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Short-Range Structure and Cation Bonding in Calcium–Aluminum Metaphosphate Glasses

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Comprehension of short- and medium-range order of phosphate glasses is a topic of interest, due to the close relation between network structure and mechanical, thermal, and optical properties. In this work, the short-range structure of glasses $(1 - x)\mathrm{Ca(PO_3)_2}\cdot x\mathrm{Al(PO_3)_3}$ with $0 \leq x \leq 0.47$ was studied using solid-state nuclear magnetic resonance spectroscopy, Raman spectroscopy, density measurements, and differential scanning calorimetry. The bonding between a network modifier species, Al, and the network forming phosphate groups was probed using high-resolution nuclear magnetic resonance spectroscopy of ^{27}Al and ^{31}P. Changes in the compositional behavior of the density, glass transition temperature, PO_2 symmetric vibrations, and Al coordination number were verified at around $x = 0.30$. ^{31}P NMR spectra show the presence of phosphorus in Q^2 sites with nonbridging oxygens (NBOs) coordinated by Ca ions and also Q^2 sites with one NBO coordinated by Al (namely, Q^2(1Al)). The changes in the properties as a function of x can be understood by considering the mean coordination number measured for Al and the formation of only Q^2 and Q^2(1Al) species. It is possible to calculate that a network formed only by Q^2(1Al) phosphates can just exist up to the upper limit of $x = 0.48$. Above this value, Q^2(2Al) species should appear, imposing a major reorganization of the network. Above $x = 0.30$ the network undergoes a progressive reorganization to incorporate Al ions, maintaining the condition that only Q^2(1Al) species are formed. These observations support the idea that bonding principles for cationic species inferred originally in binary phosphate glasses can also be extended to ternary systems.

I. Introduction

The potentiality of the phosphate glass is well-known in technological applications as sensors, solid-state batteries, hermetic seals to high expansion metals, bioactive materials, laser devices, etc....[1−4] Many studies have been carried out in this glass system because it allows modifications in its glass composition to achieve desirable properties.

In phosphate glasses, the network is composed by P tetrahedral building blocks, which are identified according to their mutual connectivity using the notation Q^n, with n being the number of bridging oxygen atoms (BOs) shared with other n P tetrahedra. Metal cations (Me) are able to coordinate the nonbridging oxygens (NBOs) according to their ionic radii and effective charge. The short-range organization of the network as a function of the cationic content is an important issue to be understood because many properties of the glasses are related to it. Correlations among the structure, bonding, and collective properties of the glass were reported elsewhere.[2−5] For example, in the sodium−aluminum metaphosphate system, the increase in T_g, frequency of PO_2 symmetric vibrations, and density as a function of Al content were explained in terms of the hardening of the network through the formation of P−O−Al linkages at the expense of weaker P−O−Na linkages.[6]

For binary oxide ultraphosphate compositions, Hoppe determined the role of the coordination number of the Me cation in the structure and properties.[7] The number of available NBOs, the valence and coordination number (CN)

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† In memoriam.

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of Me cations, and the way that Me−O coordination polyhedra share oxygen atoms among them as well as with P−O tetrahedra will determine, as a function of the composition, reconstructive transformations of the network with an effect on the properties of the material. According to Hoppe, two types of network reconstruction are likely to occur, as the oxide content in binary systems is increased.[7] The first one occurs when the oxide content is high enough to allow Q^2 tetrahedra to modify their connectivity with Me−O polyhedra from a configuration involving the sharing of their two NBOs with the same Me cation to a different configuration where NBOs are shared with *two* different Me cations. The second reconstruction occurs when the number of available BOs is insufficient to fill the coordination sphere of Me cations, so Me−O polyhedra are forced to share corners, edges, or even faces among them. This kind of process explains the minimum in packing density and T_g for several glasses observed at a concentration value dependent on the coordination number of the Me cation.[8] In a recent study on the sodium−aluminum metaphosphate system,[6] we proposed that the same type of bonding constraints are also valid in *ternary* glass systems, where two different cationic species are able to coordinate NBOs. For the sodium−aluminum metaphosphate glass it was found that (i) Al atoms tend to exploit their maximum coordination capacity according to the number of available NBOs and (ii) P tetrahedra share only *one* NBO with an AlO_n polyhedron.

The latter behavior can be considered as an extension of Hoppe's observations, in the sense that the preferred bonding for two NBOs of a single P tetrahedron is the formation of linkages not only with two different Me cations, but also with different species when they are available. Bonding constraints i and ii determine that PO_4 tetrahedra and AlO_n polyhedra ($n = 6, 5$) are linked by vertexes, and each AlO_n polyhedron is surrounded by *n* different tetrahedra. However, this kind of network connectivity cannot be sustained at arbitrary oxygen concentrations. Therefore, if the concentration of the oxides is varied to reduce the total O content, at some critical value there will be insufficient NBOs available to satisfy conditions i and ii, and a structural rearrangement of the network will occur.[6] The value of the critical concentration will depend on the valence and coordination capacity of the Me cations, and also on stereochemical constraints.[6] The latter effect can be understood as follows. According to constraints i and ii, at a given glass composition there will be a number of tetrahedra nonlinked to Al, which are able to coordinate more Al incorporated into the network, and other tetrahedra forming coordination spheres of *n* members around an Al atom. With increasing Al content, tetrahedra nonlinked to Al will decrease in number and eventually will be dispersed between spheres of tetrahedra already coordinated to Al. Although the total number of NBOs in the network is still enough to coordinate more incorporations of Al atoms, Al-free P tetrahedra will be dispersed in the glass. Eventually, conditions i and ii will not be satisfied locally. The effect of this situation can be treated by considering an extended coordination sphere around Al atoms composed by a number of phosphate groups higher than the *n* tetrahedra forming the Al−O−P linkages. Therefore, a reorganization of the connectivity should occur at concentrations lower than the values expected from stoichiometry. For sodium−aluminum metaphosphate it was verified that this first kind of reorganization occurs without violating conditions i and ii, i.e., rearranging the contact between the coordination spheres in a more efficient manner to exploit the rest of the Al-free P tetrahedra to support more Al in the network.[6]

To generalize these ideas as bonding principles valid for a wide variety of systems, it is necessary to verify if this sort of process occurs in other phosphate glasses. Also, it is expected that there will be a dependence of the concentration for network reorganization on the cation valence and coordination capacity and also on their bond strengths and ionic radii. For these reasons, in this work we studied in detail the system calcium−aluminum metaphosphate by means of high-resolution solid-state nuclear magnetic resonance (NMR) spectroscopy of ^{31}P and ^{27}Al, Raman spectroscopy, differential scanning calorimetry, and density measurements. Triple-quantum magic angle spinning (3Q-MAS) ^{27}Al NMR experiments were performed to separate the spin interaction parameters for ^{27}Al: the isotropic chemical shift δ_{iso} and the quadrupolar coupling product $P_q = [\chi^2(1 + \eta^2/3)]^{1/2}$, where χ is the coupling between the electric quadrupolar moment of the nucleus and the principal value of the electric field gradient (efg) at the nuclear site and η is the asymmetry parameter of the efg tensor.[9,10] These two parameters are sensitive to changes in the chemical bond containing the resonant species, and their measurement is important to determine if a reorganization of the network involves changes in the immediate chemical environment around the Al ions (up to second-order neighbors).

II. Experimental Procedure

Glasses $(1 - x)Ca(PO_3)_2{\cdot}xAl(PO_3)_3$ with analyzed molar fractions $x = 0$, 0.12, 0.15, 0.16, 0.22, 0.24, 0.30, 0.36, 0.38, 0.41, and 0.47 were prepared by the conventional melt quenching method. Ca_2PO_3 was synthesized using reagent grade calcium carbonate and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) as starting materials. $NH_4H_2PO_4$ was used to transform each oxide into a metaphosphate compound. Commercial reagent grade $Al(PO_3)_3$ powder was used. The metaphosphate powders were mixed at the desired proportions, melted in porcelain crucibles at temperatures between 1100 and 1250 °C in air, and poured into a brass mould previously heated. Annealing treatments were performed on each sample for 4 h at 25 °C below their respective T_g. The chemical composition of each glass was checked using an energy-dispersive X-ray spectrometer (LEO 440, EDX Oxford detector). The average compositions on three spots are shown in Table 1. The uncertainty of the measurements is ±5%. The glassy state of the samples was confirmed from X-ray diffraction experiments using a Rigaku-Rotaflex-RU 200B instrument. Densities of the glasses at room temperature were

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Table 1. Batch and Analyzed (in Parentheses) Compositions of Calcium−Aluminum Phosphate Glasses

$Al(PO_3)_3$ (molar fraction)	[CaO] (mol %)	[Al_2O_3] (mol %)	[P_2O_5] (mol %)	$Al(PO_3)_3$ (molar fraction)	[CaO] (mol %)	[Al_2O_3] (mol %)	[P_2O_5] (mol %)
0	50 (50)	0 (0)	50 (50)	0.30	38 (36.8)	6 (6.6)	56 (56.6)
0.12	41 (40.3)	1 (4.9)	51 (54.9)	0.36	35.5 (33.7)	7.25 (8.2)	57.3 (58.2)
0.15	46 (41.2)	2 (4.4)	52 (54.4)	0.38	33.5 (32.2)	8.3 (8.9)	58.3 (58.9)
0.16	44 (41.5)	3 (4.3)	53 (54.3)	0.41	31 (30.0)	9.5 (9.0)	59.5 (61.0)
0.22	42 (38.6)	4 (5.7)	54 (55.7)	0.47	28.5 (27.5)	10.8 (11.3)	60.8 (61.3)
0.24	40 (37.4)	5 (6.3)	55 (56.3)				

measured using the Archimedes method with CCl_4 as the immersion liquid. The error associated with the density measurements is about ±0.03 g/cm^3. The glass transition temperatures T_g of the samples were measured from differential scanning calorimetry (DSC) runs performed under a N_2 atmosphere in platinum crucibles with a heating rate of 10 °C·min^{-1}. The accuracy on the T_g values is about ±3 °C.

Raman spectra of optical quality polished samples were recorded on a triple-grating monochromator (Spex model 1877) with 2 cm^{-1} resolution. The excitation source was an Ar$^+$ laser (Spectra-Physics model 165) operating at 514 nm at about 300 mW power. High-resolution MAS NMR spectra of all compositions were obtained in a magnetic field of 9.4 T with a Varian Unity INOVA spectrometer. Measurements were carried out under MAS of up to 11 kHz in silicon nitride rotors. The ^{31}P NMR spectra were obtained from Bloch decay (BD) signals after $\pi/2$ pulses of 4 μs length and recycle delays of 300 s. For ^{27}Al NMR, the pulse duration was 0.3 μs ($\pi/16$) and recycle delays were 0.250 s. 3Q-MAS ^{27}Al NMR experiments were carried out using two pulses for generation−reconversion of 3Q coherences into observable ones,[11] with durations of 5 and 1.7 μs, respectively, and an intensity of 120 kHz. An additional Z-filter selective pulse of 10 μs length and 5 kHz strength was also applied.[12] Spectral widths of 30 and 40 kHz were used, respectively, for the direct and indirect dimensions. A number of 256 hypercomplex FID signals were collected, with 1024 points and 384 transients each. Recycle delays of 1 s were used in all experiments. References for ^{31}P and ^{27}Al chemical shifts were 85% H_3PO_4 and 0.1 M $Al_2(SO_4)_3$ solutions, respectively.

III. Results

III.a. Density and DSC Measurements. Density and glass transition temperature T_g values for the set of samples are plotted in Figures 1 and 2, respectively, as a function of the $Al(PO_3)_3$ concentration. With the addition of Al, the value of the density decreases from 2.64 g/cm^3 for the calcium metaphosphate glass to about 2.56 g/cm^3. With increasing Al content above $x = 0.30$, there is a more noticeable decrease in densities. On the other hand, the T_g values in Figure 2 show an increment with the Al content, with an apparent plateau for x between 0.20 and 0.30. Outside this range, the rate of increase of T_g is about 170 °C/mol. The increase in T_g can be understood in terms of the replacement of Ca−O bonds by stronger Al−O bonds bridging neighboring phosphate chains. In this way, the mobility of the phosphate segments became more restricted, causing the increase in T_g.

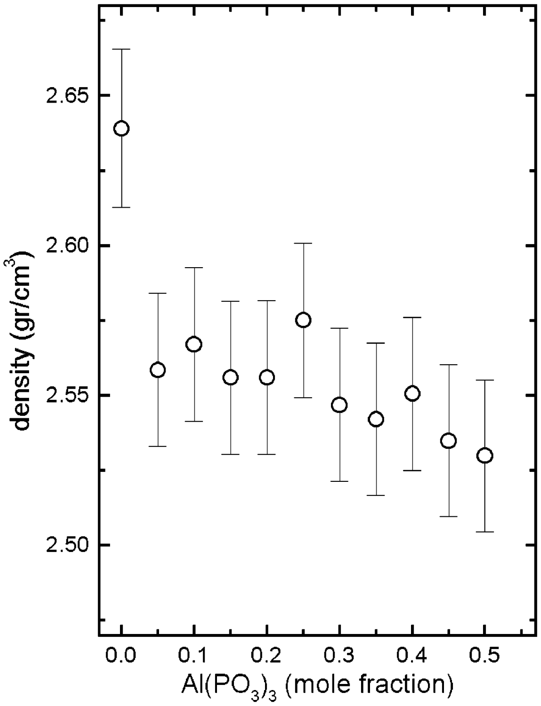

Figure 1. Density of the calcium−aluminum metaphosphate glasses as a function of composition.

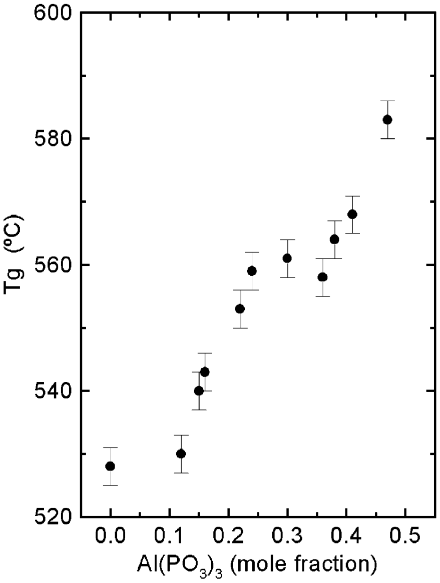

Figure 2. Glass transition temperature of the calcium−aluminum metaphosphate glasses as a function of composition.

III.b. Raman Spectroscopy. Raman spectra of some metaphosphate samples are shown in Figure 3. Two intense bands related to the symmetric stretching of P−BO and P−NBO bonds were detected around 700 and 1190 cm^{-1} in the Q^2 structures.[13] As can be seen, the frequency of the P−BO vibration practically does not change with an increase of the $Al(PO_3)_3$ concentration. On the other hand, the frequency of the P−NBO vibration is shifted from 1176 to 1204 cm^{-1} when the $Al(PO_3)_3$ content is increased due to the large interaction among the NBOs with the cation.

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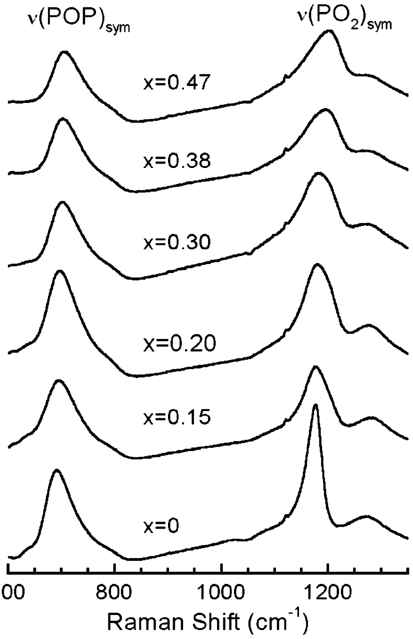

Figure 3. Raman spectra of some glasses of the system calcium−aluminum metaphosphate.

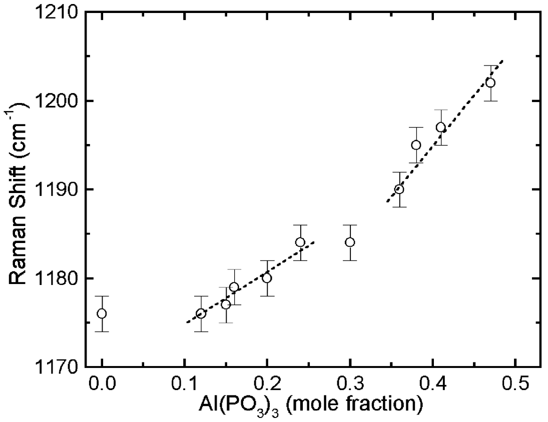

Figure 4. Raman shift of the (PO_2) symmetric vibrations as a function of the $Al(PO_3)$ mole fraction.

To evaluate the influence of the cation on the local structure of the phosphate network, it is important to investigate the dependence of the values of P−NBO frequencies on the addition of Al. Figure 4 depicts the P−NBO frequency as a function of the $Al(PO_3)_3$ mole fraction. The increase in the values of the frequencies with the addition of $Al(PO_3)_3$ occurs due to the substitution of Ca−O by Al−O bonds, which present a larger bond strength than Ca−O. Besides, in Figure 4 a change in the slope around $x = 0.30$ can also be noticed. A similar break was also verified in T_g values as a function of the $Al(PO_3)_3$ mole fraction. This behavior may indicate that structural and dynamical changes may be occurring in the metaphosphate structure for concentrations close to $x = 0.30$. It should be mentioned that Raman experiments probe structural changes in a more local manner than the T_g measurements, giving rise to some differences in the sensitivity and concentration values where the corresponding measured quantities show appreciable variations in their behavior.

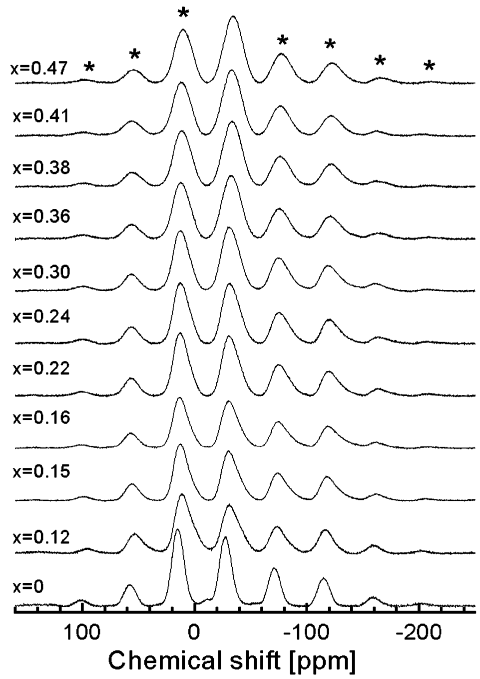

Figure 5. High-resolution ^{31}P NMR spectra of calcium−aluminum metaphosphate glasses. Asterisks indicate spinning sidebands.

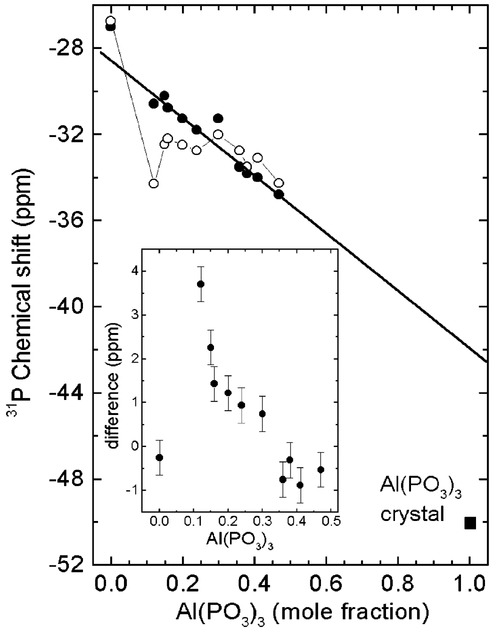

Figure 6. Black circles: chemical shift value at the peak of the ^{31}P NMR line as a function of the glass composition. Open circles: first moment of the ^{31}P NMR center band. Straight line: linear behavior of the peak position, extrapolated up to the pure aluminum metaphosphate glass ($x = 1$). Inset: difference between the first moment and the position of the maximum.

III.c. NMR Spectroscopy. III.c.1. ^{31}P NMR. Figure 5 shows the ^{31}P NMR spectra for all concentrations. There is only one resonance associated with Q^2 tetrahedra. Figure 6 shows the chemical shift values for the peak of the NMR line, showing a good linear correlation with the Al concentration. It is known that the ^{31}P resonance in phosphates shifts to lower frequencies when the bond strength of the species bound to the O atoms increases.[14] Thus, the increase of the shielding of Q^2 phosphates shown in Figure 6 is expected due to the progressive formation of more O−Al linkages having a higher bond strength than O−Ca linkages. On the other hand, it can be observed that the extrapolation of the chemical shift trend to the 100% $Al(PO_3)_3$ glass (−42 ppm) does not agree with the observed position of the Q^2 resonance of the $Al(PO_3)_3$ crystal (−50 ppm). This fact indicates a substantial difference in the bonding of Al with NBOs between the glasses and the $Al(PO_3)_3$ crystal. In fact, it is known that in the $Al(PO_3)_3$ crystal both NBOs of Q^2 phosphates are bonded to the same Al atom; i.e., AlO_6 octahedra are sharing one edge with PO_4 tetrahedra.[15] For a given Q^2 tetrahedron, we will identify the number p of NBOs shared with an Al atom by the nomenclature $Q^2(p\text{Al})$. It is known that for each P−O−Al linkage of a phosphate group there is an increase in the shielding of the ^{31}P resonance between 7 and 8 ppm.[16] So, the difference of 9 ppm measured between the extrapolation of the chemical shift of the resonance in the glasses and that of the $Al(PO_3)_3$ crystal supports the attribution of phosphate groups in the glasses as Q^2(1Al) units. A closer examination of the ^{31}P NMR line shape and width for the glasses should confirm this attribution. For glasses of low Al concentrations, the ^{31}P NMR line in Figure 5 is clearly asymmetric. This fact is related to the presence of Q^2 with both NBOs coordinated by Ca atoms, contributing to the less shielded part of the line, and some $Q^2(p\text{Al})$ groups contributing to the more shielded side. Considering, for example, the glass with $x = 0.12$, where the asymmetry is more resolved than in the other spectra, it is possible to measure a shoulder in the central NMR line at approximately 8 ppm with respect to the maximum. This difference is compatible with the 7 ppm shielding expected for phosphates with only one P−O−Al linkage, i.e., a Q^2(1Al) group. This observation reinforces the interpretation that the preferential arrangement in the coordination of Al^{3+} ions involves Q^2(1Al) phosphate species. The resolution of both kinds of phosphate species, Q^2 and Q^2(1Al), was also observed in the system sodium−aluminum metaphosphate.[6] However, in the Ca−Al glasses, the NMR lines are broader than in the Na−Al system and the inhomogeneity of the line is barely resolved for concentrations higher than 0.10. As shown in previous studies on binary phosphates,[17] this broadening is correlated with the electrostatic potential of the modifier cation and was associated with an increase in the distribution of O−P−O and P−O−P bond angles. Therefore, it is not possible to calculate the fraction of Q^2 and Q^2(1Al) species by numerical analysis of the NMR line. Instead, the asymmetry of the NMR line caused by both species can be better traced by taking the difference between the first moment and the chemical shift at the peak. This quantity was plotted as an inset in Figure 6. The variation of the asymmetry with x is determined in a complex way by the varying populations and line widths of the distributions of the isotropic chemical shift for Q^2 and Q^2(1Al) sites. For low $Al(PO_3)_3$ concentrations the difference is positive due to a higher population of Q^2 phosphates, and decreases for higher values of x due to the increment in the number of Q^2(1Al) units. For $x > 0.30$ the asymmetry becomes slightly negative and remains stable. However, we cannot conclude that this behavior is associated with the stabilization of the Q^2(1Al) fraction. An increment in structural disorder around Q^2(1Al) may also be broadening the NMR lines and masking a net increase in the integrated area of these sites.

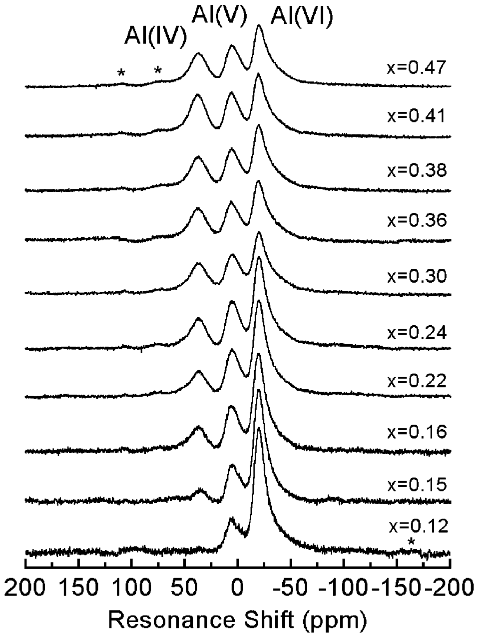

Figure 7. High-resolution ^{27}Al NMR spectra of glasses $(1 - x)Ca(PO_3)_2 \cdot xAl(PO_3)_3$.

III.c.2. ^{27}Al NMR. Figure 7 shows the ^{27}Al NMR spectra for the series of glasses. It can be readily observed that Al is present in coordinations IV, V, and VI, respectively associated with the NMR peaks observed at 37, 5.5, and −20 ppm, for all compositions. Even in the glass with the lowest x there is a small fraction of Al(IV), less than 2% of the total intensity. Figure 8 shows the integrated intensities associated with each central NMR line, obtained from least-squares fittings with multiple Gaussian functions. A number of three, two, and one Gaussian peaks were respectively fitted for Al(VI), Al(V), and Al(IV). As ^{27}Al is a species with an electric quadrupole moment, it is known that populations estimated from the line intensities may be distorted by partially selective excitation and/or contributions from satellite spinning sidebands.[10] These distortions may be especially important for sites with substantially different quadrupolar couplings. For this reason, spectra of Figure 7 were measured using short rf pulse lengths ($\pi/16$), to achieve a nonselective condition for the three sites. The most evident trend followed by the Al intensities in Figure 8, also appreciable from inspection of the NMR spectra in Figure 7, is the decrease of the Al(VI) fraction up to $x = 0.30$ and the simultaneous increase in the Al(V) and Al(IV) fractions.

For higher Al concentrations the populations remain stable in 27% ± 3% Al(IV), 27% ± 3% Al(IV), and 45% ± 5%

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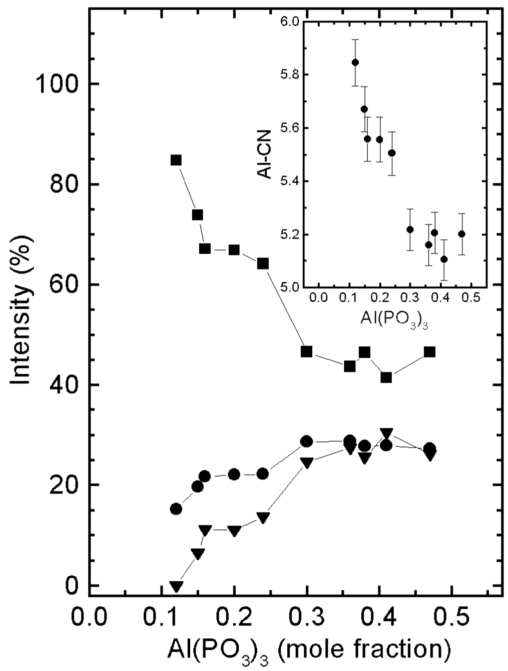

Figure 8. Intensities of each central ^{27}Al NMR line as a function of the glass composition: squares, Al(VI); circles, Al(V); triangles, Al(IV). Inset: mean coordination number for Al calculated from the NMR intensities.

Al(VI). This behavior of the Al fractions will be discussed below in terms of the oxygen content of the glasses and the formation of Q^2(1Al) units. From the populations, it is possible to calculate the mean CN for Al as a function of composition for the set of glasses. The results are plotted in the inset of Figure 8, showing a reduction of CN from 5.8 to approximately 5.2 when x increases up to 0.30, remaining stable for a higher Al content.

It is interesting to compare these results with the Al CN measured in the sodium−aluminum metaphosphate system.[6] In that system, the coordination of Al is higher than in the Ca−Al system, lying between 6 and 5.9 for the same range of Al concentrations. This difference can be explained by taking into consideration that Ca−O bonds are less ionic than Na−O, due to the higher bond strength of Ca compared with Na. As was shown by Metwalli and Brow,[18] less ionicity of the modifier−NBO bond requires greater charge donation from the Al^{3+} ion, which implies a reduction in the mean Al coordination number. For this reason, in the Ca−Al system there are substantial fractions of Al(V) and Al(IV) even for low Al concentrations, in contrast with the observations in the Na−Al system.

Figure 9 shows a typical ^{27}Al 3Q-MAS spectrum for these glasses corresponding to the glass with $x = 0.22$. The integrated projections along the isotropic and anisotropic dimensions are also shown. Signals from the three Al coordinations were clearly resolved in 3Q-MAS spectra of glasses with 0.47, 0.38, and 0.22 $Al(PO_3)_3$, except for the glass with $x = 0.12$, where the fraction of Al(IV) is too small to be appreciably excited in this experiment. With the values measured for isotropic peaks and the center of gravity of the anisotropic projections, shown in Table 2 for each site, the parameters δ_{iso} and P_q were calculated. These values are shown in Table 3, and they constitute approximations to the mean values of their respective distribution functions caused by disorder. As can be seen in Table 3, the values of P_q for each glass are of the same order of magnitude. Therefore, the nonselective rf pulse condition can be easily attained in one-dimensional ^{27}Al NMR experiments, and consequently, the intensities plotted in Figure 8 are reasonable estimations of the Al populations.

The parameters δ_{iso} and P_q determined by 3Q-MAS can be used to compare the bonding properties of the Al sites as a function of composition. The values of δ_{iso} for Al(VI), Al(V), and Al(IV) are the same for all the glasses within the uncertainty of the method, indicating that the mean chemical environment for the Al^{3+} ions does not change for the scanned range of compositions. On the other hand, there are appreciable differences in P_q values as a function of the composition. For each kind of site it is possible to observe an increment of P_q when x is increased, up to a limiting value of approximately 2 MHz for Al(VI) and Al(V) and 1.5 MHz for Al(IV). This observation indicates that for low populations the Al^{3+} ions are located in rather symmetric sites with very low values of the electric field gradient. The effect of Al on the network structure is evidenced only for higher concentrations as a reduction in the local symmetry around the Al coordination polyhedra, resulting in higher values of the electric field gradient. In summary, from the behavior of δ_{iso} and P_q it can be concluded that the structural differences in Al environments are associated mostly with distortions of the oxygen coordination polyhedra at higher Al concentrations rather than modifications in the chemical species bonded as second neighbors.

IV. Discussion

Several differences in the structural arrangement of the glass network for the calcium−aluminum metaphosphate system as a function of the composition can be inferred from the NMR parameters. The asymmetry on the ^{31}P NMR line and the populations of the Al sites show changes of behavior for concentrations higher than 0.30 $Al(PO_3)_3$. From ^{31}P NMR data it was inferred that there is one preferential way of linkage between phosphate groups and Al^{3+} cations: only one NBO per phosphate tetrahedron is shared with Al; i.e., phosphate groups are mainly Q^2(1Al) or Q^2. This behavior agrees with observations in the sodium−aluminum metaphosphate system.[6] Condition ii on the P−O−Al bonding can be satisfied as long as the composition of the glass permits, depending on the concentration and coordination number of the cations. In the sodium−aluminum metaphosphate system the trend of Al to establish bonds with the maximum coordination number compatible with the availability of NBOs for a given glass composition was verified. As the Al concentration increases, the coordination is eventually reduced to keep the condition that only Q^2(1Al) groups should exist.[6] With an increase of the Al concentration, the mean coordination number for Al could not be

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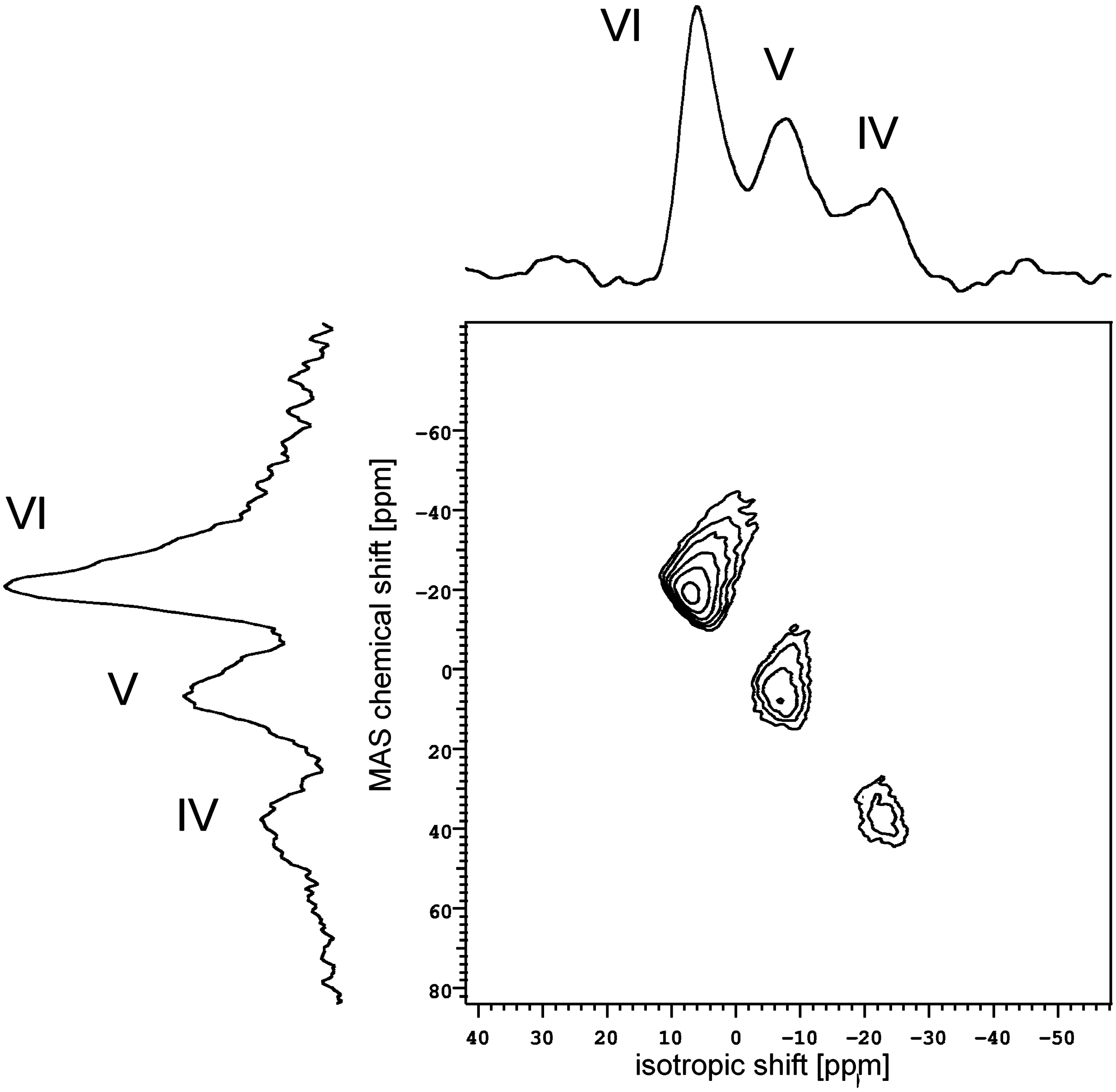

Figure 9. Typical ^{27}Al 3Q-MAS spectra for the calcium−aluminum metaphosphate glasses ($x = 0.22$).

Table 2. Measured Values for the Positions of Isotropic Peaks (δ_1) and the Center of Gravity of the Anisotropic Projections (δ_{cg}) in ^{27}Al 3Q-MAS Spectra

	δ_1 (ppm)			δ_{cg} (ppm)		
x	Al(VI)	Al(V)	Al(IV)	Al(VI)	Al(V)	Al(IV)
0.12	6.8 ± 0.2	−5.9 ± 0.2	−	−19.8 ± 0.3	10.3 ± 0.3	−
0.22	6.3 ± 0.2	−7.2 ± 0.2	−22.5 ± 0.2	−19.2 ± 0.3	7.5 ± 0.3	36.0 ± 0.4
0.38	6.1 ± 0.2	−8.3 ± 0.2	−24.6 ± 0.2	−20.8 ± 0.3	5.5 ± 0.2	36.6 ± 0.4
0.47	6.3 ± 0.3	−7.6 ± 0.3	−23.8 ± 0.3	−21.0 ± 0.5	4.8 ± 0.2	35.8 ± 0.3

Table 3. Interaction Parameters Obtained from the ^{27}Al 3Q-MAS spectra

	δ_{iso} (ppm)			P_q (MHz)		
x	Al(VI)	Al(V)	Al(IV)	Al(VI)	Al(V)	Al(IV)
0.12	−15.0 ± 0.5	10.5 ± 0.5	−	1.3 ± 0.1	0.5 ± 0.5	−
0.22	−14.5 ± 0.5	11.0 ± 0.5	39.5 ± 0.5	2.1 ± 0.1	1.5 ± 0.5	0.5 ± 0.5
0.38	−14.5 ± 0.5	11.5 ± 0.5	42.0 ± 0.5	2.10 ± 0.05	2.10 ± 0.05	1.60 ± 0.05
0.47	−15.0 ± 0.5	10.5 ± 0.5	40.5 ± 0.5	2.0 ± 0.1	1.9 ± 0.1	1.4 ± 0.1

reduced arbitrarily, and there will be a critical concentration where the network should undergo a reorganization to redistribute their NBOs in a more efficient way to coordinate Al, satisfying condition ii, or relaxing this condition to form $Q^2(2Al)$ units.

From a simplified calculation it is possible to estimate the concentration of Al from which a structural reorganization may occur in the glass network. For a calcium−aluminum metaphosphate glass with concentration x of $Al(PO_3)_3$, there will be a fraction $N_{T,av}$ of tetrahedra not coordinated to Al and therefore available to accept an additional incorporation of Al, satisfying condition ii. With N_T being the total number of tetrahedra per formula and $N_{T,coord}$ the number of those phosphates already coordinating an Al^{3+} ion (Q^2(1Al)) plus those Q^2 phosphates within an interstitial region too small to accept an Al ion, we have

$$N_{T,av} = N_T - N_{T,coord} \tag{1}$$

where the total number of phosphate tetrahedra is

$$N_T = 2 + x \tag{2}$$

If only one P−O−Al linkage per phosphate is permitted, the mean fraction of tetrahedra involved in the coordination of Al^{3+} cations, assuming a mean coordination number CN for Al, is

$$N_{T,coord} = \mathrm{CN}(1 + m)x \tag{3}$$

where (CN)m is the number of additional phosphates Q^2 in the interstitial region per Al cation. For a critical value $x = x_C$, $N_T = N_{T,coord}$:

$$x_C = \frac{2}{\mathrm{CN}(1 + m) - 1} \tag{4}$$

Through this expression, it is possible to plot x_C as a function of x using the experimental values CN(x), and considering m as a parameter. The point of intersection of the curve x_C(x) with the linear relation $x_C = x$ defines the critical concentration corresponding to a given m value. From the experimental CN(x) data, a solution with critical concentration $x_C = 0.32 \pm 0.03$ is obtained with $m = 0.50 \pm 0.02$. This x_C value lies between the range of concentrations where the stabilization of the Al populations and the changes in asymmetry of the ^{31}P lines, T_g, $(PO_2)_{sym}$ vibrations, and density are observed. Within this interpretation, a value $m \cong 1/2$ for the glass with $x = 0.30$ indicates that the region with no additional P−O−Al links around an Al ion involves a number of $[\mathrm{CN}(x)](1 + m) = 7.5$ tetrahedra.

From eq 4, it can be seen that the condition $m = 0$, corresponding to the maximum efficiency for coordination of Al by Q^2(1Al) groups, corresponds to $x_C = 0.48$, assuming CN = 5.2. Above this concentration, a glass structure with only Q^2(1Al) cannot be supported without further reduction of CN, which up to $x = 0.47$ does not occur according to the inset in Figure 8. Therefore, if the glass with $x > 0.48$ is formed, some phosphate tetrahedra should share their two NBOs with Al atoms. With this kind of bonding, higher values of T_g are expected, according to the stronger links established by the Al between neighbor phosphate chains, restricting their mobility and causing a general stiffening of the network. In fact, it should be remarked that attempts were made to prepare glasses with batch compositions above $x = 0.47$, but all of them were unsuccessful. For these compositions a substantial increase in the viscosity of the melts was observed, even at the maximum temperature of the furnace used in this study (≅1250 °C). The existence of a substantial number of Q^2(2Al) species in the melt would be compatible with the experimentally observed behavior.

For glasses with $x_C < x < 0.48$ there are changes in the compositional behavior of several properties, at atomic and macroscopic levels, with respect to lower Al concentrations. However, these changes do not seem to be as strong as expected from a major reorganization of the glass network involving Q^2(2Al) units. We believe that, in this compositional range, as x is increased, there is a progressive reorganization of the phosphate network to distribute more efficiently the NBOs to create coordination environments for Al compatible with condition ii. In terms of the description proposed in eqs 1−3, these processes would involve geometrical distortions of the phosphate chains reducing effectively the value of the parameter m. Also, some minor fraction of Q^2(2Al) species could not be ruled out, because in principle their chemical shift range is included in the low-frequency tail of the ^{31}P NMR line at these concentrations.

V. Conclusion

It was possible to determine that in the calcium−aluminum metaphosphate system the phosphate groups preferentially share only one of their NBOs with Al atoms, showing the same bonding behavior observed in sodium−aluminum metaphosphate. In contrast to the latter system, it was found that Al atoms exist with coordination less than six. This is caused by higher electronic charge donation to NBO from Al^{3+}, due to the lower ionicity of the Ca−O bonds compared with Na−O. From the ^{31}P NMR data, the existence of Q^2(2Al) phosphorus species is less likely in the studied range of glass compositions. The bonding properties inferred for P tetrahedra and Al polyhedra impose a reorganization of the network in the calcium−aluminum metaphosphate system as a function of the Al concentration. Such a process can be occurring in this system from concentrations above $x = 0.30$. On the other hand, a major reorganization is expected above $x = 0.48$, resulting in a stiffer network with phosphate tetrahedra and Al polyhedra sharing edges. The results of this study support the idea that the bonding principles inferred originally in simple binary phosphate glasses can also be extended to ternary systems. Double-resonance experiments between ^{31}P and ^{27}Al would be helpful in determining the local structure of the Q^2(nAl) moieties, probing correlation of these species through space or bonds.[19,20]

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