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Synthesis of phosphate–phenylphosphonates of titanium(IV) and their *n*-butylamine intercalates

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Layered compounds of general formula $Ti(PhPO_3)_x(HOPO_3)_{2-x}\cdot yH_2O$ have been synthesized and characterized by X-ray powder diffraction, IR spectroscopy, TG and ^{31}P magic angle spinning NMR spectroscopy. Different sources for the tetravalent metal in the synthetic process have been studied. The overall α-layered structure type is maintained while the ratio of phosphate to phenylphosphonate incorporated into the mixed derivative varies. The intercalation behaviour of mixed derivatives toward *n*-butylamine was also studied. The synthetic process shows kinetic control as a function of the tetravalent metal source; at low titanium(IV) concentration a mixture of products is obtained (phosphate + phosphonate) rather than a phosphate–phenylphosphonate single phase.

The first organic derivatives of metal(IV) phosphates were those of α-zirconium phosphate, α-$Zr(HPO_4)_2\cdot H_2O$ (α-ZrP), first prepared by Alberti *et al.*[1] in 1978 and represented by the general formula α-$Zr(O_3PR)_2\cdot$solv or α-$Zr(O_3POR)_2\cdot$solv, where R is an organic group and solv is an intercalated molecule (when present). Such compounds may be synthesized by the direct reaction of tetravalent metal ions with the acids, H_2O_3PR or H_2O_3POR, in the presence of hydrofluoric acid. These compounds adopt the α-ZrP structure type; a layered structure is maintained, but the tetrahedral O_3P–OH groups are replaced by tetrahedral O_3P–R or O_3P–OR moieties.[2] Many organic derivatives with different functional groups (alkyl, aryl, alcoholic, amino, carboxylic, sulfonic, *etc.*) have been prepared following this method.[3]

Increasing attention has been paid to layered organophosphonates of the other familiar tetravalent metals (Ti, Hf, Ce, Th), to vanadyl phosphonates,[4–7] trivalent metal (La, Sm, Ce, Fe) phosphonates[8–10] and divalent metal (Mg, Ca, Mn, Zn, Cd) phosphonates.[11–13] Such compounds offer the possibility of obtaining new materials with desired and regulated properties by changing the nature of the R group. The resulting modified materials have highly reactive sites both on the surface of the compound and in the interlayer region. They are expected to behave as intercalation hosts for Brønsted and Lewis-acid systems.[14] They have also been investigated for their ionic conductivity properties,[15–18] ion exchange,[19] photochemical reactions,[20,21] molecular recognition[4] and catalysis.[22,23]

The first reports on the synthesis of single-phase mixed-derivative compounds with two types of R group in the interlayer region were in 1982.[24] Dines *et al.*[24] reported that the surface areas of these mixed derivatives were high, presumably due to the inclusion of the sorbent species in the interlayer region by way of intercalative diffusion.[25] A number of groups have been working on the synthesis of layered mixed derivatives of tetravalent metal ions[12,26–33] and, more recently, on derivatives of tri- and di-valent metal phosphonates[34–36] with different systems, *e.g.* POH–PR, PR–PR′, POH–PH and PR–PH. The mixed phosphate–phosphonates of tetravalent metals have the general formula $M(RPO_3)_x(HOPO_3)_{2-x}\cdot$solv. These single-phase mixed compounds can be obtained by two different methods: (*i*) from a mixed solution containing phosphoric and phosphonic acids in the presence of HF;[1] (*ii*) by partial or complete substitution of the interlayer $HOPO_3{}^{2-}$ groups (in a preformed layered phosphate)[37,38] with the $RPO_3{}^{2-}$ groups of a phosphonic acid.

In recent papers we reported an alternative source of the titanium(IV) cation for the synthesis of phosphates and phosphonates by the direct precipitation method.[39,40] The reaction between the tetravalent cation and phosphoric acid yielded poorly crystalline solids.[41] To avoid this problem, the usual method is to employ a slow decomposition of a titanium(IV) fluoro complex in the presence of phosphoric acid. We used a different complexing agent (hydrogen peroxide) and the '*in situ*' generation of titanium(IV) cation by slow air oxidation of a titanium(III) solution. The objective of the current study was to examine the synthesis of mixed-derivative compounds following both the traditional and the new methods, and to study the behaviour of the different solids towards *n*-butylamine intercalation.

Results and Discussion

The formation of single-phase titanium phosphate–phenylphosphonate mixed derivatives requires coprecipitation of the metal ion with the phosphate and phenylphosphonate; a simple physical mixture of purely α-titanium phosphate **1** and phenylphosphonate **2** phases would otherwise be obtained. According to Clearfield and co-workers[35] the synthesis of mixed-derivative (phosphate–phosphonate) layered compounds is highly dependent upon the molar ratio of the phosphorus-containing reagents used. Hypothetically, such mixed compounds could be prepared with various interlamellar arrangements of the functional groups, usually one organic (R) and one inorganic (H, OH).[42] However, the most likely arrangement is a random distribution of both groups throughout both sides of the layer. Fig. 1 shows a schematic presentation of the packing of functional groups between the layers, which results in cavities (generated by the packing of the large organic groups and the small OH groups), responsible for the porosity of material. In these cavities, within the interlayer region, solvent molecules may also be accommodated.

The interlayer distance for these single-phase mixed (phosphate–phenylphosphonate) solids lies between those for the pure phenylphosphonate and phosphate phases. When

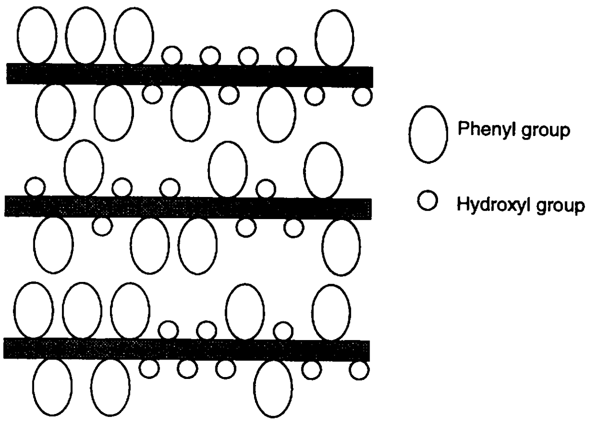


Fig. 1 Arrangement of large organic groups and small inorganic groups in the interlayer region

$x > 1$ (more phosphonate than phosphate groups) the packing for the mixed compound produces an interlayer distance almost identical to that of the single-phase phosphonate. The interlayer distance for the phenylphosphonate of titanium(IV) **2** is 15.2 Å.[40] Thus, according to the Bragg diffraction law, the first harmonic in the X-ray diffraction pattern should correspond to 7.6 Å, which is the same as the basal spacing for **1**.[43] To check for the existence of **1** as impurity, it is therefore better to use the 112 peak ($2\theta = 25.7°$).

The $TiCl_4$–HF–H_3PO_4–$PhPO_3H_2$ system

These experimental conditions produce solids of low crystallinity. Unlike other mixed derivatives,[44] the crystallinity is not improved by refluxing the samples in neutral media overnight. The X-ray diffraction (XRD) powder profiles are characteristic of layered compounds, and all display an interlayer *d* spacing of *ca.* 15 Å, together with multiple orders of this reflection (Fig. 2). It is not possible to detect any reflection typical of the phosphate **1** for these compounds, and their X-ray patterns have many features in common with the pure phenylphosphonate single phase. However, many of the reflections for the mixed derivative are broadened. The intensity of the peak at ≈ 15 Å is higher when the concentration of phenylphosphonic acid in the initial solution is increased.

Infrared spectroscopy cannot give structural conclusions regarding the mixed-derivative compounds, but it was utilized to identify the functional groups present in the solid. The phenyl ν(C=C) band at 1439, and bands at 696 and 755 (δ out-of-plane) and the typical bands for these materials at 3478 [ν(O–H)], 3048 [ν(C–H) aromatic], 1622 [δ(H–O–H)], 1248 [ν(P=O)], 1005 [$\nu_{sym}(PO_3)$] and 924 cm^{-1} [δ(P–OH)] are present.[45] For these mixed titanium(IV) phosphate–phenylphosphonates IR spectroscopy cannot be used to distinguish mixed derivatives from mechanical mixtures of the parents. Fig. 3 shows the IR spectra of phosphate **1** (*a*), a mixed derivative (*b*), and phosphonate **2** (*c*). Spectrum (*b*) is clearly an overlay of the parent spectra; there are no differences between the bands for the mixed compound and a mixture of the phosphate and phosphonate phases.

Fig. 4 shows a comparison of the XRD powder profiles of a single-phase mixed compound, prepared by using the Ti^{IV}–HF method, with its butylamine intercalate (intercalation from vapour phase). The amine is a stronger Lewis base than water, so the amine groups are not replaced by water molecules on exposure to moisture. The intercalation process takes place with a strong reordering of the solid, an increase in the interlayer distance giving lines at lower values of 2θ. This change confirms that the initial products are single-phase, solid-solution, mixed (phosphate–phenylphosphonate) derivatives.

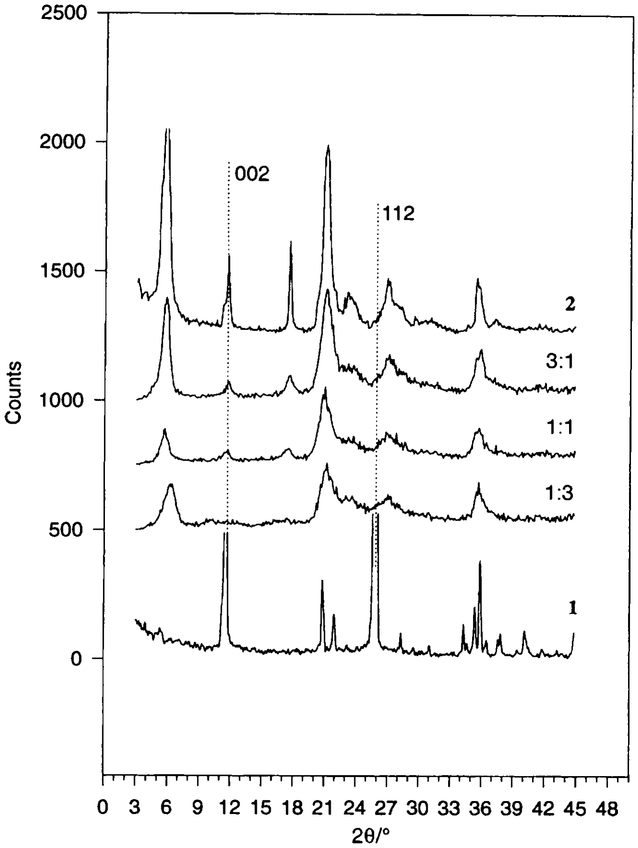


Fig. 2 The XRD powder profiles of the solids synthesized using the $TiCl_4$–HF–H_3PO_4–$PhPO_3H_2$ system (POH : PPh ratio in initial solution is indicated), and for α-titanium phosphate **1** and the phenylphosphonate of titanium(IV) **2**

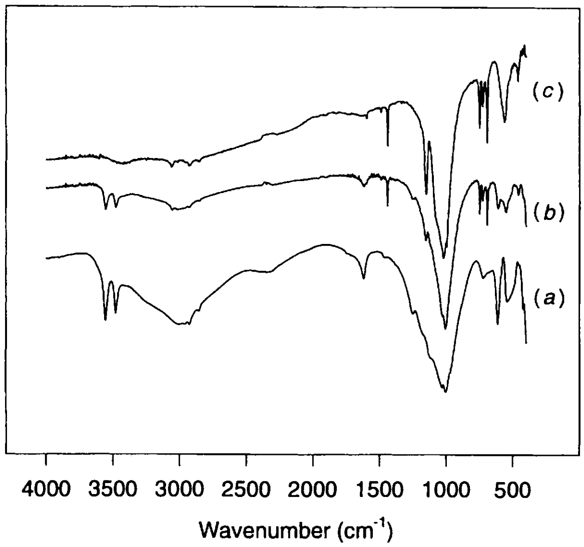


Fig. 3 Fourier-transform IR spectra of α-titanium phosphate **1** (*a*), the mixed derivative (*b*) and the phenylphosphonate of titanium(IV) **2** (*c*)

The XRD of the intercalated materials shows the coexistence of two or three different phases, depending on the synthetic condition employed to prepare the support material and the butylamine arrangement between the layers. The first reflection in the XRD profile of the butylamine-intercalated material corresponds to 18.0 Å. An interlayer *d* spacing of 18.8 Å is typical of the α-TiP–butylamine intercalate, with an extended bimolecular layer of molecules (*trans–trans* conformation, with their longitudinal axis inclined at an average of 58.7° with respect to the plane of the sheet).[46] If the position of the phenyl group remains unchanged after the intercalation process, the

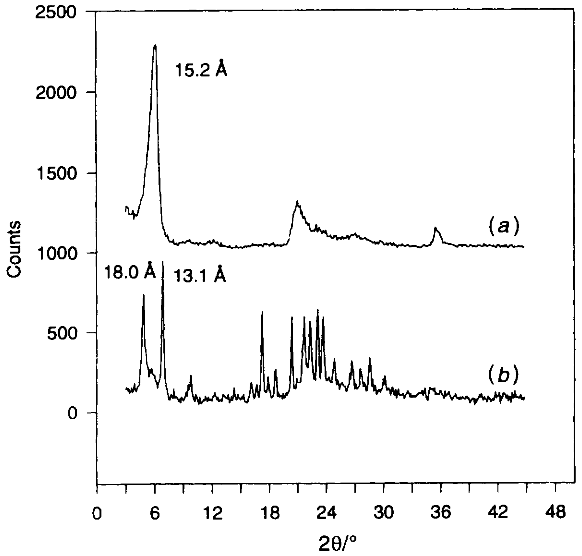


Fig. 4 The XRD patterns of a mixed derivative prepared by using the Ti^{IV}-HF method (*a*) and its butylamine intercalation derivative (*b*)

bigger *n*-alkylamine molecules should produce materials with the same or longer basal spacing, and not shorter than in the initial compounds. However, in the XRD profiles of intercalated materials a new reflection at 13.1 Å is seen, which is considerably smaller than in the initial mixed system. This fact could be explained if the amine intercalation results in phenyl-group migration or if the mixed solid was formed with the aromatic groups side-by-side. We infer that the first stage of the intercalation process, a monolayer disposition of the butylamine molecules inclined an average of 82.9°, can produce an interlayer spacing of 13.1 Å. In fact, for the phosphate **1** it was found that the monolayer intercalation of butylamine gives a solid with a 12.4 Å *d* spacing. The scheme in Fig. 5(*a*) explains the observed larger *d* value in our case; the organic packing in the mixed compound produces an interlayer distance of 15.2 Å, a larger value for the intercalation compound giving less distortion in the original layer. Similarly, if the reaction time is sufficiently long, for a bilaminar disposition the interlayer spacing must be shorter than that obtained by butylamine intercalation in **1** (18.0 Å against 18.8 Å) [Fig. 5(*b*) and (*c*)].

The $TiCl_4$–H_2O_2–H_3PO_4–$PhPO_3H_2$ system

Owing to the problems arising from the use of HF[47] and the low crystallinity of the solids obtained from the titanium fluoro complex, another complexing agent for the Ti^{IV} in solution was used, namely H_2O_2. The ratio of phosphate to phenylphosphonate in the final solid was determined from the mass percentage of carbon (elemental microanalysis) contained in the final product and mass-loss measurements (TG). X-Ray diffraction for selected samples confirmed that the cubic pyrophosphate of titanium(IV), TiP_2O_7, was the final product of the thermal treatment.

Table 1 lists the chemical composition (anhydrous material), interlayer distance and the experimental conditions used to obtain three of these mixed derivatives **3**–**5** of general formula $Ti(PhPO_3)_x(HOPO_3)_{2-x}$. By using POH:PPh ratios close to 1:1 in the initial solution, the solids obtained show XRD profiles similar to those resulting from the Ti^{IV}–HF system, with x values close to 2 (not listed in Table 1). When this ratio is raised we obtain single-phase mixed compounds with interlayer distances between those for the single pure phases (Fig. 6). The degree of crystallinity of these solids increases with reaction time, and no reflections for phosphate **1** were detected. So, the reactivity of the Ti^{IV} is not the same in both cases, and it is necessary to increase the phosphoric acid concentration in order to obtain mixed compounds with a chemical composition close to 1:1. When x is close to 1 the packing produces solids with *d* spacing similar to that of phosphonate **2**, but if $x < 0.7$ $d = 12.6$ Å. For POH:PPh > 50:1 in the initial solution pure **1** was obtained.

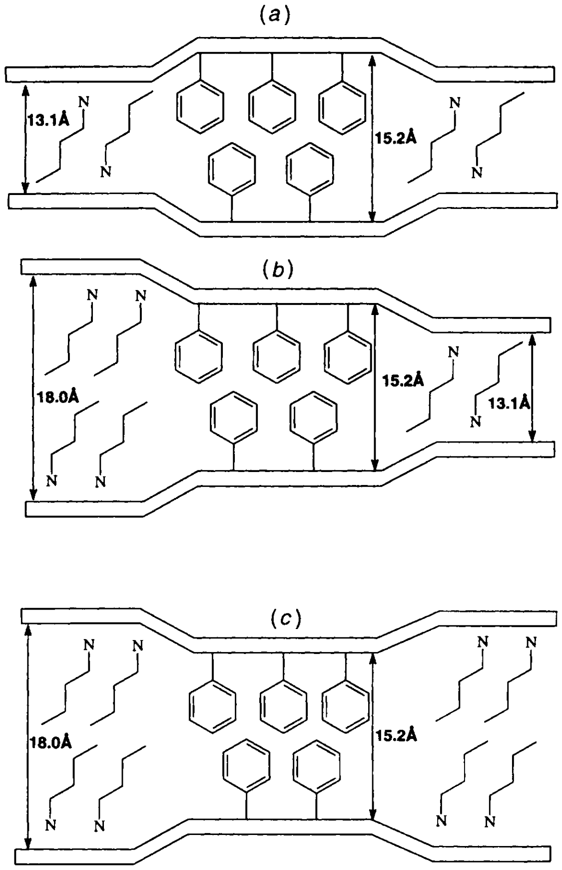


Fig. 5 An idealized structure of a monolayer of amine molecules and a bilayer of aromatic rings (*a*), mono- and bi-layers of amine molecules and bilayers of aromatic rings (*b*) and bilayers of amine and phenyl groups (*c*)

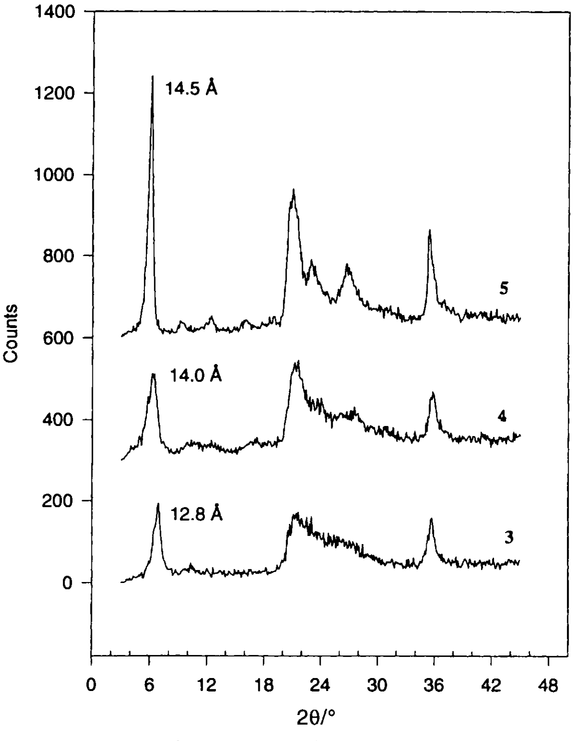


Fig. 6 The XRD profiles for three mixed phosphate–phenylphosphonates of titanium(IV), samples **3**–**5**

The thermal stability for these single-phase mixed compounds is closer to that of the titanium(IV) phosphonate than to that of the phosphate. Fig. 7 shows the TG traces for samples prepared under similar conditions, but with different reaction temperatures, 20 and 100 °C. Both show a high thermal stability, but the behaviour in the thermal process is different. The mass loss for the material synthesized at the higher temperature is greater. Thus, the amount of organic moiety in the solid increases when the reaction temperature is higher. The representative TG traces show two major mass-loss regions. The first involves dehydration which occurs between 50 and 200 °C. The second region, between 400 and 550 °C, involves oxidation of the organic portion and dehydration to titanium pyrophosphate (the final product).

Amine intercalation also gives interesting information. The *d* spacing of *n*-butylamine intercalates in mixed compounds prepared *via* the Ti^{IV}–H_2O_2 system is between 15 and 18 Å. Fig. 8 shows the XRD profiles; the original first reflection of the starting material disappears, as a single-phase starting compound is involved. A 17.3 Å *d* spacing could be associated with a bimolecular arrangement of amine molecules in the interlayer region. However, it is more likely (taking into consideration the degree of intercalation) that the solid arrangement is as shown in Fig. 9, with the apolar part of the amine molecule in front of the aromatic ring. It is possible to approximate the value of the amount of amine molecule intercalated. A simple method is to compare the mass gain by the material before and after the intercalation procedure. Of course this may not be exact, because the solvent contents could differ. The TG results obtained in this manner are, however, in excellent agreement with the calculated values (± 1.5%).

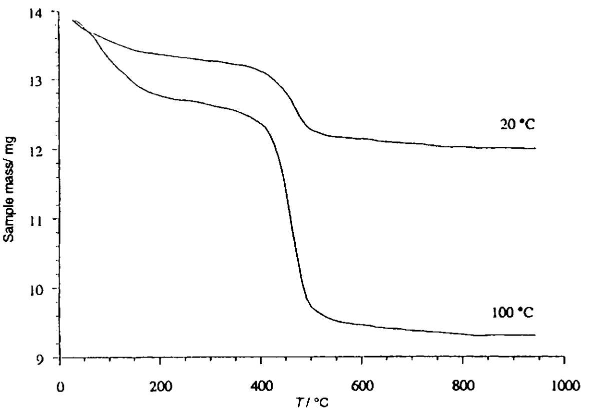


Fig. 7 The TG traces for two mixed phosphate–phenylphosphonates of titanium(IV) (**3** and **5**) prepared at differing reaction temperatures, 20 and 100 °C

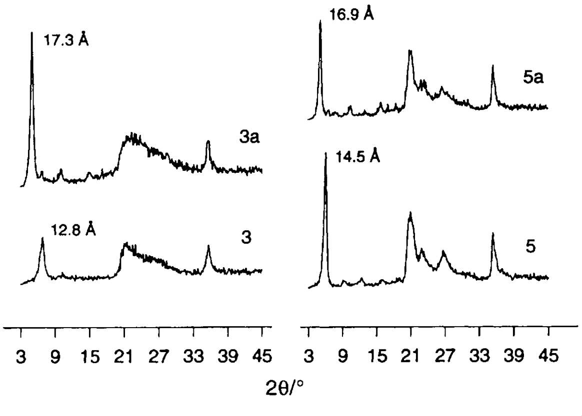


Fig. 8 The XRD profiles of two compounds prepared using the Ti^{IV}–H_2O_2 method (**3**, **5**) and their butylamine intercalation derivatives (**3a**, **5a**)

The ^{31}P magic angle spinning (MAS) NMR spectra were recorded again to confirm that the solid is a single phase rather than a physical mixture. To establish a comparison the spectra for the pure phases were also recorded. As anticipated, for each of the pure phosphate **1** and phosphonate **2** only one very sharp peak was registered, centred at δ −18.5 and −4.0. These values are in good agreement with the data obtained by Clayden[48] for the zirconium-based solids, determined by the Herzfeld–Berger method.[49] In Fig. 10, the spectra are shown for the mixed material. Two intense ^{31}P resonances were detected, with their spinning sidebands. The spectra confirm that there are only two different types of chemical environments for the phosphorus atoms in the mixed material. More important information is given by chemical shifts. These are δ −3.2 and −19.4, so the signals appear to be displaced by ≈1

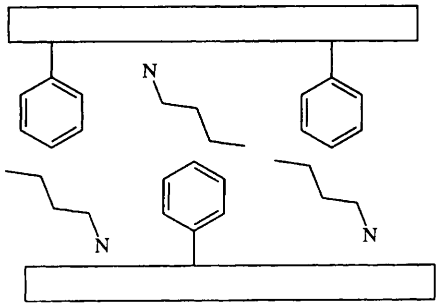


Fig. 9 Schematic representation of the arrangement of amine molecules between the layers of a mixed derivative

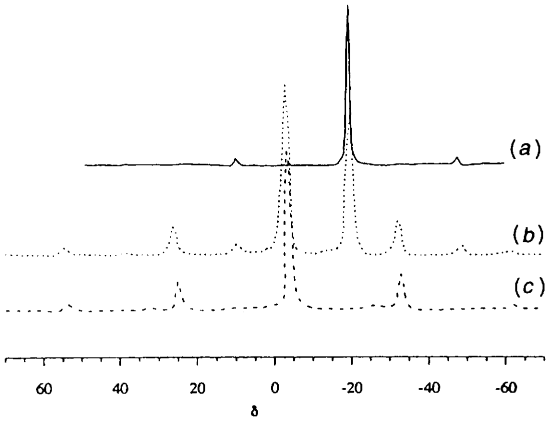


Fig. 10 The 121 MHz ^{31}P MAS NMR spectrum for phosphate **1** (*a*), the mixed phosphate–phenylphosphonate phase **5** (*b*) and the phosphonate **2** (*c*)

Table 1 Experimental conditions used for the synthesis of three compounds by the Ti^{IV}–H_2O_2 route, interlayer distance and chemical composition (obtained from TG and elemental microanalysis) for the anhydrous materials

Sample	POH : PPh	*T*/°C	*t*/h	d_{002}/Å	Composition
3	25	60	17	12.8	$Ti(PhPO_3)_{0.65}(HOPO_3)_{1.35}$
4	30	100	48	14.0	$Ti(PhPO_3)_{0.94}(HOPO_3)_{1.06}$
5	10	80	72	14.5	$Ti(PhPO_3)_{1.50}(HOPO_3)_{0.5}$

ppm from the position for the single phases, and this eliminates the possibility that the solid obtained is a simple mechanical mixture of the pure parent compounds. Chemical shifts obtained for a physical mixture (50%, by mass) of **1** and **2** samples were δ −18.8 and −3.8, respectively, which is similar to an overlay of spectra for those compounds.

Fig. 11 shows the thermal analysis for the solid obtained after *n*-butylamine intercalation of mixed material **5**. The TG presents several steps: the first, between room temperature and 145 °C, involves solvent molecule elimination; from 145 to 350 °C a second mass-loss step is associated with the desorption–decomposition of amine molecules (the DTG shows two ratios for this process); and from 350 to 650 °C there is a third step involving phenyl-group elimination. There is a shoulder in the DTG at 500 °C which indicates the dehydration process from titanium(IV) phosphate to pyrophosphate, the final product. Based on the data obtained we deduce the following chemical composition for this solid, $Ti(PhPO_3)_{1.50}(HOPO_3)_{0.50}\cdot 0.5NH_2Bu^n\cdot 1.26H_2O$ **6**. This confirms that butylamine has access to the acid centres in the mixed solid and it is in good agreement with the arrangement shown in Fig. 9. Such a behaviour of the amine in the intercalation process further supports the identity of the initial solid as a single phase rather than a physical mixture.

The differences in the amine intercalation process for materials prepared by using Ti^{IV}–HF and Ti^{IV}–H_2O_2 systems can be explained by consideration of steric and electronic effects. If the amount of aromatic groups is low the layered mixed solid has galleries enabling the diffusion of amine molecules; this is accompanied by a homogeneous expansion of the interlayer region. However, if the amount of aromatic groups is high 'walls' formed by organic molecules block the access to internal pores, which results in the appearance of several interlayer distances, as was stated in the case of the Ti^{IV}–HF system.

The $TiCl_3$–H_3PO_4–$PhPO_3H_2$ system

The oxidation of Ti^{III} to Ti^{IV} in air takes place rather slowly, which enables the synthesis of highly crystalline titanium(IV) phosphates and phosphonates.[39–41] This system was studied for the synthesis of mixed derivatives, seeking to obtain materials with higher crystallinity than was obtained for the titanium(IV) methods above. Solids were prepared by exploring all the variables which influence the synthesis (Table 2): reaction time, temperature, the molar ratio P:Ti and the POH:PPh ratio. The white solids obtained were highly crystalline, but in all cases only mechanical mixtures of the two parent compounds were obtained (no single-phase mixed compounds).

The positions and relative intensities of the XRD patterns of the materials are given in Table 2. For pure phosphonate **2** the intensity ratio between the first and second reflections $I_1:I_2$ is ≈8:1 (this value depends slightly on the sample preparation for XRD, but it is always ≈8); lower values indicate some **1** (pure phosphate) present. Samples **13**–**15** were synthesized using P:Ti ratios lower than the stoichiometric ratio. Fig. 12 shows the XRD patterns of these materials. All three solids are poorly crystalline materials, with the characteristic reflections of the pure phases at 15.2 and 7.6 Å. There is also a reflection centred at 10.1 Å. This reflection is assigned to the $Ti(OH)_2(HPO_4)\cdot H_2O$ phase described previously.[41] For sample **14** there is also a weak reflection in the XRD at 11.6 Å, typical of γ-$Ti(H_2PO_4)(PO_4)\cdot 2H_2O$. So, this route gives a physical mixture of four different materials, but no single-phase phosphate–phosphonate.

To provide additional information that solids prepared by this route are physical mixtures of the pure parent phases an intercalation study was carried out. Fig. 13 shows the XRD of sample **8** and the product obtained after contact with butylamine vapour for 2 d. The original solid does not contain detectable phosphate **1**. The resulting solid, however, presents an unmistakable reflection at 18.8 Å, typical of the α-titanium

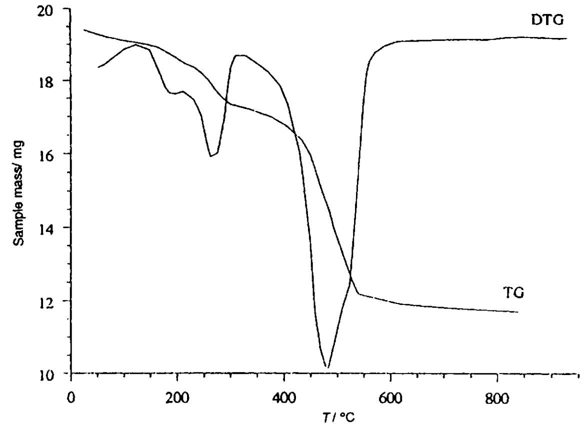


Fig. 11 The TG and DTG traces of the solid obtained by *n*-butylamine intercalation in the mixed titanium(IV) phosphate–phenylphosphonate **5**

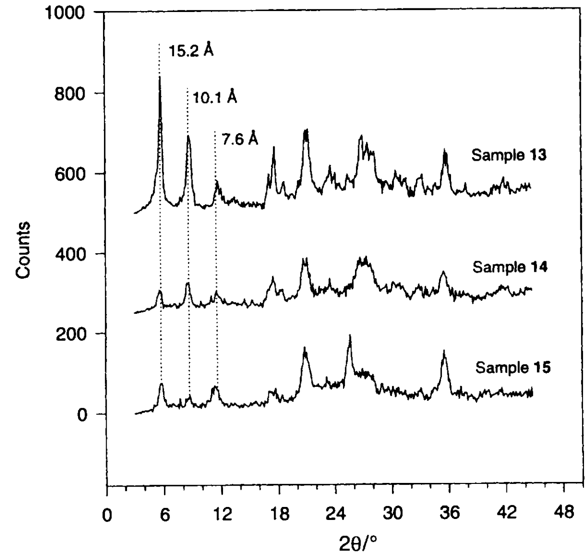


Fig. 12 The XRD profiles for samples obtained by the titanium(III) route

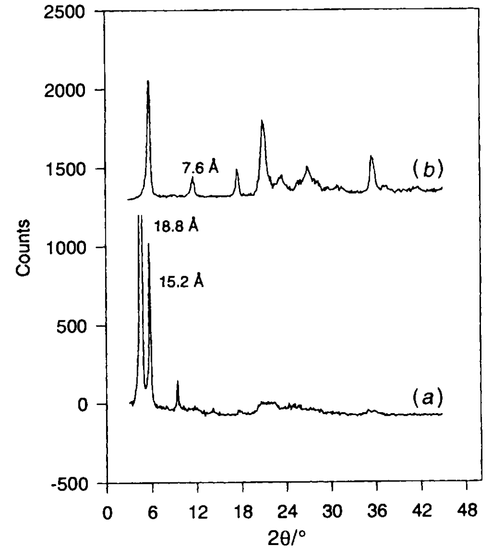


Fig. 13 The XRD powder pattern of (*a*) sample **8** compared with that of its *n*-butylamine intercalate (*b*)

phosphate-*n*-butylamine intercalation compound. Moreover, the reflection at 7.6 Å disappears and reflections for **2** (phosphonate) remain in the intercalated solid. The intercalation behaviour is completely different from that of the single-phase phosphate–phosphonate materials.

Topotactic reaction

The topotactic process consists of the substitution of O_3POH tetrahedra in a preformed layered phosphate by O_3PR tetrahedra, whilst retaining the original layer structure. An idealized mechanism is shown in Fig. 14. Using an isotopic marker, it has been possible to show that the phosphonic group can be completely exchanged in the layered structure.[37]

Using this method it is difficult to obtain complete substitution of the OH for R groups,[33] as an equilibrium takes place: $Ti(HPO_4)_2 + 2\,RPO_3H_2 \rightleftharpoons Ti(RPO_3)_2 + 2\,H_3PO_4$. This method might, however, be excellent to obtain mixed derivatives. Fig. 15 shows the X-ray diffractograms of the samples obtained following a topotactic exchange. The materials obtained possess higher crystallinity than those prepared by the direct precipitation method. Two reflections are observed in the XRD patterns, at 15.2 and 7.6 Å, which unfortunately correspond to those of the pure parent compounds. The reflection between these two peaks, characteristic of the mixed derivatives, was not observed. The amine intercalation process, carried out on these solids, produced materials with very similar XRD patterns to those obtained for intercalation into the solids made from titanium(III) solutions (preceding section).

The synthesis of physical mixtures may be due to the phosphonic groups incorporating in layers with the aromatic rings together, generating a pure phosphonate layer. This would, however, obstruct the amine intercalation process.

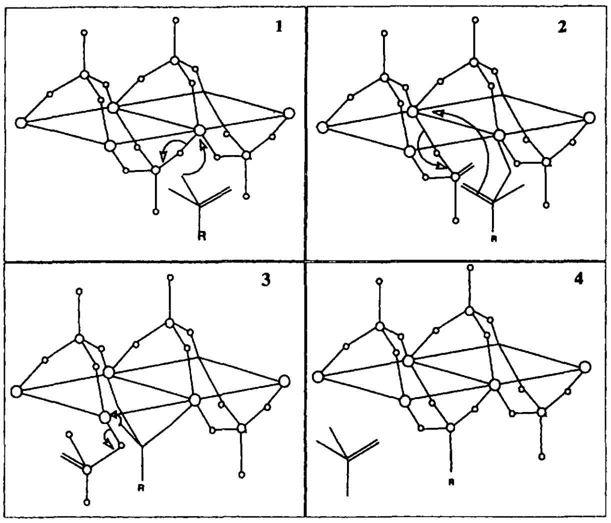


Fig. 14 Idealized mechanism for the topotactic substitution of phosphate tetrahedra by phosphonate tetrahedra in a preformed layered phosphate

Table 2 Experimental conditions used for the synthesis, at 80 °C, of nine compounds by the titanium(III) route, positions of the two first reflections in XRD profiles and their relative intensities

Sample	P:Ti	POH:PPh	t/h	d_1/Å	d_2/Å	$I_1:I_2$
7	4	0.5	168	15.0	7.5	7.70
8	4	1	168	14.9	7.5	5.04
9	4	2	168	14.9	7.5	1.41
10	4	5	96	14.9	7.5	1.47
11	4	7	96	14.9	7.5	0.79
12	4	15	96	13.3	7.7	0.52
13	1	1	96	14.9	8.8	1.75
14	1.5	2	96	15.5	10.2	0.80
15	2	4	96	14.9	7.5	1.17

Another possibility (Scheme 1) is a reaction between the phenylphosphonic acid in solution and the Ti^{IV} (produced by hydrolysis of phosphate **1** at the working pH). This would produce low concentrations of Ti^{IV} and this species then reacts with the most reactive and more concentrated phosphonic acid in solution, the phenylphosphonic acid, producing highly crystalline phosphonate **2**.

Conclusion

The synthesis of mixed derivatives demonstrates the presence of kinetic control. When the tetravalent metal is present in

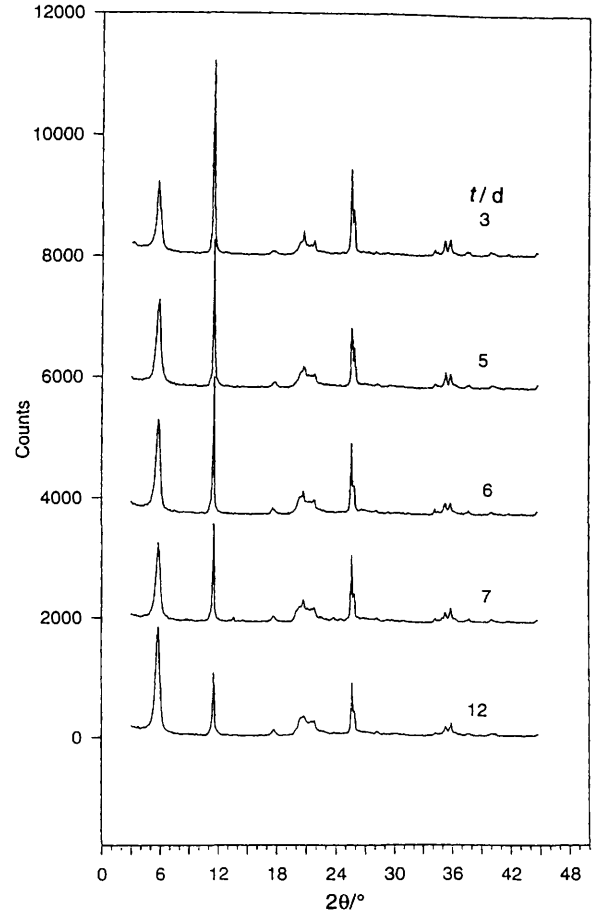
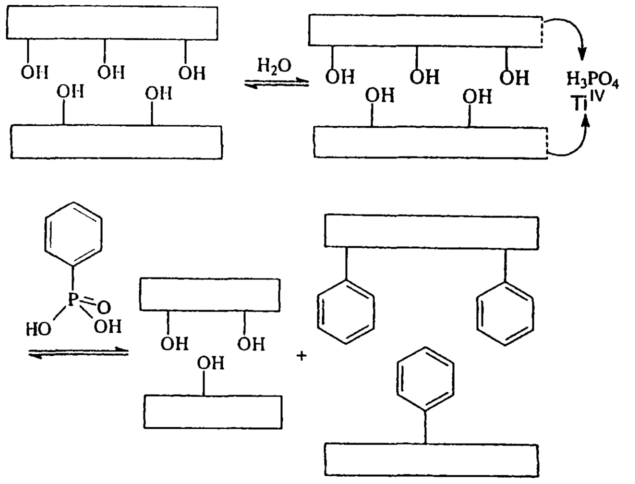


Fig. 15 The XRD profiles for samples of materials prepared from phosphate **1** by a topotactic process. The reaction time is indicated



Scheme 1 Hydrolysis of phosphate **1** to give a sufficient amount of free titanium(IV) to react with phenylphosphonic acid solutions, yielding phosphonate **2**

solution at high concentration, it reacts rapidly with both the species present, and this results in coprecipitation of both species, yielding single-phase mixed (phosphate–phenylphosphonate) compounds. When the concentration of titanium(IV) in solution is low, or it is slowly generated in the reaction medium, the cation can distinguish the most reactive agent (in our case the phenylphosphonic acid) from the least reactive (phosphoric acid), giving physical mixtures of single phosphate and phosphonate phases.

Experimental

Materials and methods

Reagents used were obtained from Merck ($TiCl_4$, HF, H_2O_2, H_3PO_4), Aldrich ($TiCl_3$) and Fluka (phenylphosphonic acid) and used without further purification.

$TiCl_4$–HF–H_3PO_4–$PhPO_3H_2$ system

Mixed aqueous solutions of the acids H_3PO_4 and $PhPO_3H_2$ in variable ratios were prepared from the 1 mol dm^{-3} acids. For all samples a constant molar ratio P:Ti = 4:1 was used (P is the amount of phosphorus from phosphoric acid plus phosphonic acid). A titanium(IV) fluoro complex solution was prepared by the addition of $TiCl_4$ [1 mol dm^{-3} in 1.5 cm^3 HCl(aq)] and 40% HF(aq) (0.2 cm^3) to deionized water (25 cm^3). This solution was mixed with a solution (60 cm^3) of known phosphoric:phosphonic acid (POH:PPh) ratio. The reaction mixtures were heated at 80 °C in an oil-bath, under reflux conditions for 7 d.

$TiCl_4$–H_2O_2–H_3PO_4–$PhPO_3H_2$ system

Titanium(IV) chloride [1 mol dm^{-3} in 1.1 cm^3 HCl(aq)] was added to 30% H_2O_2 solution (20 cm^3) to give the strongly coloured $[TiO_2(OH)(H_2O)_x]^+$ complex in solution (pH < 1). The P:Ti molar ratio was 4:1 in all cases. A molar ratio phosphoric acid:phenylphosphonic acid (POH:PPh) between 1 and 50:1 was used. The influence of the reaction temperature was studied.

$TiCl_3$–H_3PO_4–$PhPO_3H_2$ system

A 30% solution (13 cm^3) of $TiCl_3$ in HCl(aq) was added to a mixture (60 cm^3) of H_3PO_4 and $PhPO_3H_2$ solutions in variable ratios. The influence on the crystallinity and composition of the solid of the P:Ti molar ratio, temperature and reaction time was studied.

Topotactic reaction

The compound α-$Ti(HPO_4)_2{\cdot}H_2O$ **1** (0.4 g), prepared as described previously,[39] was dispersed in aqueous 1 mol dm^{-3} $PhPO_3H_2$ (20 cm^3) at 40 °C. The process was carried out using a batch technique. The materials were obtained using reaction times from 1 to 12 d.

Sample purification

All the prepared solids were filtered off, washed with distilled water (until the pH of the washings was 4), air dried overnight at 50 °C and then stored over a saturated aqueous solution of NaCl (relative humidity 75%).

n-Butylamine intercalation

Samples (0.5 g) of materials prepared by the above methods were stored in a desiccator above a 97% aqueous *n*-butylamine solution, at room temperature for 4 d. The resulting white solids were oven dried at 50 °C for *ca.* 12 h.

Sample characterization

Powder X-ray diffraction measurements were carried out with a Philips 1050/23 diffractometer equipped with a graphite monochromator using Cu-Kα, radiation (λ = 1.5418 Å). The diffractometer was calibrated with a thin film of tetradecanol. Infrared spectra were recorded in KBr pressed discs on a Perkin-Elmer 1720-X FT spectrometer, proton-decoupled solid-state NMR spectra on a Bruker MSL-300 spectrometer. The ^{31}P MAS NMR spectra were acquired at a frequency of 121 MHz employing cross-polarization with flip-back. Samples were packed into a sapphire tube and spun at 4.5 kHz in a MAS probe supplied by Doty Scientific. A lorentzian-to-gaussian transformation was used to improve resolution for chemical shift determination.[50] Chemical shifts are reported in ppm with respect to that for analytical grade 85% H_3PO_4. A Mettler [TA 4000 (TG50)] thermal analyser unit was used in thermogravimetry (TG) at a typical heating rate of 10 °C min^{-1}, in flowing air (25–900 °C). The empirical results of TG and elemental (C, H, N) microanalysis were in excellent agreement with the theoretical values deduced from formulations given for the materials.

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References

1 G. Alberti, U. Costantino, S. Allulli and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1113.
2 D. M. Poojary, C. Bhardwaj and A. Clearfield, *J. Mater. Chem.*, 1995, **5**, 171.
3 G. Alberti and U. Costantino, in *Inclusion Compounds*, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Oxford University Press, Oxford, 1992, vol. 5, ch. 5.
4 J. W. Johnson, A. J. Jacobson, W. M. Butler, S. E. Rosenthal, J. F. Brody and J. T. Lewandowski, *J. Am. Chem. Soc.*, 1989, **111**, 381.
5 L. A. Vermulen and M. E. Thompson, *Nature (London)*, 1992, **358**, 656.
6 G. Huan, A. J. Jacobson, J. W. Johnson and E. W. Corcoran, *Chem. Mater.*, 1990, **2**, 91.
7 J. W. Johnson, J. F. Brody, R. M. Alexander, B. Pilarki and A. R. Katritzky, *Chem. Mater.*, 1990, **2**, 198.
8 R.-C. Wang, Y. Zhang, H. Hu, R. R. Frausto and A. Clearfield, *Chem. Mater.*, 1992, **4**, 864.
9 B. Bujoli, P. Palvadeau and J. Rouxel, *Chem. Mater.*, 1990, **2**, 582.
10 B. Bujoli, A. Courilleau, P. Palvadeau and J. Rouxel, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 171.
11 G. Cao, H. Lee, V. M. Lynch and T. E. Mallouk, *Inorg. Chem.*, 1988, **27**, 2781.
12 C. Y. Ortiz-Avila, P. R. Rudolf and A. Clearfield, *Inorg. Chem.*, 1989, **28**, 2137.
13 G. Cao, V. M. Lynch, S. J. Swinnea and T. E. Mallouk, *Inorg. Chem.*, 1990, **29**, 2112.
14 G. L. Rosenthal and J. Caruso, *Inorg. Chem.*, 1992, **31**, 3104.
15 G. Alberti, M. Casciola, U. Costantino, A. Peraio and E. Monterini, *Solid State Ionics*, 1992, **50**, 3104.
16 G. Alberti, M. Casciola, R. Palombari and A. Peraio, *Solid State Ionics*, 1992, **58**, 339.
17 R. C. T. Slade, C. R. M. Forano and A. Peraio, *Solid State Ionics*, 1993, **61**, 23.
18 M. Casciola, U. Costantino, A. Peraio and T. Rega, *Solid State Ionics*, 1995, **77**, 229.
19 A. Clearfield, *Chem. Rev.*, 1988, **88**, 125.
20 C. F. Lee and M. E. Thompson, *Inorg. Chem.*, 1991, **30**, 4.
21 M. Ogawa and K. Kuroda, *Chem. Rev.*, 1995, **95**, 399.
22 G. Alberti and U. Costantino, *J. Mol. Catal.*, 1994, **27**, 235.
23 A. Clearfield, in *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis*, ed. J. M. Basset, Kluwer Academic Publishers, Norwell, MA, 1988, pp. 269–271.

24 M. B. Dines, P. Di Giacomo, K. P. Callahan, P. C. Griffith, R. H. Lane and R. E. Cooksey, *ACS Symp. Ser.*, 1982, **192**.

25 M. B. Dines and P. Di Giacomo, *Inorg. Chem.*, 1981, **20**, 92.

26 M. B. Dines, R. E. Cooksey, P. C. Griffith and R. H. Lane, *Inorg. Chem.*, 1983, **22**, 1003.

27 *Inorganic Ion Exchange Materials*, ed. A. Clearfield, CRC Press, Boca Raton, FL, 1982.

28 G. Alberti, U. Costantino, F. Marmottini and G. Perego, *Mater. Chem. Phys.*, 1988, **9**, 267.

29 G. Alberti, U. Costantino, F. Marmottini, R. Vivani and P. Zappelli, in *Pillared Layered Structures: Current Trends and Applications*, ed. I. V. Mitchell, Elsevier Applied Science, New York, 1990, pp. 119–126.

30 J. G. Wang, G.-Z. Peng and A. Clearfield, *Mater. Chem. Phys.*, 1993, **35**, 208.

31 B.-Z. Wan, R. G. Anthony, G.-Z. Peng and A. Clearfield, *J. Catal.*, 1986, **101**, 19.

32 G. Huan, A. J. Jacobson, J. W. Johnson and D. P. Goshorn, *Chem. Mater.*, 1992, **4**, 661.

33 G. Alberti, R. Vivani, R. K. Biswas and S. Murcia-Mascaros, *React. Polym.*, 1993, **19**, 1.

34 G. Cao and T. E. Mallouk, *Inorg. Chem.*, 1991, **30**, 1434.

35 K. J. Scott, Y. Zhang, R.-C. Wang and A. Clearfield, *Chem. Mater.*, 1995, **7**, 1095.

36 Y. Zhang, K. J. Scott and A. Clearfield, *J. Mater. Chem.*, 1995, **5**, 315.

37 S. Yamanaka and M. Hattori, *Inorg. Chem.*, 1981, **20**, 1929.

38 S. Yamanaka, K. Sakamoto and M. Hattori, *J. Phys. Chem.*, 1984, **88**, 2067.

39 A. Bortun, E. Jaimez, J. R. García and J. Rodríguez, *Mater. Res. Bull.*, 1995, **30**, 413.

40 M. A. Villa-Gracía, E. Jaimez, A. Bortun, J. R. García and J. Rodríguez, *J. Por. Mater.*, 1995, **2**, 293.

41 A. Bortun, V. V. Strelko, E. Jaimez, J. R. García and J. Rodríguez, *Chem. Mater.*, 1995, **7**, 249.

42 J. D. Wang, A. Clearfield and G.-Z. Peng, *Mater. Chem. Phys.*, 1993, **35**, 187.

43 G. Alberti, P. Cardini-Galli, U. Costantino and E. Torraca, *J. Inorg. Nucl. Chem.*, 1967, **26**, 571.

44 K. J. Martin, P. J. Squattrito and A. Clearfield, *Inorg. Chim. Acta*, 1989, **155**, 7.

45 B. Bujoli, P. Palvadeau and M. Queignec, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 141.

46 F. Menéndez, A. Espina, C. Trobajo, J. R. García and J. Rodríguez, *J. Incl. Phenom. Mol. Recog. Chem.*, 1993, **15**, 215.

47 R. Llavona, Ph.D. Thesis, Oviedo University, 1985.

48 N. J. Clayden, *J. Chem. Soc., Dalton Trans.*, 1987, 1877.

49 J. Herzfeld and A. E. Berger, *J. Chem. Phys.*, 1980, 6021.

50 G. A. Pearson, *J. Magn. Reson.*, 1987, **8**, 541.

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