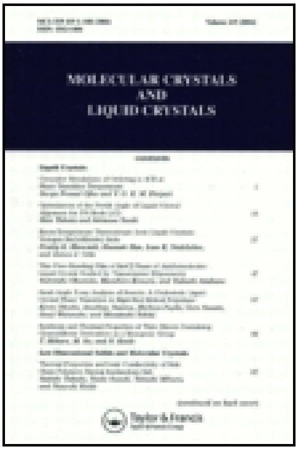

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: Sabrina Foglia & Anthony A.G. Tomlinson (1998): Interstratified Group IV Phosphates and Phosphate / Smectite Clays, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 227-232

To link to this article: http://dx.doi.org/10.1080/10587259808042390

Mol. Cryst. Liq. Cryst., 1998, Vol. 311, pp. 227–232
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Interstratified Group IV Phosphates and Phosphate / Smectite Clays

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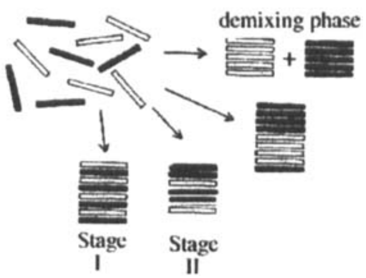
Abstract. Colloidal platelet re-assembly can be used to obtain interstratified phosphates and phosphate/smectite clays. For Group IV phosphates, Stage 1 materials alone are obtained and ^{31}P MAS-NMR and AFM probing show that the materials are composed of crystalline and mobile phases.

Keywords: Interstratification, phosphates, smectites, MAS-NMR, AFM

INTRODUCTION

Most soft intercalation reactions can now be mapped in detail, due to recent refinements in XRPD and local structure probes[1]. However (with few exceptions[2]) manipulations have been confined to homogeneous layered materials, i.e. those with layers of the same type and charge, one reason being the greater sensitivity of colloids to surface hydrolysis, coagulation and other effects with respect to bulk. Conversely, in Nature, layered materials often occur in interstratified forms, as in illite and rectorite ('fat clay')[3].



Nevertheless, the differing specific layer charges in interstratifieds (between smectites, phosphates, oxides, etc.) are expected to modify rheological, intercalation and other chemical properties, to give a range of new materials useful in, for example, pillaring. We have found that characterisable interstratified Group IV phosphate-containing materials can be obtained *via* the simple re-stacking reaction above, provided they are first colloidised[4] *via* pre-intercalation with *n*-$PrNH_2$ (PA). Typically, a phosphate dispersed in the colloidal existence zone (i.e. 60% of theoretical c.e.c.) in 0.1 mol dm^{-3} PA is added in fixed mole ratio to a second phosphate, dispersed similarly, and the flocculate stirred, centrifuged and dried (vacuum/70°C).

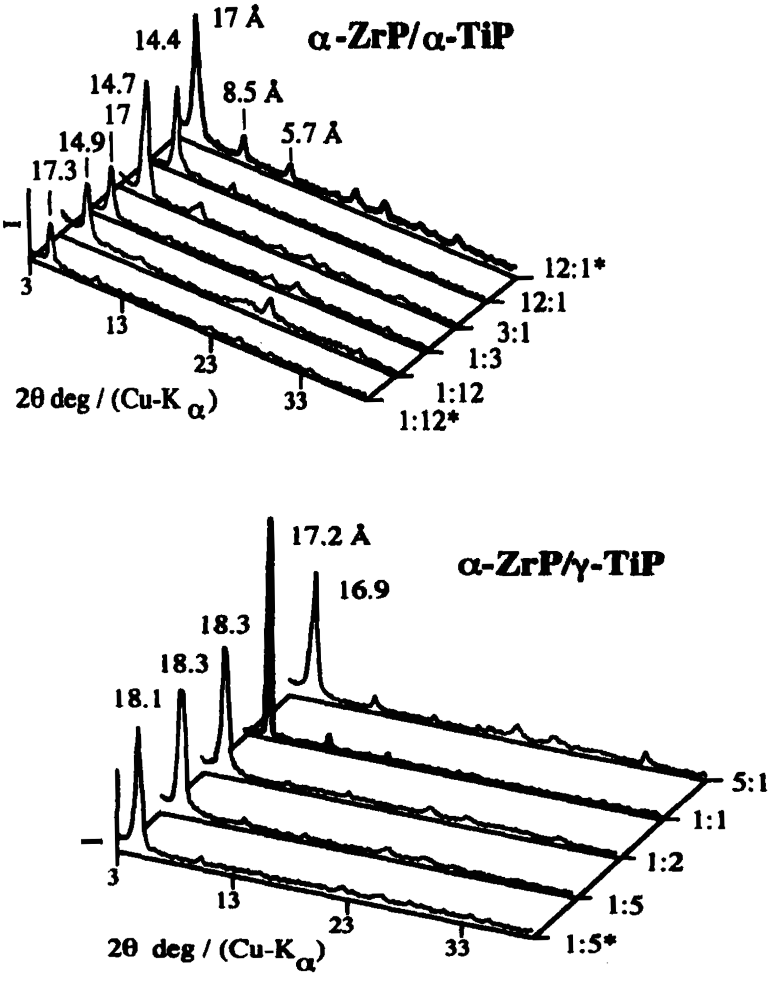


FIGURE 1. XRPD of interstratified materials (* after redispersion in PA, —, pure phases discussed below)

Stage I materials alone are obtained for α/α and α/γ-Group IV phosphates throughout the molar ratio range $M_IP : M_{II}P \gtrless$ 12:1 [M_I = Zr; M_{II} = α, γ Ti; P = $(HPO_4)_2 \cdot H_2O$ and γ-TiP refers to $Ti(PO_4)(H_2PO_4) \cdot 2H_2O$]. No phase demixing occurs, and all are redispersible in PA. For α/α ZrP/TiP two major phases are obtained, one impure with d= 14.7 ± 0.2 Å and the second from 12:1 ZrP:TiP pure after re-dispersion, having d = 17±0.2 Å. Conversely, α/γ ZrP/TiP gave the most crystalline phase at 1:1. Stoichiometries of these two materials are (from metal, C,H,N and TG/DTA analyses) :

$$12{:}1\ \alpha/\alpha : Zr_{0.97}\,Ti_{0.03}\,(HPO_4)_8 \cdot PA \cdot (H_3O^+)_{12} \cdot 12 \cdot H_2O$$

$$1{:}1\ \alpha/\gamma : Zr_{0.7}Ti_{0.3}\,(HPO_4)_7 \cdot PA \cdot (H_3O^+)_{10} \cdot H_2O$$

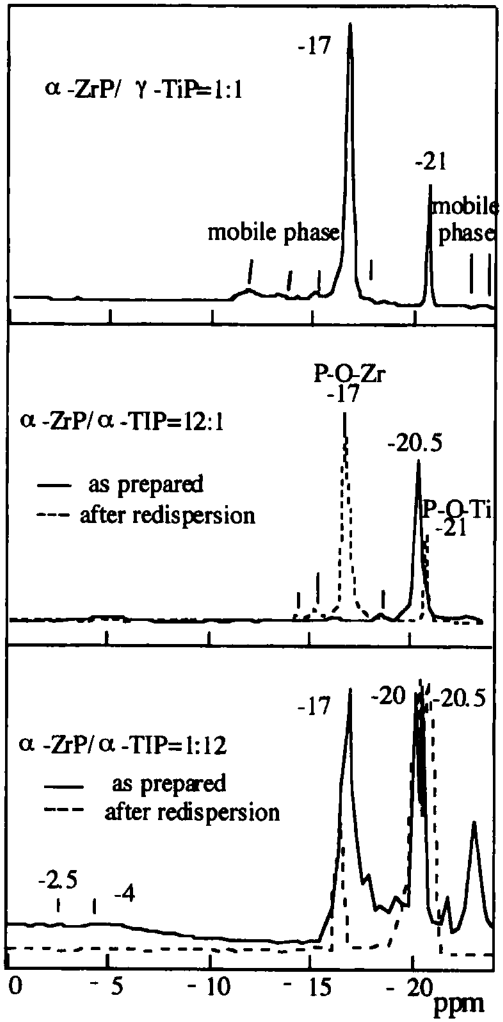
At several α/α–Zr/TiP ratios a phase with an interlayer distance (14.7 ± 0.2 Å) different from that of the components (α–ZrP/PA = 17.3Å; as also probably α–TiP/PA) is given (see FIG. 1). The same is the case for α/γ–Zr/TiP : at 5:1 ratio, a phase is present with d = 16.9 Å and at ratio 1: 2 - 1 : 5 a phase with d = 18.1 ± 2Å predominates. The unusual decrease in interlayer is attributed to possible nesting of PA in the TiP component, as found previously for phen in γ–TiP[5]. The same methods are successful for Gp. IV phosphate-montmorillonite. Again, only Stage I materials could be obtained, whatever the α-, γ-TiP :smectite ratios used (10:1-->1:10). Compared with those of montmorillonite itself (15 Å), the interlayer distances are unusually short : 12.2 Å (α-TiP/PA) and 13.0 Å (γ-TiP:PA) Å indicative of flat PA molecules.

That crystalline, rather than delaminated amorphous phases (such as expected, for example, from 'cut' platelets) phases are given indicates that hydrolysis effects are not as important as suggested previously[6]. Crucial factors determining clean phases are : i) the presence of differing colloidal existence zones for each component, ii) differential drying of each platelet-ordered material; iii) influence of redispersion time on different platelets hydrolysis; iv) delamination on re-dispersion for the phosphate/clay systems.

^{31}P MAS-NMR show that three different phases are present in both α/γ and α/α materials. For 1:1 α/γ, resonances at -17 and -21 ppm (of high intensity) are due to P-O-Zr and P-O-Ti groups respectively. They do not change on cross-polarization and are ascribed to the major, highest-ordered phase visible by XRPD. A second, very disordered phase (not detectable by XRPD) is also present as indicated by a series of low-intensity resonances. Integration shows this mobile phase predominates over the crystalline phase (despite its low intensities, see ratios in Fig.2).

Turning to the α/α system, the NMR spectrum of the fresh 12:1 sample shows two main peaks at -17.5 and -20.5 ppm, which do not change after cross-polarization. After redispersion - i.e. after increase in platelet ordering - these peaks shift to -17 ppm (corresponding to the P-O-Zr group resonance) and -21 ppm (corresponding to P-O-Ti group resonance) with intensities now comparable with those in the α/γ system. Further, there is an increase in importance of the mobile phase and after cross-polarization only the resonance at -20.5 forms a doublet (-20 and -20 ppm). This phase is neither crystalline, nor amorphous and the low degree of crystallinity with respect to the P environment, caused by the presence of low-ordered stacked layers beyond XRPD measurement, indicates that they are probably ordered with respect to a H$^+$ environment.

The latter NMR spectrum indicates that a third phase is present, albeit in low amount. Resonances due to amorphous phases disappear CP-MAS and those related to crystalline phases increase in intensity (hence this spectrum may be compared with the XRPD one). The signal at -20.5 ppm (ascribed to P-O-Ti group), in this sample, is split in CP (-20 and -20.5 ppm). This is brings to light the presence of a third phase (different from both crystalline and "mobile" ones). This has intermediate order, *via* stacked and differently ordered layers, and is less predominant than the other phases.



	Crystalline %	Mobile %
	19	81
	23.5	76.5
---	19.5	80.5
	3	97
---	43.5	56.5

FIGURE 2 Mas-nmr of some interstratified Group IV phosphates (modified Bruker AC200; CP-MAS sequence; external standard ref.: $(NH_4)H_2PO_4$)

Examination of NMR spectra of the α-ZrP/ α-TiP=1:12 material reveals that the P-O-metal group resonances become doublets. More importantly, the large excess of α-TiP present in this material enhances observation of the third phase, which has only short range order. In the fresh sample, this phase imparts disorder to the system, but after redispersion it contributes to the higher-crystallinity-degree phase. The combined XRPD + MAS-NMR results point to the presence of three differently ordered domains in the materials. The observable XRPD derive from the high *c*-axis ordered platelets, whereas low c-axis ordered platelets are unobservable. Full fits of the crystalline MAS-NMR are being completed to obtain distance information in both.

AFM provides further insight into the morphology of the materials, especially as regards temperature changes. For both α–α and α–γ-phosphates variable-size domains are present on (001) mica, as shown in Fig. 3. Platelet bundles are roughly perpendicular to the mica surface in both cases, which is comparable to previous studies, which have shown that the mica surface partially orients smectite platelets[7]. For 12 : 1 α–α, there is clear parallel stacking, corresponding to ca 90 single platelets. PA loss leads to disruption of ordering, L' now being in agreement with ca 27 platelets.

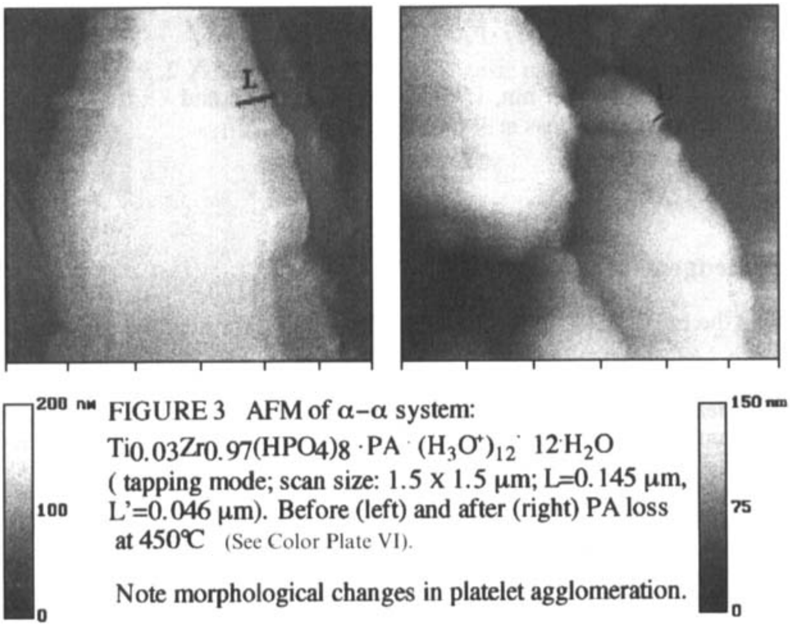


FIGURE 3 AFM of α–α system: $Ti_{0.03}Zr_{0.97}(HPO_4)_8 \cdot PA \cdot (H_3O^+)_{12} \cdot 12H_2O$ (tapping mode; scan size: 1.5 x 1.5 μm; L=0.145 μm, L'=0.046 μm). Before (left) and after (right) PA loss at 450°C (See Color Plate VI).

Note morphological changes in platelet agglomeration.

Conversely, the α–γ Zr/TiP gives a stacking of 49 nm, corresponding to only 28 single platelets, which increases, to 42 platelets, on PA loss. In addition, the agglomeration produced gives rise to tilted (ca 80° to the surface) sheaf-like moieties on the mica (001) surface.

In conclusion, despite complications (hydrolysis and other effects) interstratified materials can be obtained from both similarly (Group IV phosphates) and differently (phosphate/smectite clay) charged layered materials by colloidal re-assembly. The method is being extended to other systems and the above materials utilised as substrates in pillaring, and molecular modelling of the platelet reorganization is underway.

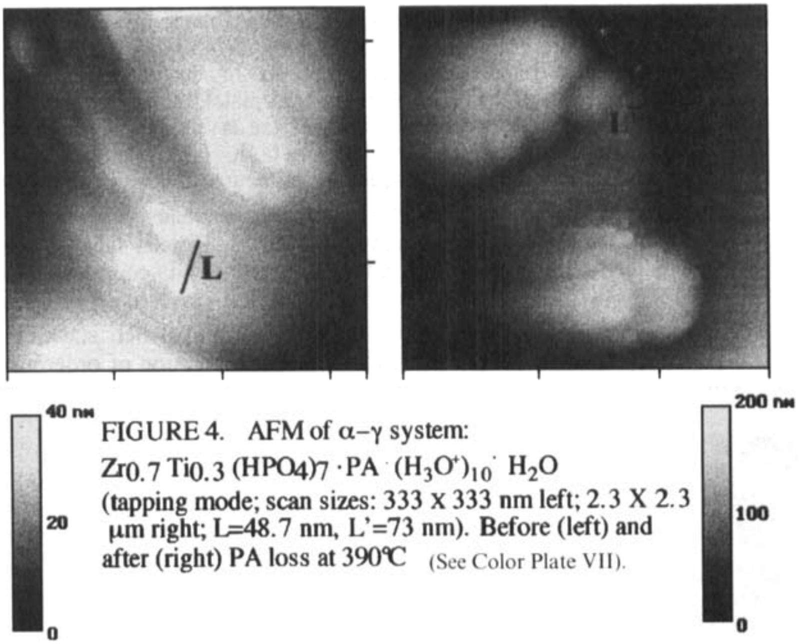


FIGURE 4. AFM of α–γ system: $Zr_{0.7}Ti_{0.3}(HPO_4)_7 \cdot PA \cdot (H_3O^+)_{10} \cdot H_2O$ (tapping mode; scan sizes: 333 X 333 nm left; 2.3 X 2.3 μm right; L=48.7 nm, L'=73 nm). Before (left) and after (right) PA loss at 390°C (See Color Plate VII).

Acknowledgement

We thank the EC (BRITE-EuRam, BRE2-CT93-0450) for financial support.

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