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Phosphorus speciation in sodium–calcium–phosphate ceramics

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A series of ceramics derived from glasses of general formula $(P_2O_5)_{0.45}(CaO)_{0.2+x}(Na_2O)_{0.35-x}$ (x = 0.0–0.12) were prepared and one- and two-dimensional ^{31}P magic-angle spinning NMR spectroscopy confirmed the predominant speciation of Q^1 phosphorus as Na_4-, Na_2Ca-, and α- and β-Ca_2-P_2O_7, but did not show any Q^1–Q^2 connectivity characteristic of short metaphosphate chains.

We have recently completed[1] a combined solid-state nuclear magnetic resonance and X-ray powder diffraction study of a series of potentially bioactive glasses and glass ceramics of general formula $(P_2O_5)_{0.45}(CaO)_{0.24}(Na_2O)_{0.31-x}(Al_2O_3)_x$ (x = 0.0–0.05). The ceramics are of intrinsic interest, and in addition we seek to use the more detailed structural information obtained from the ceramics to model phosphorus speciation in the glasses. The principal phosphate species were deduced[1] to be cyclic trimetaphosphates (Q^2) bridged by Ca, *i.e.* $Na_4Ca(PO_3)_6$ (by comparison of the ceramic X-ray powder pattern with that of an authentic sample) and various $P_2O_7^{4-}$ (Q^1) containing phases. The assignment of the Q^1 phosphorus species was not conclusive, and we have continued our study through the measurement of the solid-state ^{31}P magic-angle spinning (MAS) NMR spectra of a related series of glass ceramics of general formula $(P_2O_5)_{0.45}(CaO)_{0.20+x}(Na_2O)_{0.35-x}$ (x = 0.0–0.12), wherein there is no complication from structural modification induced by the presence of aluminium, in order to confirm the nature of the Q^1 species. Hartmann and co-workers[2–4] reported one-dimensional ^{31}P MAS spectra and two-dimensional dipolar recoupled ^{31}P spectra of sodium–calcium–aluminium–phosphate glasses and glass ceramics which showed strong connectivities within the Q^1 region and weaker Q^1–Q^2 and Q^2–Q^2 connectivities. The connected Q^1–Q^1 resonances were assigned to mixed sodium–calcium pyrophosphates, and the Q^1–Q^2 and Q^2–Q^2 connectivities to the presence of short chain metaphosphate species, but the precise structures of the species was not discussed.

Four glass samples (x = 0.0, 0.04, 0.08 or 0.12) were prepared using appropriate molar quantities of $CaCO_3$, NaH_2PO_4 and P_2O_5, which were blended together and melted at 1250 °C in a platinum crucible for 2 h. The melt was poured into a preheated graphite mould at 350 °C and furnace cooled. Subsequent conversion to ceramic samples was carried out by heating the glasses on gold foil for approximately 2–3 h just below the crystallisation temperature (*ca.* 450 °C, determined by differential scanning calorimetry).

The Q^2 regions (δ −18 to −25) of the 121.4 MHz ^{31}P single-pulse MAS NMR spectra of the four ceramic samples were similar to each other, and also similar to that of the spectra from the samples studied previously,[1] suggesting the predominance of the cyclic trimetaphosphate phase $Na_4Ca(PO_3)_6$. However the appearance of the Q^1 regions (δ 0 to −12) of the 121.4 MHz ^{31}P spectra were quite distinctive (Fig. 1). The major Q^1 ^{31}P resonances occur in pairs: for x = 0.0 at δ −2.4 and −3.9, 0.04 at δ −0.7 and −4.9, 0.08 at δ −0.7 and −4.9 and at δ −7.7 and −10.2, 0.12 at δ −7.1, −8.0, −8.8 and −10.3. This appearance of the spectra is consistent with each pair of resonances being due to a single $P_2O_7^{4-}$ species wherein the two phosphorus atoms are crystallographically distinct. Our

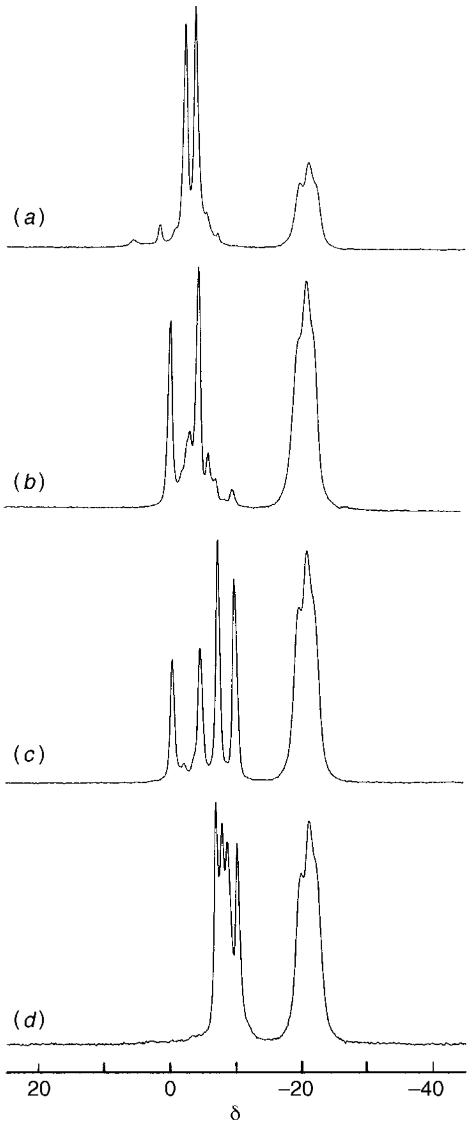

Fig. 1 Centre band regions of the 121.4 MHz ^{31}P MAS NMR spectra (Bruker MSL-300) of the ceramic samples $(P_2O_5)_{0.45}(CaO)_{0.2+x}$-$(Na_2O)_{0.35-x}$: (*a*) x = 0.0, (*b*) 0.04, (*c*) 0.08 and (*d*) 0.12. The ^{31}P chemical shifts are referenced to external H_3PO_4, and typical measurement conditions were 16 scans with a 100 s relaxation delay, and MAS rates *ca.* 7 kHz with the samples contained in a 4 mm outer diameter rotor

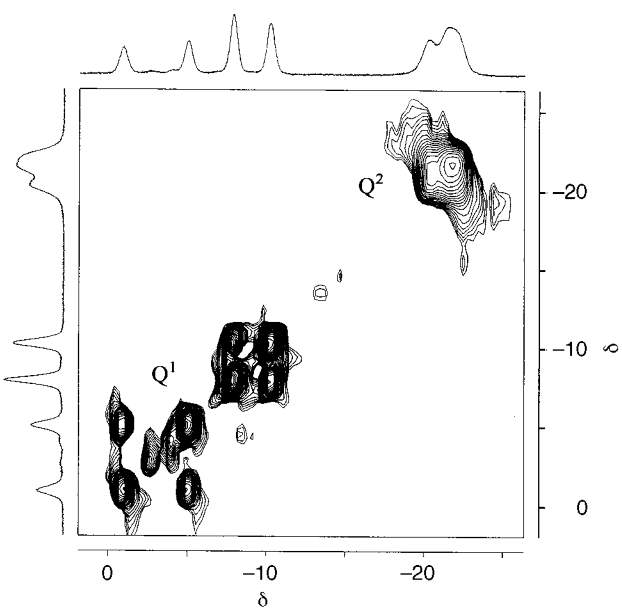

Fig. 2 Centre band region of the 242.9 MHz ^{31}P dipolar recoupled two-dimensional spectrum (Bruker AMX-600) of the ceramic with $x = 0.08$. The MAS rate was 12.0 kHz using a 4 mm outer diameter rotor, and the mixing time was 2.7 ms. Eight scans were acquired, with a relaxation delay of 12 s, for each of 512 experiments

assignment for the pair of resonances from the $x = 0.0$ sample is $Na_4P_2O_7$ for which the reported[5] shifts are *ca.* δ +3.0 and +1.5, the absolute δ values are not the same as those here but the *difference* is identical (1.5 ppm). For the lower sodium-content sample with $x = 0.08$ the signals at δ −7.7 and −10.2 are very similar in position to those reported[5] for α-$Ca_2P_2O_7$. There were four ^{31}P signals reported[5] for β-$Ca_2P_2O_7$ in the range δ −7 to −9 and the spectrum for the $x = 0.12$ sample shows four resolved signals attributable to the β-form. The pairs of signals at δ −0.7 and −4.9 for the samples with $x = 0.04$ and 0.08 are reasonably assigned to $Na_2CaP_2O_7$, with the higher frequency resonances due to phosphorus in the vicinity of sodium in the structure.

As described above the reported[5] ^{31}P spectrum for β-$Ca_2P_2O_7$ showed four resolved resonances, consistent with the X-ray structural determination[6] for β-$Ca_2P_2O_7$ which showed two crystallographically distinct pyrophosphate groups (the X-ray determination[7] of the α-modification showed just one distinct $P_2O_7^{4-}$ unit). Our 121.4 MHz ^{31}P spectrum showed just four resonances attributable to $Ca_2P_2O_7$, but the improved spectral dispersion of a 242.8 MHz ^{31}P MAS NMR spectrum showed four resonances at δ −7.0, −7.9, −8.6 and −10.1 with approximately equal intensity (β-$Ca_2P_2O_7$), and two lesser, equal intensity resonances δ −6.6 and −9.6 (α-$Ca_2P_2O_7$). The total α : β ratio was *ca.* 1 : 10.

To obtain additional evidence for the dominance of the $P_2O_7^{4-}$ species in the Q^1 region, we used the homonuclear dipolar-recoupled two-dimensional NMR experiment described by Jäger and co-workers.[8,9] In this experiment the homonuclear dipolar interaction is reduced by the MAS, but is recoupled by a train of rotor-synchronised 180° pulses during a mixing period. The result of the experiment applied to our ceramic sample with $x = 0.08$ is shown in Fig. 2. The ^{31}P–^{31}P dipolar coupling constant is *ca.* 795 Hz (dependent upon the P–O–P geometry, here taken as that found[10] for $Na_4P_2O_7$), and the MAS rate was adjusted to 12 kHz. The mixing time used was 2.7 ms. In contrast to the published data on the sodium–calcium–aluminium–phosphate glasses and ceramics[3,4] we do not observe any correlation peak between the Q^1 and Q^2 spectral regions, but we do see strong correlations within the Q^1 region, linking the resonances in a pair-wise manner; δ −0.7 with −4.9, and δ −7.7 with −10.2. The lack of the Q^1–Q^2 correlation means that we do not have significant amounts of *short* linear metaphosphate chains, and is consistent with our earlier deductions[1] that cyclic trimetaphosphate species dominate the Q^2 region. The pair-wise correlations within the Q^1 region are entirely consistent with the above conclusion, based on the chemical shifts and intensities of the resonances, that the dominant Q^1 species are pyrophosphates. The experiment was repeated with a mixing time of 10 ms, and a very similar result obtained.

In conclusion we have shown by a combination of one- and two-dimensional ^{31}P MAS NMR that the ceramics all have Q^1 phosphorus mainly present as pyrophosphate. For the sodium rich sample ($x = 0$) the principal component is $Na_4P_2O_7$; with less sodium ($x = 0.04$) the principal component is most likely $Na_2CaP_2O_7$; less sodium still ($x = 0.08$) and there is a mixture of $Na_2CaP_2O_7$ and α-$Ca_2P_2O_7$; and in the sodium depleted sample ($x = 0.12$) there is a mixture of the α- and β-forms of $Ca_2P_2O_7$, with the latter dominating.

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