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Combined Single-Crystal X-ray Diffraction and Magic Angle Spinning NMR Study of α-$CaZn_2(PO_4)_2$

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Abstract: α-$CaZn_2(PO_4)_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 4.960$ (2) Å, $b = 8.418$ (4) Å, $c = 8.940$ (4) Å, $\alpha = 113.75$ (4)°, $\beta = 102.45$ (5)°, and $\gamma = 94.20$ (6)°. In agreement with the ^{31}P magic angle spinning NMR (MAS NMR) spectrum, which shows two isotropic resonances, the structure contains two crystallographically distinct phosphorus sites. There are also two zinc sites, one four- and the other five-coordinated, which are linked to the phosphate tetrahedra to form layers between which the calcium ions lie. ^{31}P MAS NMR has been used to investigate members of a solid solution $CaZn_{2-x}Mg_x(PO_4)_2$ with the α-$CaZn_2(PO_4)_2$ structure. The position and intensity of the ^{31}P isotropic resonances are found to be sensitive to changes in the local environment of the phosphorus caused by magnesium substitution in the five-coordinated zinc site, thus facilitating an assignment of the α-$CaZn_2(PO_4)_2$ spectrum and a rationalization of the nature of the cation substitution.

Magic angle spinning NMR (MAS NMR) is now widely used in solid-state chemistry and has found particular application in structural studies. Nuclei on crystallographically distinct sites are generally found to give rise to separate isotropic resonances (exceptions can be attributed to coincidence), as do equivalent nuclei with different local environments. For example, ^{29}Si isotropic chemical shifts can usually be attributed to crystallographically inequivalent silicon atoms[1] (although this is often complicated by overlapping resonances), but they also display a marked sensitivity to the number of next-nearest-neighbor aluminums in aluminosilicates, in which a maximum of five resonances are obtained from crystallographically equivalent silicon atoms.[2] The sensitivity of MAS NMR isotropic chemical shifts in continuous solids to the local environment of the nuclei has been further demonstrated in a study of the solid solution $Zn_{3-x}Mg_x(PO_4)_2$ by ^{31}P MAS NMR.[3] In this case, an analysis of the intensities of the four resonances, which arise from the four possible local environments of the crystallographically equivalent phosphorus atoms, has enabled a quantitative description of the cation distribution for a variety of compositions. This is possible because the phosphorus chemical shift is sensitive to the nature of a single cation with which the PO_4^{3-} tetrahedra share two oxygens. A second, and more general, approach to the problem of interpreting chemical shifts has been taken with phosphates by using empirical correlations between chemical shifts and features related to the structure, such as the summed bond strength at the phosphate oxygens,[4] or cation electronegativity and charge radius ratio.[5] Part of the rationale for the present investigation has been the search for a system that facilitates a comparison of the allocation of resonances by these two different approaches.

A ^{31}P MAS NMR study of samples with the stoichiometry $CaZn_2(PO_4)_2$ has confirmed the existence of two separate phases, which are stable (or metastable) at room temperature.[6] These two phases correspond to the α- and δ-phases identified from their X-ray powder diffraction patterns by Kreidler and Hummel;[7] two other phases, which are stable above room temperature, were also identified. One of these, β-$CaZn_2(PO_4)_2$, which is reported as being stable in the temperature range 870–997 °C, was indexed in a hexagonal space group with $a = 5.13$ Å and $c = 7.67$ Å. Kreidler et al.[7] have suggested that this β-phase is isostructural with $BaAl_2Si_2O_8$, which has $a = 5.25$ Å and $c = 7.84$ Å.[8] The X-ray powder diffraction patterns of the other $CaZn_2(PO_4)_2$ phases, although reported, have not been indexed.

The slow-spinning ^{31}P MAS NMR spectrum of a sample of α-$CaZn_2(PO_4)_2$ (Figure 1) shows two narrow isotropic resonances, one at 10.0 ppm and the other at 2.2 ppm, with a corresponding array of spinning sidebands separated at the sample spinning speed (of 1595 Hz). Such a spectrum is consistent with a structure in which there are two phosphorus atoms in the asymmetric unit. An NMR study of samples with stoichiometries on either side of $CaZn_2(PO_4)_2$ (i.e. $x < 2$ or $x > 2$ in $Ca_{3-x}Zn_x(PO_4)_2$) confirms that these contain additional phases. The stoichiometry of the α-phase is then definitely $CaZn_2(PO_4)_2$ and, furthermore, the zinc and calcium sites must be quite different so that zinc will not go on to the calcium sites and vice versa; this is not unexpected on size grounds. We report here the crystal structure of α-$CaZn_2(PO_4)_2$ and show how, by comparison with the results of a study of the solid solution $CaZn_{2-x}Mg_x(PO_4)_2$ by ^{31}P MAS NMR, we can make an allocation of resonances in the α-$CaZn_2(PO_4)_2$ spectrum and a qualitative description of the nature of the magnesium substitution.

Experimental Section

A polycrystalline sample of α-$CaZn_2(PO_4)_2$ was prepared by dissolving the salts $CaCO_3$, ZnO, and $NH_4H_2PO_4$ in acid solution in the mole ratio 1:2:2. After drying, the residual white powder was ground and fired at 800 °C for 24 h before being checked by X-ray powder diffraction and ^{31}P MAS NMR for impurities. Single crystals of α-$CaZn_2(PO_4)_2$, suitable for X-ray diffraction, were grown from a $ZnCl_2$ melt. A total of 1.8 g of the polycrystalline sample of $CaZn_2(PO_4)_2$ was thorougly mixed with $ZnCl_2$ (dried at 500 °C) in the approximate molar ratio of 1:10 and then sealed in an evacuated quartz tube. Crystals were grown by slow cooling from 900 °C to room temperature over 10 days in a programmable furnace, with subsequent washing with water to dissolve the zinc chloride. A crystal of dimensions 0.50 × 0.55 × 1.05 mm was selected and mounted on an Enraf-Nonius CAD 4 X-ray diffractometer equipped with monochromatic Mo Kα radiation. After crystal alignment, 25 intense diffraction maxima were measured and used to obtain the cell parameters and the orientation matrix. The reflections were indexed in a triclinic cell with the following dimensions: $a = 4.960$ (2), $b = 8.418$ (4), $c = 8.940$ (4) Å; $\alpha = 113.75$ (4), $\beta = 102.45$ (5), $\gamma = 94.20$ (6)°; $V = 328.2$ Å^3. This gives a calculated density of 3.65 g cm^{-3} for $Z = 2$ (with the formula unit $CaZn_2(PO_4)_2$), which corresponds well to that of α-$Zn_3(PO_4)_2$ ($D_{calcd} = 3.88$ g cm^{-3}).[10] Since the ^{31}P MAS NMR spectrum shows that there are only two crystallographically in-

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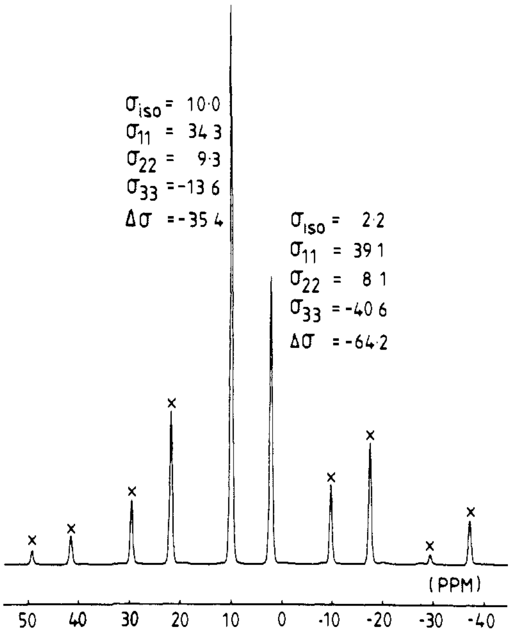

Figure 1. Slow-spinning ^{31}P MAS NMR spectra of α-$CaZn_2(PO_4)_2$ with chemical shifts (ppm) for each resonance. There are two sets of spinning sidebands, separated by the spinning speed of 1595 Hz and indicated by crosses, at each side of the central resonances, which occur at the isotropic shifts. The anisotropic chemical shifts are calculated from the sideband intensities[9] and the chemical shift anisotropies from $\Delta\sigma = \sigma_{33} - {}^1/_2(\sigma_{11} + \sigma_{22})$.

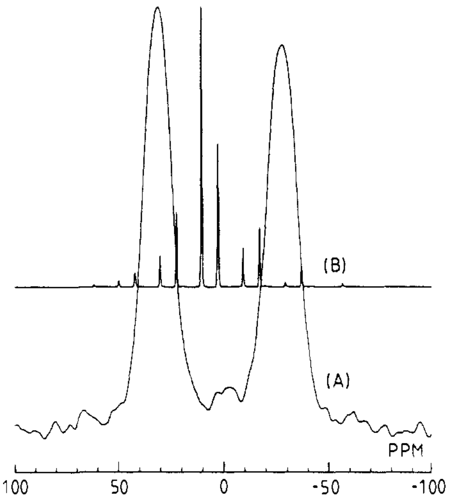

Figure 2. ^{31}P NMR (static) spectrum of a single crystal of α-$CaZn_2(PO_4)_2$, of unknown orientation to the field (A) compared to the MAS NMR spectra (B). The broad line widths of the resonances from the single crystal result from the ^{31}P–^{31}P dipolar interactions.

equivalent phosphorus atoms, the space group can be unambiguously assigned as $P\bar{1}$. In some cases further information about the crystallographic space group may be obtained from the NMR spectrum of a single crystal. In such an experiment, in contrast to data collected from polycrystalline samples, different resonances are observed from atoms that are *magnetically* inequivalent, that is, those not related by translation or inversion, unless there is coincidence caused by the orientation of the crystal in the magnetic field. Such a spectrum from a single crystal of α-$CaZn_2(PO_4)_2$ is shown in Figure 2; two lines are observed, as expected.

A total of 7105 reflections was collected from $0 < \theta < 45.0°$, and they were merged to yield 4862 unique relections with $I > 3\sigma(I)$. Data were collected in the ω–2θ mode. The scan angle was calculated with $\omega = 0.90 + 0.35 \tan\theta$, with scan speeds varying between 1 and 6.67° min^{-1} in ω. The data were treated in the usual way for Lorentz and polarization effects. An empirical absorption correction was applied[11] as well as a θ absorption correction.[12] The transmission factors for the crystal (μ(Mo Kα) = 8.73 mm^{-1}) varied from 1.0 to 4.08.

Table I. Fractional Coordinates and Isotropic Temperature Factors for α-$CaZn_2(PO_4)_2$ (Esd's in Parentheses)

atom	x	y	z	U_{iso}
Zn(1)	0.16241 (3)	0.92142 (2)	0.71522 (2)	0.0093
Zn(2)	0.37615 (4)	0.60709 (2)	0.41045 (2)	0.0096
Ca	0.22509 (5)	0.73242 (3)	0.05449 (3)	0.0085
P(1)	0.68549 (7)	0.79356 (4)	0.81995 (4)	0.0061
P(2)	0.11101 (7)	0.28089 (4)	0.69375 (4)	0.0067
O(1)	0.6210 (3)	0.7478 (2)	0.9560 (2)	0.0128
O(2)	0.4241 (2)	0.2899 (2)	0.7044 (1)	0.0102
O(3)	0.0062 (2)	0.8307 (1)	0.8522 (1)	0.0096
O(4)	0.5654 (3)	0.6338 (1)	0.6437 (1)	0.0098
O(5)	0.0060 (2)	0.8838 (1)	0.2911 (1)	0.0098
O(6)	0.9423 (2)	0.2735 (2)	0.5212 (1)	0.0100
O(7)	0.5639 (2)	0.9504 (1)	0.8036 (1)	0.0088
O(8)	0.9615 (3)	0.5604 (1)	0.1709 (1)	0.0107

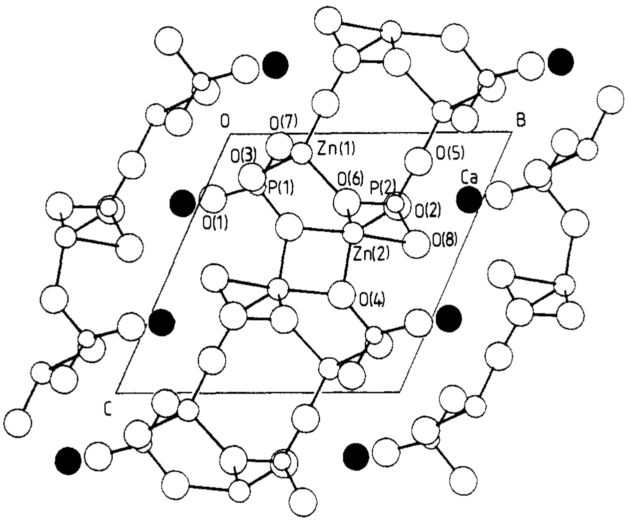

Figure 3. Projection of the structure of α-$CaZn_2(PO_4)_2$ onto the (100) plane. The coordination about the calcium atoms (filled circles) has been omitted for clarity.

The NMR spectra were acquired on a Bruker CXP200 spectrometer operating at 80.9 MHz for ^{31}P. Magic angle sample spinning was carried out with ~400-mg samples in Delrin-Andrews type rotors, with a range of spinning speeds between 2 and 4 kHz. A variety of pulse conditions were used according to the nature of the experiment, but typically 100 transients were collected, with a 5-μs pulse and a recycle delay sufficient to allow full relaxation (up to 500 s was found necessary). Chemical shifts were measured with respect to an external reference of 85% H_3PO_4 and are reported, taking upfield as negative.

Results and Discussion

Single-Crystal X-ray Results. The X-ray crystal structure of α-$CaZn_2(PO_4)_2$ was solved in $P\bar{1}$, on the basis of an asymmetric unit of $CaZn_2(PO_4)_2$, by the heavy-atom method. Initial coordinates for all 10 non-oxygen atoms in the unit cell (2 Ca, 4 Zn, and 4 P) were obtained from the Patterson map, and the remaining oxygen atoms were located by a series of difference Fourier maps. A full-matrix least-squares refinement on all positional and isotropic thermal parameters was carried out with the CRYSTALS suite of programs.[13] During the final cycles of refinement a three-term Chebyshev weighting scheme was used whose parameters were 15024.4, 20672.8, and 6797.0,[14] and an overall isotropic extinction parameter[15] was applied. The final R value was 0.040, and R_w = 0.049.

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Table II. Bond Distances (Å) and Angles (deg) (Esd's in Parentheses) for α-$CaZn_2(PO_4)_2$

Zn(1)–O(3)	1.939 (1)	O(3)–Zn(1)–O(5)	109.61 (5)
–O(5)	1.909 (1)	–O(6)	106.58 (5)
–O(6)	2.010 (1)	–O(7)	104.01 (5)
–O(7)	1.935 (1)	O(5)–Zn(1)–O(6)	108.30 (5)
		–O(7)	120.63 (4)
		O(6)–Zn(1)–O(7)	106.89 (4)
Zn(2)–O(2)	1.954 (1)	O(2)–Zn(2)–O(4)	120.07 (5)
–O(4)	2.006 (1)	–O(4)	110.76 (5)
–O(4)	1.946 (1)	–O(6)	113.61 (5)
–O(6)	2.008 (1)	–O(8)	83.35 (4)
–O(8)	2.505 (1)	O(4)–Zn(2)–O(4)	80.33 (4)
		–O(6)	94.82 (4)
		–O(8)	154.61 (5)
		O(4)–Zn(2)–O(6)	130.84 (5)
		–O(8)	101.43 (4)
		O(6)–Zn(2)–O(8)	64.62 (4)
Ca–O(1)	2.963 (1)	Ca–O(5)	2.510 (1)
–O(1)	2.334 (1)	–O(7)	2.475 (1)
–O(2)	2.543 (1)	–O(8)	2.533 (1)
–O(3)	2.372 (1)	–O(8)	2.420 (1)
P(1)–O(1)	1.502 (1)	O(1)–P(1)–O(3)	108.48 (7)
–O(3)	1.539 (1)	–O(4)	109.90 (7)
–O(4)	1.555 (1)	–O(7)	115.68 (7)
–O(7)	1.537 (1)	O(3)–P(1)–O(4)	107.51 (7)
		–O(7)	109.14 (6)
		O(4)–P(1)–O(7)	105.83 (6)
P(2)–O(2)	1.530 (1)	O(2)–P(2)–O(5)	110.44 (6)
–O(5)	1.531 (1)	–O(6)	110.99 (6)
–O(6)	1.563 (1)	–O(8)	114.73 (7)
–O(8)	1.528 (1)	O(5)–P(2)–O(6)	108.29 (6)
		–O(8)	107.27 (6)
		O(6)–P(2)–O(8)	104.77 (7)

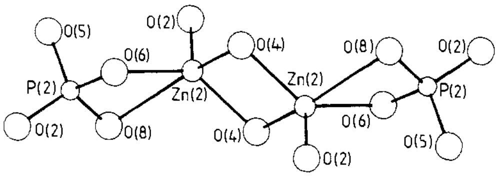

Figure 4. Bridging unit in α-$CaZn_2(PO_4)_2$.

Final atomic coordinates and isotropic temperature factors are shown in Table I, and a projection of the α-$CaZn_2(PO_4)_2$ structure on to the (100) plane is shown in Figure 3. The main framework of the structure is made from connected zinc and phosphorus polyhedra, which form layers parallel to the (001) plane. The calcium cations are coordinated between these layers. Selected bond lengths and bond angles are given in Table II. The two phosphorus atoms have regular tetrahedral coordination, as does Zn(1). Zn(2), on the other hand, has four neighboring oxygens at normal Zn–O distances with a fifth, O(8), at 2.505 Å. A bond strength analysis of the Zn(2)–O bonds by the empirical formula of Brown and Shannon[16] gives a value of 1.85 valence units (vu) for four-coordination and 1.99 vu for five-coordination. The latter is clearly a better statement of the Zn(2)–oxygen coordination. The long Zn(2)–O(8) bond forms part of a short chain of edge-sharing Zn(2) polyhedra and P(2) tetrahedra that stretches across the center of symmetry of the unit cell. This unit, seen in Figure 3 and shown schematically in Figure 4, is very similar to the grouping found in the γ-$Zn_3(PO_4)_2$ (γ-$Zn_3(PO_4)_2$ is a generic term for members of $Zn_{3-x}M^{II}{}_x(PO_4)_2$ solid solutions that have the $Mg_3(PO_4)_2$ structure[17,18]) structure and in β-$Zn_3(PO_4)_2$, a zinc phosphate phase stable above 942 °C.[19] It appears, therefore, to be common in zinc phosphates despite the fact that the group contains, in α-$CaZn_2(PO_4)_2$, a four-membered ring with a Zn(2)–O(4)–Zn(2) bond angle of 99.7° and a O(4)–Zn(2)–O(4) bond angle of 80.3°. One consequence of this is that the coordination about Zn(2) is quite irregular, with O–Zn–O angles ranging from 130.8° to 80.3° for the four short oxygen bonds and from 154.6° to 64.6° when the fifth bond, Zn(2)–O(8), is included.

There is some similarity between the structure of α-$CaZn_2(PO_4)_2$ and that of $BaAl_2(SiO_4)_2$, which Kreidler et al. have suggested is isostructural with the high-temperature phase, β-$CaZn_2(PO_4)_2$ (stable above 875 °C).[7] $BaAl_2(SiO_4)_2$ has a regular array of connected (AlO_4 and SiO_4) tetrahedra sandwiched between layers of barium cations.[8] These tetrahedra form connected eight-membered rings similar to the P(2)–O–Zn(1)–O–P(2), etc., rings of α-$CaZn_2(PO_4)_2$, although, in the phosphate, the structure is further complicated by the formation of the linkage shown in Figure 4.

Study of Cation Substitution into α-$CaZn_2(PO_4)_2$ by ^{31}P MAS NMR. The structure determination of α-$CaZn_2(PO_4)_2$ has confirmed that there are two crystallographically independent phosphorus atoms that give rise to the isotropic resonances at 10.0 and 2.2 ppm. Despite this, there is no direct evidence for which phosphorus atom gives rise to which resonance. There are, however, ways in which we can attempt to address this problem. One route is to make an analysis of the bonding around the phosphorus atoms and use an empirical relationship between bond strengths and chemical shifts to make the assignment; this method has been discussed elsewhere.[4] A second possible route, which will form the rationale for this part of the study, involves distinguishing between the resonances by inducing small local structural changes around the phosphorus atoms by cation substitution. This method can only succeed if such changes affect one phosphorus differently from the other. With this in mind and with consideration of the similarity of the grouping in α-$CaZn_2(PO_4)_2$ to that found in the solid solution $Zn_{3-x}Mg_x(PO_4)_2$,[3] the cation substitution chosen will be of magnesium for zinc in the hope that similar local environment effects may be found.

Samples of stoichiometry $CaZn_{2-x}Mg_x(PO_4)_2$, with $x = 0.1$, 0.2, 0.5, 0.75, and 1.0, were prepared by the method described above from an acid solution of the salts $CaCO_3$, ZnO, MgO, and $NH_4H_2PO_4$. The samples were dried, ground, and fired at 800 °C for 12 h before cooling rapidly to room temperature. There are several competing phases in this system, including $Ca_{3-x}Zn_x(PO_4)_2$, $Ca_{3-x}Mg_x(PO_4)_2$, and $Zn_{3-x}Mg_x(PO_4)_2$. These competing phases appear to complicate the picture, and it is evident from the X-ray powder diffraction patterns that the targeted phases with the α-$CaZn_2(PO_4)_2$ structure can only be prepared in a small temperature region around 800 °C and even then not in a pure state. The X-ray powder diffraction patterns of the preparations with $x = 0.1$, 0.2, and 0.5 show the major component to be an α-$CaZn_2(PO_4)_2$-like phase. As x increases beyond 0.5, the α-$CaZn_2(PO_4)_2$ phase becomes harder to prepare; it is only a small component of the $x = 0.75$ preparation, and for samples with $x = 1.0$, no evidence for it can be found. This indicates a limited solid solution that is in agreement with the observation that there is no analogous $CaMg_2(PO_4)_2$ phase in the calcium/magnesium system. The ^{31}P MAS NMR spectra of three of the compositions prepared at 800 °C are shown in Figure 5, and these reveal something of the complexity of the system. A preliminary inspection of these spectra shows the dominant features still to be the resonances at 10.0 and 2.2 ppm characteristic of the α-$CaZn_2(PO_4)_2$ phase. There are, however, two sets of additional resonances, those just to the upfield side of the 10.0 ppm signal (at 8.7 and 7.2 ppm) and those grouped around the 2.2 ppm resonance. It is possible to demonstrate that the resonances grouped around the 2.2 ppm peak are, in fact, due to impurities while those at 8.7 and 7.2 ppm are associated with the same phosphorus that gives rise to the 10.0 ppm resonance. In order to make this distinction, we have studied samples prepared under different thermal conditions and collected spectra with a variety of NMR parameters. These latter experiments enable one to distinguish between phosphorus atoms that have different spin-lattice relaxation times (T_1) and chemical shift anisotropies. As expected, these parameters are equivalent for the 10.0, 8.7, and

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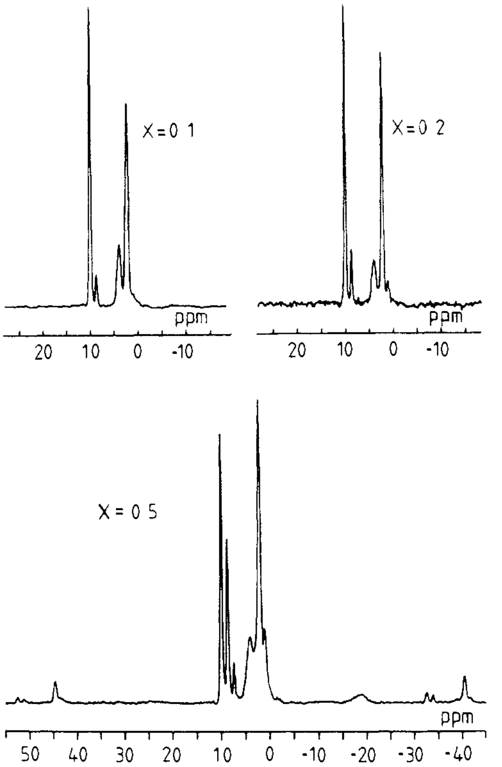

Figure 5. ^{31}P MAS NMR spectra of three preparations from the system $CaZn_{2-x}Mg_x(PO_4)_2$, with initial stoichiometries $x = 0.1$, 0.2, and 0.5.

7.2 ppm resonances, indicating their similar origin, while the same is not found for those resonances around 2.2 ppm.

It appears, therefore, that the differential effect that is required to distinguish between the 10.0 and 2.2 ppm resonances exists, but if this is to be used for an allocation, we must be able to interpret the satellite resonances in terms of a perturbation to a particular phosphorus atom. We have done this by analogy with the ^{31}P MAS NMR chemical shift effects observed in the $Zn_{3-x}Mg_x(PO_4)_2$ solid solution.[3] Both structures contain the bridging unit shown in Figure 4, and we conclude that the 10.0 ppm resonance can be assigned to P(2) and the associated satellite peaks to the local structure perturbation on this phosphorus when magnesium is substituted at the Zn(2) site. This is consistent with the known preference of Mg^{2+} for coordination numbers greater than 4 in phosphates.[20] As magnesium fills the Zn(2) site, therefore, the P(2) resonance at 10.0 ppm diminishes in real terms (compare with the intensity of the 2.2 ppm peak as x increases to 0.5 in Figure 5), because many of the phosphorus atoms, while still being in P(2)-like sites, are experiencing new local environments. This causes the phosphorus resonances to shift to higher field. In contrast, the isotropic resonance of the P(1) phosphorus, presumably because of its weaker linking to Zn(2), is essentially unchanged by the magnesium substitution.

The primary objective of this cation substitution has been accomplished: the resonances at 2.2 and 10.0 ppm have been allocated to P(1) and P(2) in the α-$CaZn_2(PO_4)_2$ structure. Furthermore, this allocation is in agreement with an independent analysis on the basis of oxygen bond strength, in which the upfield resonance (at 10.0 ppm) is assigned to the phosphorus with the highest summed bond strength at the neighboring oxygens. In addition, the same assignment is also made if the largest chemical shift anisotropy, $\Delta\sigma$, is allocated to the phosphorus with the greatest range in the bond strengths at the oxygens.[4]

Figure 6. ^{31}P MAS NMR spectra of a sample with initial stoichiometry $CaZn_{1.25}Mg_{0.75}(PO_4)_2$.

A more detailed investigation of the intensities of the satellite resonances indicates that the magnesium distribution over the bridging unit is nonrandom, that double substitution (Mg–Mg) is significantly disfavored over the other arrangements, and that the limit of solution in α-$CaZn_2(PO_4)_2$ is reached when all the bridging units are singly substituted (i.e. $CaZn_{1.5}Mg_{0.5}(PO_4)_2$). The three resonances can be allocated to (1) a phosphorus with an edge-sharing zinc cation (10.0 ppm), (2) a phosphorus with an edge-sharing magnesium cation but with a zinc in the next nearest bridging site (8.7 ppm), and (3) a phosphorus next to the doubly substituted Mg–Mg link of limited stability (7.2 ppm). As a consequence of this allocation, the spectra of a sample at the solution limit is expected to show two resonances at 10.0 and 8.7 ppm of equal intensity. Such a situation is observed in the ^{31}P MAS NMR spectra of a sample prepared with an initial stoichiometry of $x = 0.75$ (Figure 6), despite the high percentage of impurity phase present, which is manifested by the broad resonance around 3 ppm.

Conclusion

In this study we have shown that MAS NMR can provide a complementary technique to the more classical methods of structural analysis in the solid state, enabling us in this instance to choose between two possible space groups, $P1$ and $P\bar{1}$. Furthermore, with a knowledge of the structure and with exploitation of the sensitivity of the nucleus to local environment changes, it may be possible to make an allocation of the MAS NMR resonances by means of selective cation substitution. By such a method, the two ^{31}P resonances obtained in a MAS NMR spectrum of α-$CaZn_2(PO_4)_2$ have been allocated to particular phosphorus atoms in the structure. The resonance at 10.0 ppm was assigned to P(2) because of the satellite resonances that appear upfield of it when zinc was substituted by magnesium at Zn(2). The intensity of these satellite resonances suggests that the magnesium is distributed over the Zn(2) sites in a nonrandom manner and that this is due to a preference for Mg–Zn occupation of the P–Zn(2)–Zn(2)–P link. It has also been noted that this "cation substitution" allocation is wholly consistent with an independent analysis based on the summed bond strengths of the coordinating oxygens.[4]

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Registry No. $CaZn_2(PO_4)_2$, 15974-07-9; $CaZn_{1.9}Mg_{0.1}(PO_4)_2$, 111769-77-8; $CaZn_{1.8}Mg_{0.2}(PO_4)_2$, 111769-78-9; $CaZn_{1.5}Mg_{0.5}(PO_4)_2$, 111743-31-8; $CaZn_{1.25}Mg_{0.75}(PO_4)_2$, 111743-32-9.

Supplementary Material Available: Table of anisotropic temperature factors for α-$CaZn_2(PO_4)_2$ (1 page). Ordering information is given on any current masthead page.

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