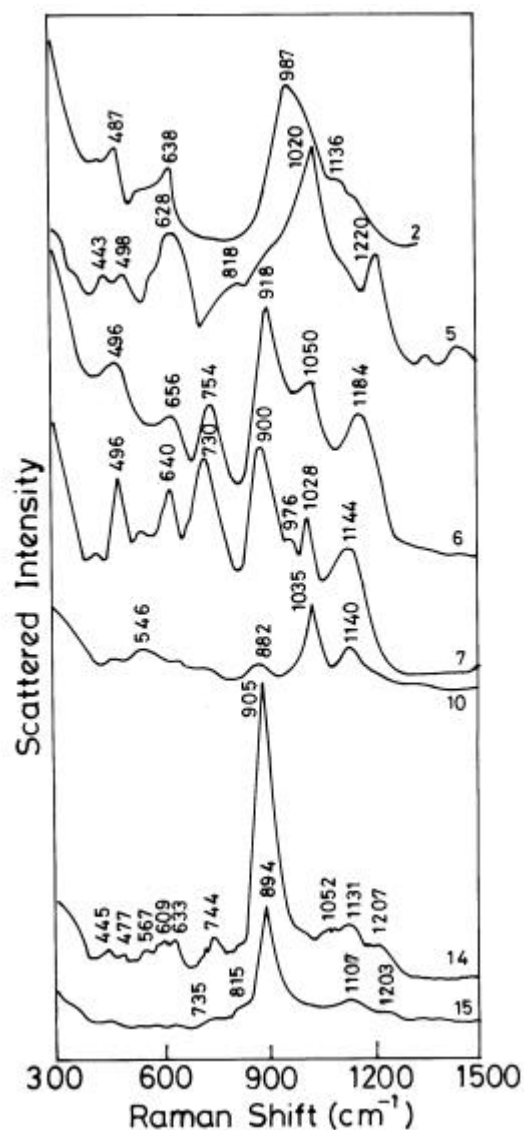


Figure 8. Raman spectra of the glasses (table 2 gives the exact compositions).

some major differences can be seen between the Raman spectra of the glass and the crystal in the 1100 cm^{-1} region, which arises from the stretching modes of the PO_4 units. The implications of these observations are discussed later.

The Raman spectra of the glasses exhibit considerable differences. Here again most differences are found in the region of the P–O stretching modes. The highest intensity band in KGP and NJP spectra is observed at 1020 cm^{-1} , which may be assigned to P–O stretching³⁰. The bending modes at 638 cm^{-1} and 487 cm^{-1} are found in almost all the cases. There are several bands common to both IR and Raman spectra of the glasses. But it is difficult to identify and compare quantitatively the various bands due to their large

half-widths. An important feature of the Raman spectra is that for the same B ion (say Ti) the spectra of glasses with different alkalis are very similar. But with different B atoms (say Ge, Fe and Nb) the spectra are significantly different. This again is consistent with the observations made in the previous section.

3.3 General

3.3a *Evidence for $[P_2O_7]^{4-}$ species:* Some of the systems reported here have been studied using vibrational spectroscopy by other workers also. El Jazouli *et al*¹³ compared the Raman spectra of $Na_4NbP_3O_{12}$ glass and crystal, and concluded that the structure of the glass and the crystal are very similar and consistent with NASICON-type structure with distorted and isolated PO_4 tetrahedra. Wang *et al*¹⁶ from their IR spectroscopic study of NNP glass and crystal concluded that the crystal consisted of pyrophosphate units which were present in the glass also. While Wang *et al*¹⁶ attributed the 1175 cm^{-1} band to pyrophosphate units, Krimi *et al*¹⁵ associated the weak 1027 cm^{-1} stretching mode with $[P_2O_7]^{4-}$. The spectra of NNP (also KNP) glass in figure 4 are in very good agreement with those of Wang *et al*¹⁶. The 1180 cm^{-1} band due to P–O stretching along with the 725 cm^{-1} band due to P–O–P bending may be considered as evidence for the presence of $[P_2O_7]^{4-}$ in our glasses as well. Presence of 1175 cm^{-1} and 715 cm^{-1} absorption peaks in the crystalline NNP (figure 1) appear therefore to support the conclusion of Wang *et al*¹⁶ that crystalline NNP also contains pyrophosphate groups. We may also note that Sales and Chakoumakos³² found evidence for the presence of only $[P_2O_7]^{4-}$ ions in crystalline NNP from high performance liquid chromatography (HPLC) experiments. It would however be difficult to understand how the chemistry of $A_xB_y(PO_4)_3$ is consistent with the presence of $[P_2O_7]^{4-}$ groups in either crystalline or glassy form unless there are facile chemical and structural disproportionations of phosphate anions occurring in them. This is possible only when the $[BO_{1/2}]^{n-}$ behave as strong structural entities so that the phosphate moiety is present as meta or ultra phosphate units in the structure. On this basis, the likely types of $[BO_{1/2}]^{n-}$ and the associated phosphate units present in the various NASICON compositions have been listed in table 2. The NASICONs in which $[P_2O_7]^{4-}$ units can form can be directly inferred from table 2. We may now examine the important spectroscopic features in the light of the suggested disproportionation of phosphate units.

3.3b *$A_3B_2P_3O_{12}$ glasses:* $Na_2O-Ga_2O_3-P_2O_5$ glasses were studied by Berthet *et al*¹⁷, using IR and Raman spectroscopies. They assigned the band at $600-660\text{ cm}^{-1}$ in the IR spectrum to the GaO_4 groups and the Raman peaks at 636 cm^{-1} and 350 cm^{-1} were assigned to GaO_4 and GaO_6 groups respectively. In alkaline earth gallate glasses, the Raman peaks at 515 cm^{-1} and 540 cm^{-1} were assigned to Ga–O–Ga bonds between GaO_4 tetrahedra, and the band at 675 cm^{-1} to the vibrations involving non-bridging oxygens from the GaO_4 tetrahedra³³⁻³⁵. Clearly $600-660\text{ cm}^{-1}$ vibrations present in good intensity in KGP (figures 6 and 8) and NGP (figure 6) glasses provide evidence for the presence of $[GaO_{4/2}]$ groups in our glasses. This is consistent (table 2) with the proposed presence of $[POO_{3/2}]^0$ and $[POO_{2/2}O]^-$ units in these glasses. The presence of pronounced shoulders at $\sim 1200\text{ cm}^{-1}$ due to P=O, prominent peaks around 650 cm^{-1} due to modes of $[POO_{3/2}]^0$ ³⁰ (figure 3) and bands at $\sim 540\text{ cm}^{-1}$ attributable to $[GaO_4]$, together confirm the presence of the proposed entities. Absence of absorption between 515 cm^{-1} and 550 cm^{-1} (due to Ga–O–Ga) also suggests that $[GaO_{4/2}]$ units in the structure are largely isolated by

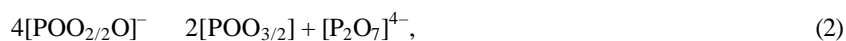
intervening phosphate groups. These phosphate units are again isolated in the structure since 730 cm^{-1} IR absorption due to P–O–P linkages²³ are absent. In fact, Tarte *et al*¹⁴ have pointed out that the phosphate tetrahedra are essentially isolated in the $\text{Na}_3\text{Ga}_2\text{P}_3\text{O}_{12}$ glass, based on the absence of the above peak.

From the similarities of valences of Ga and Fe, we should expect Fe-containing glasses to exhibit similar spectroscopic features. However, there is evidence from Mössbauer spectroscopy that Fe^{3+} is octahedrally coordinated in alkali phosphate glasses³⁶. Fe^{3+} acts more like a modifier in such a coordination and only orthophosphate, PO_4^{3-} ions can be present in the glass as suggested in table 2. The Raman bands at 550 cm^{-1} and 487 cm^{-1} (figure 8) support the presence of PO_4^{3-} in the NFP glass³⁷. However, presence of the weak IR band at $\sim 730\text{ cm}^{-1}$ (figure 3) and the Raman shoulder near 1170 cm^{-1} (figure 8) can only be due to the presence of other types of phosphatic species³⁸. It is reasonable to expect that Fe, like Ga, occupies tetrahedral positions also, as has been suggested in the literature^{5,28,29}. Formation of the $[\text{FeO}_{4/2}]$ unit leads to the formation of $[\text{POO}_{3/2}]$ and $[\text{POO}_{2/2}\text{O}]^-$ groups as in the case of Ga glasses. However, spectroscopic features due to $[\text{POO}_{3/2}]$ are absent. This, we feel is a consequence of the reaction between PO_4^{3-} and the $[\text{POO}_{3/2}]$ which leads to the formation of $[\text{POO}_{2/2}\text{O}]^-$,



The presence of Fe^{3+} as $[\text{FeO}_4]$ is also consistent with $530\text{--}560\text{ cm}^{-1}$ absorptions (figures 3 and 6)^{5,26,28,29,39}. Vibrations below 450 cm^{-1} in figure 6 could also be attributed to motions involving Fe^{5,26,28,29,39}.

Whenever $[\text{POO}_{2/2}\text{O}]^-$ groups are present in glass-forming melts an equilibrium of the kind,



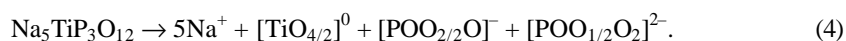
may be expected to be established⁴⁰. Reactions (1) and (2) can be combined to



A strong depletion of $[\text{POO}_{3/2}]$ units is expected at the expense of which $[\text{POO}_{2/2}\text{O}]^-$ and $[\text{P}_2\text{O}_7]^{4-}$ species are produced. While cooling the glass-forming melts there is a likely thermodynamic motivation in the system for the above reaction because it decreases the number of species present and helps the system to eschew configurational entropy, which it should. Therefore, Fe-containing glasses should also contain pyrophosphate units. The peaks at $\sim 1170\text{ cm}^{-1}$ (P=O stretching) and 730 cm^{-1} (P–O–P stretching)²⁶ in Fe-containing glasses (figures 3 and 8) support this view.

3.3c $A_5BP_3O_{12}$ glasses: In Ti-containing glasses a strong Raman band near 900 cm^{-1} has been thought to arise from $[\text{TiO}_4]$ groups^{34,41}. Recently Krimi *et al*¹⁵ have assigned the band at 750 cm^{-1} and 905 cm^{-1} to $[\text{TiO}_6]$ and $[\text{TiO}_5]$ entities respectively. The particularly strong IR absorption of the NTP glass (figure 4) at 545 cm^{-1} and the Raman bands at 640 cm^{-1} (figure 8) may be taken as indication of octahedrally coordinated Ti, whereas the strong Raman peak near 750 cm^{-1} in the Raman spectra of LTP and NTP (figure 8) may be assigned to tetrahedrally coordinated Ti in comparison with the literature reports on crystalline titanates⁴². As a result of the tendency of titanium to form

tetrahedral $[\text{TiO}_{4/2}]^0$, square pyramidal $[\text{TiO}_{5/2}]^-$ and octahedral $[\text{TiO}_{6/2}]^{2-}$ units, several types of phosphate units are also expected to form (table 2). Thus the interpretation of the vibrational spectra of LTP and NTP glasses is quite difficult. $[\text{TiO}_{4/2}]^0$ units readily lead to the formation of pyrophosphate units,



Peaks in IR (and also in Raman) in $1020\text{--}1100\text{ cm}^{-1}$ region along with features in the region of $700\text{--}750\text{ cm}^{-1}$ (P–O–P linkage) support the presence of $[\text{P}_2\text{O}_7]^{4-}$. ($[\text{TiO}_4]$ vibrations also contribute to the absorption in this region.) There is no absorption at $\sim 665\text{ cm}^{-1}$ and therefore $[\text{POO}_{3/2}]$ units are absent supporting the occurrence of the above reaction.

Ge has the same valency as Ti and germanium glasses also exhibit very similar IR spectra. Only $[\text{GeO}_{4/2}]^0$ and $[\text{GeO}_{6/2}]^{2-}$ species are known in literature. Presence of $1080\text{--}1100\text{ cm}^{-1}$ band together with $740\text{--}780\text{ cm}^{-1}$ band (figure 4) (except in NJP where 710 cm^{-1} peak is seen) again suggests presence of pyrophosphate units. Further the signature frequency of tetrahedrally coordinated Ge at $\sim 900\text{ cm}^{-1}$ ⁴³ present in all Ge glasses and absence of IR bands at $580\text{--}600\text{ cm}^{-1}$ (figure 4), together with the absence of a Raman band at 710 cm^{-1} (figure 8) attributable to octahedrally coordinated Ge^{43,44}, suggest that Ge is present only in $[\text{GeO}_{4/2}]^0$ units.

3.3d *A₄BP₃O₁₂ glasses:* Although vanadium has the same valency as Nb, it tends to form $[\text{VOO}_{3/2}]$ units in glass⁴⁵, similar to phosphorus which forms $[\text{POO}_{3/2}]$ units. Unfortunately the IR spectra of vanadium-containing glasses in this work are poorly resolved. Presence of a peak at 740 cm^{-1} can be associated with $[\text{VOO}_{3/2}]$ units in addition to P–O–P linkages⁴⁵. However vanadium glass should also contain pyrophosphate units (table 2) and the presence of 1100 cm^{-1} (NVP) and 1060 cm^{-1} (KVP) support this possibility.

3.3e *Pyrophosphate units and spectra of crystalline NNP:* ³¹P MAS NMR evidence clearly points to the presence of at least two distinguishable phosphate units in crystalline NNP^{46,47}. But only one (averaged) ³¹P resonance was identified in the glass, where it is easy to visualize the formation of pyrophosphate units because in the melt an equilibrium of the type represented by (2) (§3.3b) can occur. Structurally $[\text{P}_2\text{O}_7]^{4-}$ is an apically fused ditetrahedron. One can visualize the occurrence of a *structural and chemical* disproportionation of the type represented by (2) even in crystalline compounds like NNP (or NTP) resulting in two types of phosphate species. Topochemical constraints fix the positions of the phosphate units in the structure in the lattice and high resolution magic angle spinning nuclear magnetic resonance (HR MAS NMR) can distinguish between them even though the chemical shift difference between them is small. But the two ³¹P signals possibly get merged into a single NMR peak of larger FWHM in the glass. Presence of $[\text{POO}_{3/2}]$ units in the glasses is suggested in the IR absorption features at $>1200\text{ cm}^{-1}$ in NNP (figure 5) and several other glasses (figures 3 and 4) which is due to P=O stretching. Features at $\sim 650\text{ cm}^{-1}$ due to P=O bending further confirm the presence of $[\text{POO}_{3/2}]$ groups in the glass²⁷. The absorption peak at 530 cm^{-1} (figure 5) can be attributed to Nb–O vibrations¹⁶. A 525 cm^{-1} peak is particularly prominent in the FTIR spectrum of NNP which again supports this conclusion. The strong absorption peak at $\sim 900\text{ cm}^{-1}$ present in IR and Raman spectra of the Nb glasses may include contributions

from the $[\text{NbO}_6]$ vibrations¹³. Spectroscopic features of KNP and NNP glasses (figures 5 and 6) are very similar.

Two aspects of the literature reports regarding the vibrational spectrum of NASICON glasses need to be considered further. El Jazouli *et al*¹³ reported that the crystal and glass structures are very similar on the basis of Raman spectroscopic studies but it was found that glass and crystal do have distinguishable structures on the basis of ^{31}P MAS NMR studies. However, studies of Wang *et al*¹⁶, HPLC studies of Sales and Chakoumakos³² and the present spectroscopic studies together suggest that pyrophosphate units are likely to be present in both crystalline and glassy NASICONs containing Nb. Formation of pyrophosphate units can be visualized only through the reaction represented by (2). It is possible only if there is *dynamic switching* of bonds among the tetrahedral phosphate units surrounding the B ions in the crystal structure. Four phosphate tetrahedral units, (2), in close proximity can switch the bonds forming one pyrophosphate unit and two 3-connected $[\text{POO}_{3/2}]$ units. This requires only a slight reorientation of the four phosphate tetrahedra in such a way that a binary ditetrahedral unit is formed which snaps all its other links forming the $[\text{P}_2\text{O}_7]^{4-}$ unit. At the same time the other two units form two additional links resulting in the formation of $[\text{POO}_{3/2}]$ units. Thus there is both charge and bond conservation. At ordinary temperatures, a *dynamical bond switching* as envisaged here can still enable distinguishing the different phosphate units by NMR experiments if the time scales of switching are less than 10 ns. Similarly, presence of P–O–P linkages characteristic of pyrophosphates, are also identified from IR spectra in which time constants are less than 10 ns. Secondly, association of 1175 cm^{-1} IR absorption features with pyrophosphate units¹⁶ does not appear to be unequivocal. In our investigation, we found that formation of pyrophosphate units was always associated with the 1027 cm^{-1} absorption as suggested by Krimi *et al*¹⁵. An absorption feature around 650 cm^{-1} (figures 3–5) attributable to $[\text{POO}_{3/2}]$ units was also present in many spectra since the latter forms together with $[\text{P}_2\text{O}_7]^{4-}$ units.

4. Conclusions

Vibrational properties of several phosphates with NASICON chemistry have been examined using IR, Raman and FTIR spectroscopies considered together, the vibrational spectra of glasses reveal the following.

- (1) The IR spectra is dominated by the vibrational properties of phosphates which also provide vital clues to understand the structure of the glasses.
- (2) Phosphate units establish equilibria among various phosphatic species through disproportionation reactions which conserve both charges and bonds.
- (3) B atoms seem to be present in different possible coordinations to oxygen atoms and generally tend to have lower coordination numbers with higher covalency of bonding. Different phosphatic species are therefore present in glasses (table 2). Although the spectra are dominated by vibrational features due to phosphate ions, B ions also register their presence in the middle region of $400\text{--}800\text{ cm}^{-1}$. Notable in the spectra shown in figures 3–5 are the specific peaks due to Fe ($530\text{--}550\text{ cm}^{-1}$), Ga ($600\text{--}675\text{ cm}^{-1}$) and Ti (905 cm^{-1} , 750 cm^{-1} and 640 cm^{-1}) containing oxypolyhedra. Alkali ion vibration in oxygen cages have been identified in FTIR spectra. However, this region of spectrum is complicated by the excitation of external modes of the various structural groups present in the glasses. Thus the

vibrational spectroscopic investigations have helped identify unique structural features of glasses with NASICON chemistry.

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