Structural study of phosphate groups in layered metal phosphates by high-resolution solid-state ^{31}P NMR spectroscopy

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In studies of a series of crystals of layered metal phosphate compounds by magic angle spinning (MAS) NMR spectroscopy, it has been found that there is a distinct correlation between the ^{31}P isotropic chemical shift value and the type of phosphate group. The isotropic ^{31}P chemical shifts of $(H_2PO_4)^-$, $(HPO_4)^{2-}$ and $(PO_4)^{3-}$ groups appear around δ −10, −20 and −30, respectively. These assignments were made unambiguously by measuring the ^{31}P MAS NMR spectra with and without ^1H high-power decoupling together with the cross-polarization transfer technique between ^1H and ^{31}P nuclei (CP MAS spectra).

Since two different layered zirconium phosphates, α-$Zr(HPO_4)_2{\cdot}H_2O$ (α-ZrP) and γ-$Zr(H_2PO_4)(PO_4){\cdot}2H_2O$ (γ-ZrP), were discovered by Clearfield and co-workers,[1,2] a lot of extensive experimental studies on the preparation of intercalation compounds between these materials and various guest molecules have been carried out.[3–5] These intercalation compounds have been characterized mainly by X-ray powder diffraction (XRD), differential thermal analysis (DTA), thermogravimetry (TG) and elemental analyses. The static and dynamic nature of the guest molecules in the interlayer space has been discussed on the basis of the interlayer distance determined by XRD studies. The above two host compounds differ in their capability to intercalate various guest molecules.

In order to understand this different intercalation behaviour between α- and γ-ZrP, Clearfield and co-workers tried to determine the crystal structure by XRD and reported the crystal structure of α-ZrP.[6,7] The position of the hydrogen atom was later determined by a neutron diffraction study.[8] α-ZrP has two crystallographically inequivalent $(HPO_4)^{2-}$ moieties in the unit cell. In contrast, the crystal structure of γ-ZrP was solved in 1995 by applying the Rietveld method to the powder X-ray diffraction pattern.[9] There exist two chemically different phosphate groups, $(H_2PO_4)^-$ and $(PO_4)^{3-}$ in γ-ZrP. These results are consistent with the structural models proposed by Clayden on the basis of ^{31}P CP MAS spectra.[10] The $(H_2PO_4)^-$ group in γ-ZrP is thought to be the origin of the very strong ion-exchange capability of γ-ZrP.

It is, therefore, important to characterize the three phosphate groups, $(H_2PO_4)^-$, $(HPO_4)^{2-}$ and $(PO_4)^{3-}$, for a particular host layered phosphate in order to design a new intercalation compound with various functions. However, it has been found to be very difficult to distinguish unambiguously these phosphate groups by XRD studies because the determination of the hydrogen position is accompanied by a fairly large uncertainty in these compounds. Recently, we succeeded in obtaining various layered metal phosphates in their pure forms. In order to characterize layered zirconium(IV), titanium(IV), cerium(IV) and aluminium phosphates, we measured the ^{31}P NMR spectra of these phosphates in the solid state. The crystallographic data of the layered titanium(IV), cerium(IV) and aluminium phosphates are as yet unclear.

Experimental

Synthesis

α-ZrP was prepared by mixing zirconium(IV) hydroxide and phosphoric acid at a molar ratio ($P_2O_5:ZrO_2$) of 1.2:1 in a PTFE vessel and keeping it at 175–200 °C for 5 h in an autoclave. The water vapour pressure in the autoclave was maintained at 10 atm.[11]

In the syntheses of $Ti(HPO_4)_2{\cdot}H_2O$ (α-TiP) and $Ti(H_2PO_4)(PO_4){\cdot}2H_2O$ (γ-TiP), a mixture of phosphoric acid and titanium(IV) hydroxide at a molar ratio ($P_2O_5:TiO_2$) of 1.2–1.5:1 was kept at 200–225 °C for α-TiP and at 225–250 °C for γ-TiP for 5 h.[12,13]

$Ce(HPO_4)_2{\cdot}1.33H_2O$ (CeP) was synthesized by keeping a mixture of cerium(IV) oxide and phosphoric acid at a molar ratio ($P_2O_5:CeO_2$) of 1.5–2.0:1 at 175–200 °C for 5 h under a water vapour pressure of 5.0–7.0 atm.[14]

Aluminium dihydrogentriphosphate dihydrate, $AlH_2P_3O_{10}{\cdot}2H_2O$ (AlP), was synthesized by mixing aluminium hydroxide and phosphoric acid at a molar ratio ($P_2O_5:Al_2O_3$) of 3.0:1 and keeping the mixture at 120 °C in a porcelain crucible until it hardened into a solid mass. When the mass was heated at 300 °C for 20 h, type I $AlH_2P_3O_{10}$ was formed;[15] this was allowed to stand in air, whereupon it readily adsorbed moisture and transformed completely into the dihydrate, $AlH_2P_3O_{10}{\cdot}2H_2O$.

The layered phosphates obtained were washed with distilled water and dried in air.

α-$Zr(HPO_4)(NaPO_4){\cdot}H_2O$ was obtained by substituting half of the protons in α-$Zr(HPO_4)_2{\cdot}2H_2O$ by ion exchange with 0.1 M sodium hydroxide solution.[16]

The compositions of the above seven compounds were determined by elemental analyses. X-Ray powder diffraction patterns of the above compounds were consistent with the reported values of the interlayer spacing, *d*.[11–17]

NMR measurements

A Bruker MSL-200 spectrometer operating at 81.0 MHz for ^{31}P was used to measure the solid-state NMR spectra. A single $\pi/2$ pulse sequence with a pulse length of 2 μs was applied to obtain the MAS and the static spectra with and without ^1H high-power decoupling. A cross-polarization (CP) pulse sequence followed by ^1H high-power decoupling was used to measure the ^{31}P CP MAS and the CP static spectra in each

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of the substances. The MAS rate was 3–4 kHz and the Fourier transform was done on the free induction decay (FID) signals obtained after 8 accumulations, with a recycle time of 10 s in a typical measurement. Accumulation of more than 240 FIDs was necessary to obtain the static broad-line spectra for the determination of the anisotropy of the chemical shift tensors.

Results and Discussion

The isotropic chemical shift values (δ_{iso}) of α-ZrP and γ-ZrP listed in Table 1 agree with those reported by Clayden.[10] Although α-ZrP has two crystallographically inequivalent $(HPO_4)^{2-}$ anions,[6–8] only one sharp peak was observed. For γ-ZrP, two peaks were observed at δ −9.4 and −27.4[10] and were assigned according to the CP MAS spectra as follows. The CP MAS technique is usually used to enhance the signal intensity of rare spins, *e.g.* ^{13}C and ^{15}N. Since ^{31}P is an abundant nucleus, it is not necessary to enhance the signal through the cross-polarization effect between ^{31}P and ^{1}H. However, this technique is useful to estimate the strength of the dipolar interaction between ^{31}P and ^{1}H and therefore to count the number of hydrogens bonded to the PO_4 group concerned. The degree of signal enhancement in the cross-polarization experiment is determined by the efficiency of magnetization transfer, provided that the Hartmann–Hahn condition, $\gamma_P H_1{}^P=\gamma_H H_1{}^H$, is fulfilled.[18–20] The magnetization M of ^{31}P depends on the contact time (or cross-polarization period) t_m according to eqn. (1):

$$M(t_m)=M_0\lambda^{-1}\left\{1-\exp\left(-\frac{\lambda t_m}{T_{PH}}\right)\right\}\exp\left(-\frac{t_m}{T_{1\rho}(^1H)}\right) \qquad (1)$$

where M_0 is the value of the static magnetization of ^{31}P, T_{PH} the dipolar cross-relaxation time between ^{31}P and ^{1}H, $T_{1\rho}(^1H)$ the proton spin–lattice relaxation time in the rotating frame, and

$$\lambda=1+\frac{T_{PH}}{T_{1\rho}(^{31}P)}-\frac{T_{PH}}{T_{1\rho}(^1H)}$$

Eqn. (1) shows that the magnetization M increases with a time constant $\lambda^{-1}T_{PH}$ during the short contact time t_m between ^{31}P and ^{1}H, when T_{PH} is sufficiently short compared with $T_{1\rho}(^1H)$ and $T_{1\rho}(^{31}P)$, the spin–lattice relaxation time of ^{31}P in the rotating frame. Subsequently, a reduction in the magnetization occurs owing to the relaxation of the protons in the rotating frame with a time constant $T_{1\rho}$. The magnitude of the dipole–dipole interaction between ^{1}H and ^{31}P, $T_{PH}{}^{-1}$, is proportional to r^{-6}, where r denotes the P—H distance. Therefore, the enhancement factor of the ^{31}P signal due to cross-polarization increases as number of protons bonded to the PO_4 group is increased. In the case of γ-ZrP, Clayden found that the enhancement was larger for the peak at $\delta-9.4$ than for that at $\delta-27.4$, and hence assigned the peak at $\delta-9.4$ to the $(H_2PO_4)^-$ group and that at $\delta-27.4$ to the $(PO_4)^{3-}$ group. This assignment was validated by a recent X-ray structure analysis.[9]

In the present study we applied the above technique to the other layered metal phosphates, together with high-power decoupling to identify the ^{31}P signal to the specific phosphate group. The measured values of the chemical shifts and their assignments to the specified phosphate ions are recorded in Table 1. The values of δ_{iso} of α-TiP and γ-TiP are close to those for the corresponding layered zirconium phosphates, α-ZrP and γ-ZrP, respectively. α-TiP[21] is found to be isomorphous to α-ZrP and to contain $(HPO_4)^{2-}$ groups in the structure. Although the existence of two inequivalent $(HPO_4)^{2-}$ groups in α-TiP has been reported by an X-ray structure analysis,[21,22] these sites could not be distinguished in our MAS NMR spectrum of α-TiP. Two compounds, γ-ZrP and γ-TiP, are isomorphous, from the XRD data, although the crystal structure of γ-TiP has not yet been solved. Two δ_{iso} values for γ-TiP appeared individually in the regions of the δ_{iso} values for γ-ZrP, confirming that γ-TiP and γ-ZrP are isostructural.

The ^{31}P MAS spectra of the titanium phosphates with and without ^{1}H high-power decoupling are shown in Fig. 1. The dipole–dipole interaction between ^{1}H and ^{31}P causes a considerable broadening of the signal of ^{31}P in the MAS-only spectra. The ^{1}H high-power decoupling technique diminishes this interaction by saturating the magnetization of ^{1}H nuclei and brings about a sharp resonance line, as can be seen in Fig. 1. Hence one can distinguish protonated and unprotonated phosphate anions. The broad peak at $\delta-10$ in the spectrum of γ-TiP without ^{1}H decoupling indicates strong ^{1}H and ^{31}P dipole–dipole interactions. Therefore, the peaks at $\delta-10.8$ and −33.0 can be assigned to $(H_2PO_4)^-$ and $(PO_4)^{3-}$, respectively. This assignment is also confirmed by the contact time dependence of the CP MAS spectrum shown in Fig. 2.

The α-$Zr(HPO_4)(NaPO_4)\cdot H_2O$ crystal gives two peaks ($\delta-17.3$ and −15.0) with equal intensity (Table 1). According to the X-ray structure analysis, $(HPO_4)^{2-}$ and $(NaPO_4)^{2-}$ units are stacked alternately in the layer structure.[16] The α-$Zr(NaPO_4)_2\cdot H_2O$ crystal has two peaks at $\delta-14.6$ and −15.9,[23] and α-$Zr(HPO_4)_2\cdot H_2O$ has a single peak at $\delta-18.7$ as mentioned above.[10] Therefore, the peak at $\delta-17.3$ is assigned to $(HPO_4)^{2-}$ and that at $\delta-15.0$ to $(NaPO_4)^{2-}$.

In the ^{31}P MAS spectrum of $Ce(HPO_4)_2\cdot 1.33H_2O$ crystal, two peaks are observed at $\delta-10.6$ and −28.3. The contact time dependence of the CP MAS spectrum shown in Fig. 3 and of the MAS spectrum without ^{1}H decoupling implies that the peaks at $\delta-10.6$ and −28.3 are assigned to $(H_2PO_4)^-$ and $(PO_4)^{3-}$, respectively. Although the crystal structure of $Ce(HPO_4)_2\cdot 1.33H_2O$ (CeP) is unknown, the existence of $(H_2PO_4)^-$ and $(PO_4)^{3-}$ suggests that it belongs to the γ-type

Table 1 Isotropic and anisotropic chemical shifts for layered metal phosphates

	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	site	ref.
α-$Zr(HPO_4)_2\cdot H_2O$	−18.7	4.3	−23.7	−36.8	$(HPO_4)^{2-}$	10
α-$Ti(HPO_4)_2\cdot H_2O$	−18.4	4	−22	−37	$(HPO_4)^{2-}$	this work
α-$Zr(HPO_4)(NaPO_4)\cdot H_2O$[a]	−15.0	*ca.* 2	*ca.* −15	*ca.* −32	$(NaPO_4)^{2-}$	this work
	−17.3	*ca.* −7	*ca.* −17	*ca.* −41	$(HPO_4)^{2-}$	
γ-$Zr(HPO_4)_2\cdot 2H_2O$	−9.4	18.5	−17.7	−30.0	$(H_2PO_4)^-$	10
	−27.4	−16.0	−24.7	−34.0	$(PO_4)^{3-}$	
γ-$Ti(HPO_4)_2\cdot 2H_2O$	−10.6	20	−19	−32	$(H_2PO_4)^-$	this work
	−32.6	−15	−34	−48	$(PO_4)^{3-}$	
γ-$Ce(HPO_4)_2\cdot 1.33H_2O$	−10.6	28	−22	−39	$(H_2PO_4)^-$	this work
	−28.3	−1	−28	−55	$(PO_4)^{3-}$	
$AlH_2P_3O_{10}\cdot 2H_2O$[a]	−20.8	*ca.* 44	*ca.* −15	*ca.* −95	$(HPO_4)^{2-}$	this work
	−22.9	*ca.* 44	*ca.* −15	*ca.* −95	$(HPO_4)^{2-}$	
	−29.6	*ca.* 48	*ca.* −24	*ca.* −123	$(PO_4)^{3-}$	

[a] For α-$Zr(HPO_4)(NaPO_4)\cdot H_2O$ and $AlH_2P_3O_{10}\cdot 2H_2O$, the uncertainties in anistropic chemical shift values are relatively large because these spectra consist of a closely spaced doublet.

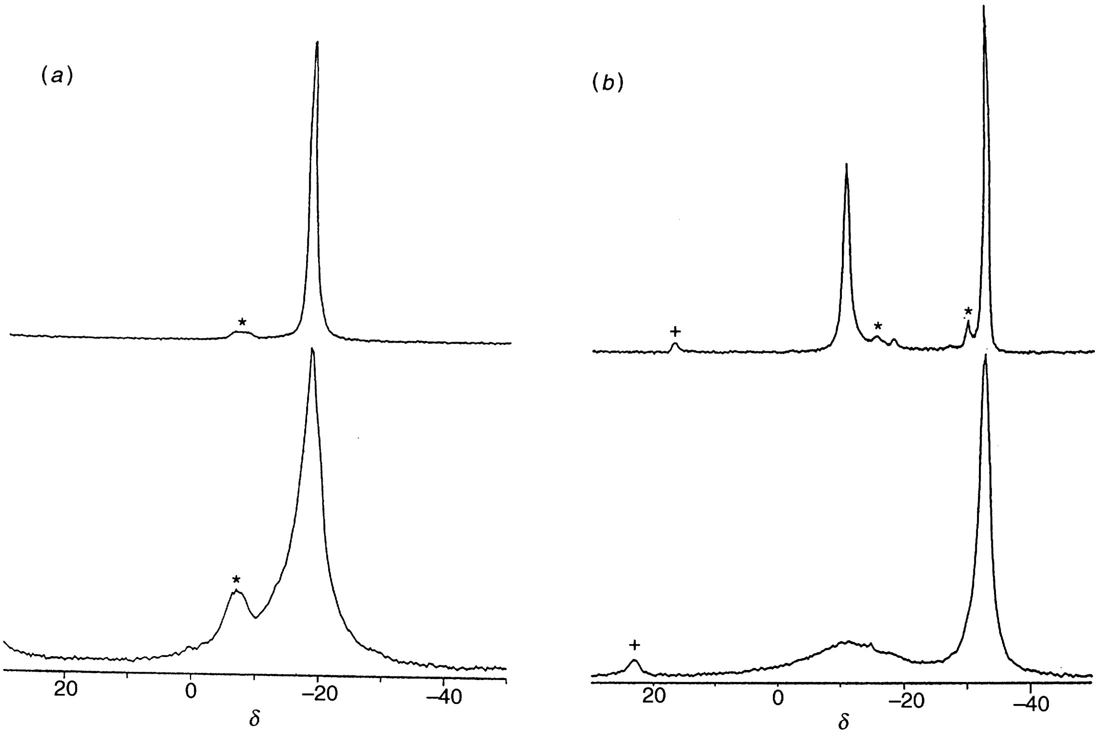

Fig. 1 ^{31}P MAS NMR with (top) and without (bottom) ^{1}H decoupling for (a) α-Ti(HPO$_4$)$_2$·H$_2$O and (b) γ-Ti(HPO$_4$)$_2$·2H$_2$O. Peaks marked * are due to impurities and + indicates the spinning side bands.

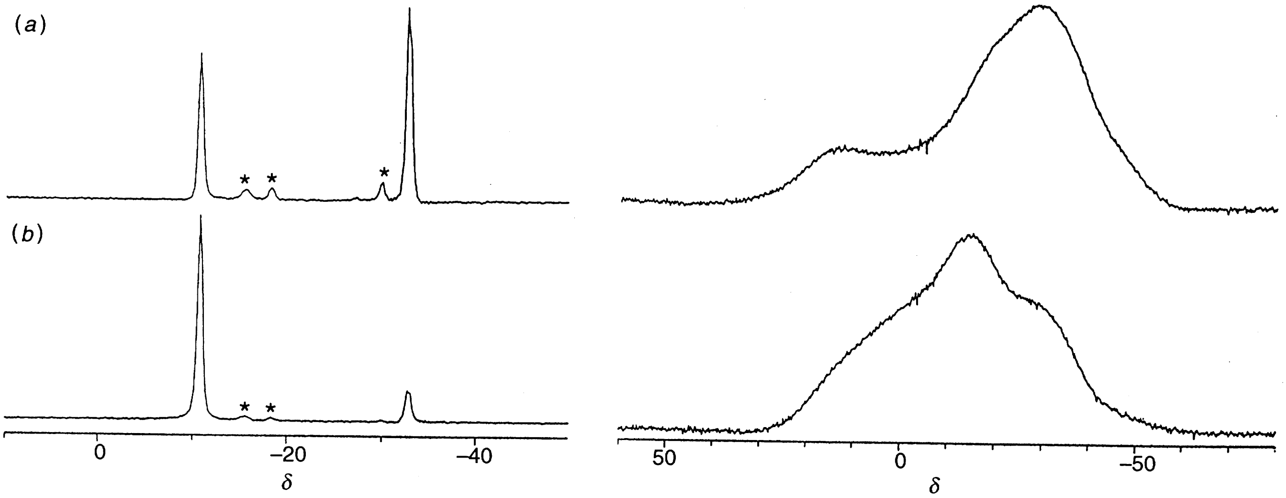

Fig. 2 Contact time dependence of ^{31}P CP MAS (left) and CP static spectra (right) of γ-Ti(HPO$_4$)$_2$·2H$_2$O with τ_m=(a) 100 µs and (b) 4 ms. Peaks marked * are due to impurities.

of layered phosphates M^{IV}(H$_2$PO$_4$)(PO$_4$)·2H$_2$O (M=Zr, Ti). The γ-type phosphates usually contain two molecules of water of crystallization. Therefore, CeP has one-third too few water molecules. The lack of water of crystallization may fulfil an important role in producing a large difference in the structure and bonding characteristics of (H$_2$PO$_4$)$^-$ and (PO$_4$)$^{3-}$ groups.

The ^{31}P NMR spectrum of AlH$_2$P$_3$O$_{10}$·2H$_2$O (AlP) has three peaks at δ −20.8, −22.9 and −29.6, suggesting that the structure of layered aluminium phosphate is completely different from those of layered zirconium(IV), titanium(IV) and cerium(IV) phosphates. In M^{IV}(HPO$_4$)$_2$·H$_2$O and M^{IV}(H$_2$PO$_4$)(PO$_4$)·2H$_2$O (M=Zr, Ti, Ce) mentioned above, each (PO$_4$)$^{3-}$ is isolated from the others and coordinates individually to the metal atom. In contrast, three phosphate groups in AlP form a triphosphate ion (P$_3$O$_{10}$)$^{5-}$ with a P—O—P—O—P bond by sharing the apical oxygens of three PO$_4$ groups. The contact time dependence of the CP MAS spectrum indicates the existence of a weak but significant dipole–dipole interaction between ^{1}H and ^{31}P for the peak at δ −29.6. The other two peaks in the ^{31}P MAS spectrum are very broad when the ^{1}H high-power decoupling is absent. These facts suggest that the peaks at δ −20.8 and −22.9 are assigned to the end (HPO$_4$)$^{2-}$ groups of the triphosphate anion, and the peak at δ −29.6 to the central (PO$_4$)$^{3-}$ group.

We also measured the broad-band powder spectra of all the samples in order to determine the chemical shift anisotropy in the ^{31}P signals. The chemical shift anisotropy originates from the asymmetric distribution of electrons around the resonant nuclei. In the case of phosphates, the degree of chemical shift anisotropy is a measure of the deformation of the (PO$_4$)$^{3-}$ tetrahedra. If (PO$_4$)$^{3-}$ forms a regular tetrahedron, the chemical shift anisotropy is zero, *i.e.* $\delta_{11}=\delta_{22}=\delta_{33}$. However, in layered phosphates the (PO$_4$)$^{3-}$ group is deformed to some extent and its ^{31}P chemical shift tensor becomes anisotropic. The chemical shift anisotropy in the three α-type compounds [α-ZrP, α-TiP and Zr(HPO$_4$)(NaPO$_4$)·H$_2$O] falls in a similar

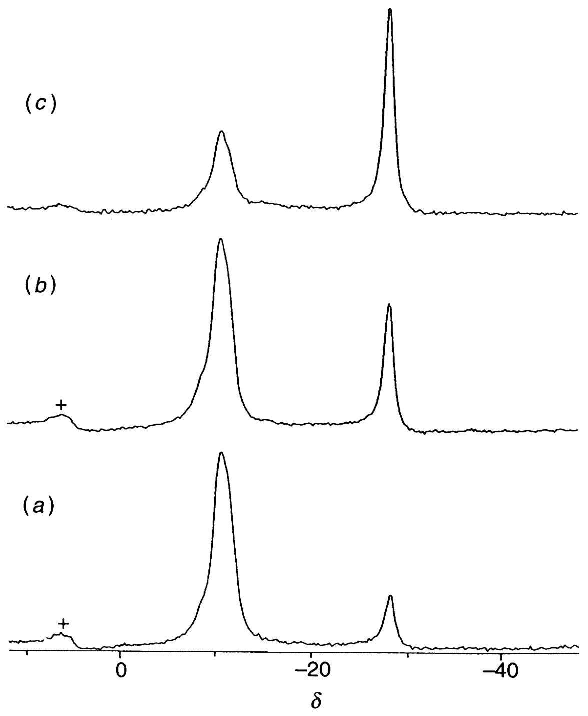

Fig. 3 Contact time dependence of ^{31}P CP MAS spectrum of $Ce(HPO_4)_2 \cdot 1.33H_2O$ with τ_m = (a) 100 μs, (b) 1 ms and (c) 3 ms. Peaks marked + are due to spinning side bands.

range. In contrast, the chemical shift anisotropy in the γ-type compounds differs from compound to compound. The chemical shift anisotropy for both $(H_2PO_4)^-$ and $(PO_4)^{3-}$ sites increases in the order of zirconium, titanium and cerium phosphate. As the chemical shift anisotropy increases, the distortion of the $(PO_4)^{3-}$ groups from the regular tetrahedron becomes large. This might be related to the ion-exchange capability of these compounds, *i.e.*, strong ion exchange can occur in zirconium phosphate with small distorted anions, but only a weak ion-exchange capability is recognized for cerium phosphate which contains highly distorted anions.

In aluminium triphosphate there is no discrete $(PO_4)^{3-}$ group and the very large chemical shift anisotropy of the end and central ^{31}P in the triphosphate anion may be brought about by a relatively large distortion of the component PO_4 tetrahedra because the apical oxygens of the three PO_4 groups are shared in the triphosphate ions $(P_3O_{10})^{5-}$.

The site assignment for the ^{31}P resonances is summarized in Table 1 together with the values of the ^{31}P chemical shift tensor components for the present compounds. The isotropic chemical shift values for $(H_2PO_4)^-$, $(HPO_4)^{2-}$ and $(PO_4)^{3-}$ groups appeared in distinctly separate regions, *i.e.*, δ *ca.* −10, −20 and −30, respectively. These assignments can be established by observing the CP MAS spectra with different contact times and by ^{1}H high-power decoupling. The layered metal phosphate compounds with one and two molecules of water of crystallization are usually assigned to as the so-called α- and γ-types for the titanium phosphates [α-$Ti(HPO_4)_2 \cdot H_2O$, γ-$Ti(H_2PO_4)(PO_4) \cdot 2H_2O$] and for zirconium phosphates [α-$Zr(HPO_4)_2 \cdot H_2O$, γ-$Zr(H_2PO_4)(PO_4) \cdot 2H_2O$ and α-$Zr(HPO_4)(NaPO_4) \cdot H_2O$], but not for cerium phosphate [γ-$Ce(HPO_4)_2 \cdot 1.33H_2O$]. It is concluded that by using ^{31}P MAS NMR spectra with ^{1}H high-power decoupling, α- and γ-types of layered phosphates can be definitely distinguished.

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