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Intercalation and interlayer amidation properties of *n*-alkylmonoamines for γ-zirconium (2-carboxyethyl)phosphonate phosphate

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The uptake of *n*-alkylmonoamines $C_nH_{2n+1}NH_2$ ($n = 2$–10) by γ-zirconium (2-carboxyethyl)phosphonate phosphate, $ZrPO_4(H_2PO_4)_{0.36}(HO_3PCH_2CH_2CO_2H\text{-}2)_{0.64}\cdot 2.3H_2O$, derived from γ-zirconium phosphate has been studied at 25 °C. The alkylamines with $n \geqslant 4$ form an intercalated phase in which the amine molecules are arranged as a bilayer with their axes perpendicular to the inorganic layers, whereas the shorter-chain amines cannot be stably held in the interlayer space. The amine uptake increases with increasing carbon number until it reaches a constant value of 0.32 mol per formula weight for the amines with $n \geqslant 6$. The amine uptake and IR data indicate that the ammoniated guest molecules replace primarily the protons of the interlayer carboxyl groups. On heating at 220 °C, the ionically bonded $CO_2^-NH_3^+$ group in the ammonium-exchanged solids is thermally condensed into the amide CONH form without any significant release of the amine guest.

Layered zirconium phosphate is represented by two fundamental forms, α- and γ-zirconium phosphates.[1] Organic derivatives of α-zirconium phosphate, $Zr(HPO_4)_2\cdot H_2O$, can be synthesized by the direct reaction of tetravalent zirconium ions with organophosphoric or organophosphonic acids, as first reported by Alberti *et al.*[2] in 1978. This method has been applied to the preparation of an enormous variety of zirconium organophosphates or organophosphonates with α-layer structures containing organic groups such as alkyl, phenyl, carboxyl and sulfonyl.[3] Much attention has been paid to the applications of α-organic derivatives concerned with their useful functions such as ion exchange,[4] ionic conduction[5] and catalysis.[6] Recently, some interesting findings were reported concerning the intercalation properties of carboxyethylated derivatives of α-zirconium phosphate.[7–9] Burwell and Thompson[7] extended the method of Alberti *et al.*[2] to prepare amide- and ester-functionalized zirconium phosponates *via* amine and alcohol intercalation reactions of the acyl chloride compound of α-zirconium phosphonate derived from its carboxylic acid form. We reported a simpler route in which a similar amide-functionalized zirconium phosphonate can be obtained by thermal condensation of the alkylmonoammonium or alkyldiammmonium-exchanged form of a carboxyethylated zirconium phosphonate.[8] A similar condensation of carboxyl with amino groups in the interlayer space of layered systems was observed for α,ω-amino acids or their related compounds intercalated in α-zirconium phosphate[10] and montmorillonites.[11] It was also found that the intercalation of *n*-alkylmonoamines by a α-carboxyethylated zirconium phosphonate occurs only for *n*-heptylamine, leading to a new class of host–guest process based on molecular assembly recognition.[9]

The organic derivatives of γ-zirconium phosphate, on the other hand, are obtainable by its topotactic reaction with various organophosphoric or organophosphonic acids, as reported by Yamanaka[12] in 1976. At that time the γ-zirconium phosphate erroneously formulated as $Zr(HPO_4)_2\cdot 2H_2O$ was believed to have a structure similar to that of the α form in which each layer consists of a plane of zirconium atoms linked through HPO_4 groups located alternately above and below this plane.[1] Recent structural studies, however, revealed that the γ-zirconium phosphate must be formulated as $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$.[13] In each layer two planes of zirconium atoms are bridged with PO_4 groups and tetrahedral $PO_2(OH)_2$ groups while the hydroxyl groups projecting out of the layer are bonded to two zirconium atoms through their oxygen atoms. On the basis of this new structural information, Alberti *et al.*[14] have confirmed the above-mentioned topotactic reaction and examined the ion-exchange properties of some alkylated or phenylated derivatives of γ-zirconium phosphate.

Previously, a striking contrast between the two parent α- and γ-zirconium phosphates as host matrices was observed for the reactivity in intercalation or thermal stability of intercalated phases with pyridine,[15] histamine (imidazole-4-ethanamine),[16] basic amino acids,[17] and aminated β-cyclodextrins.[18] These observations suggest that it would be of interest to compare the intercalation and interlayer amidation properties of carboxyethylated derivatives of α- and γ-zirconium phosphates.

Attempts were thus made to investigate the intercalation of *n*-alkylmonoamines $C_nH_{2n+1}NH_2$ ($n = 2$–10) in γ-zirconium (2-carboxyethyl)phosphonate phosphate and the subsequent interlayer amidation.

Experimental

Reagents and materials

The γ-zirconium phosphate sample was prepared by a method similar to that of Clearfield *et al.*,[19] as previously described.[15b] The γ-zirconium (2-carboxyethyl)phosphonate phosphate sample **2** used in this study was prepared in a manner similar to that applied by Yamanaka and Hattori[20] to the synthesis of γ-zirconium phenyl phosphate. A 1.0 g sample of the γ-zirconium phosphate was added to $HO_2CC_2H_4PO(OH)_2$ (0.100 mol, 5.39 g) dissolved in acetone–water (1 : 1, 100 cm^3) and then refluxed for 10 h. The product was filtered off, washed with acetone and then dried in air.

Intercalation reaction

A 0.05 g sample of compound **2** was mixed with aqueous alkylamine solution (5 cm^3) at a fixed ratio of [amine] : [Zr] = 2.0 : 1, followed by stirring at 25 °C for 9 d. This reaction time was selected by reference to the equilibration time

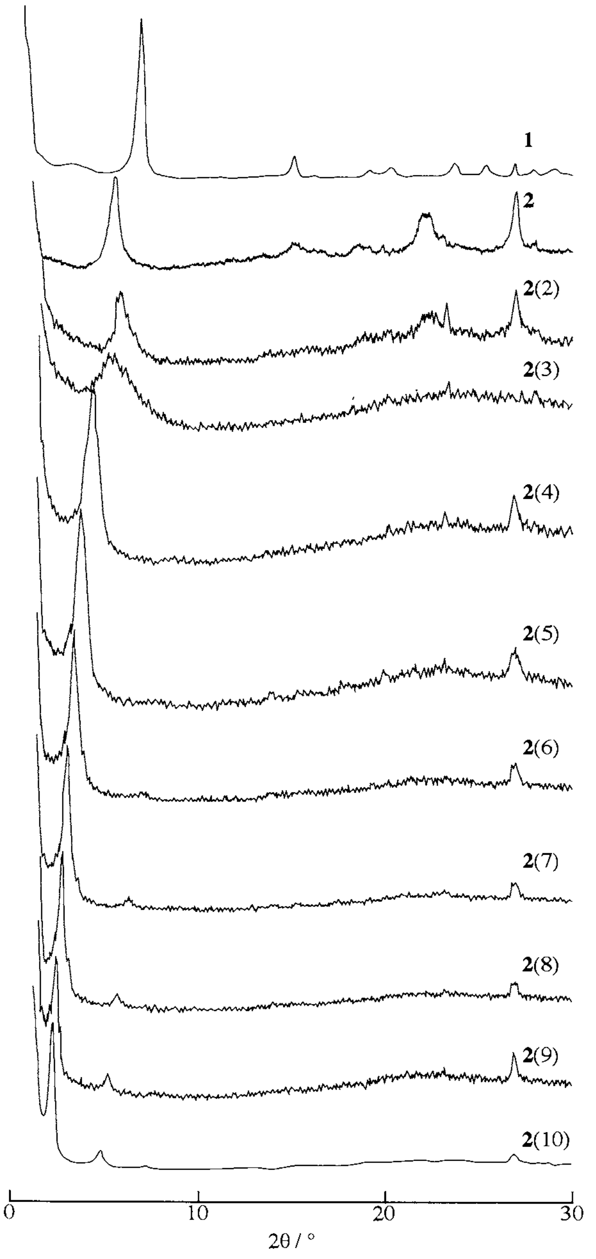

Fig. 1 X-Ray diffraction patterns of γ-zirconium phosphate **1**, $ZrPO_4(H_2PO_4)$, its 2-carboxyethylphosphonate derivative **2**, $ZrPO_4(H_2PO_4)_{0.36}(HO_3PCH_2CH_2CO_2H\text{-}2)_{0.64}\cdot 2.3H_2O$ and their amine intercalates **2(*n*)**, where *n* is the number of carbon atoms of the intercalated amine

observed for the α-zirconium (2-carboxyethyl)phosphonate–alkyldiamine or –heptylamine systems.[8] The resulting mixtures were centrifuged, fully washed with water and freeze-dried.

Sample characterization

Thermogravimetry (TG) was carried out with a Shinku Riko instrument at a heating rate of 10 °C min^{-1} in air. X-Ray diffraction measurements were made on a Shimadzu diffractometer with Cu-Kα radiation using tetradecan-1-ol as an external standard. Infrared absorption spectra were measured by the KBr-pellet method using a Nippon Bunko spectrometer.

Results and Discussion

Preparation of γ-zirconium (2-carboxyethyl)phosphonate phosphate

The X-ray diffraction patterns of the γ-zirconium (2-carboxyethyl)phosphonate phosphate sample **2** and its parent phosphate **1** are shown in Fig. 1. The major peaks at low angles attributable to the 002 reflections for both samples indicate that the parent phosphate with an interlayer spacing of 12.3 Å was converted into a layered compound with an interlayer spacing of 15.4 Å. The IR spectrum of **2** exhibited an absorption band at 1710 cm^{-1} due to the C=O stretching of the CO_2H group, as shown in Fig. 2(*a*). Additional X-ray data revealed that the solid is totally converted into ZrP_2O_7 upon heating at 1000 °C for 1 h. The carbon and hydrogen contents of this sample were

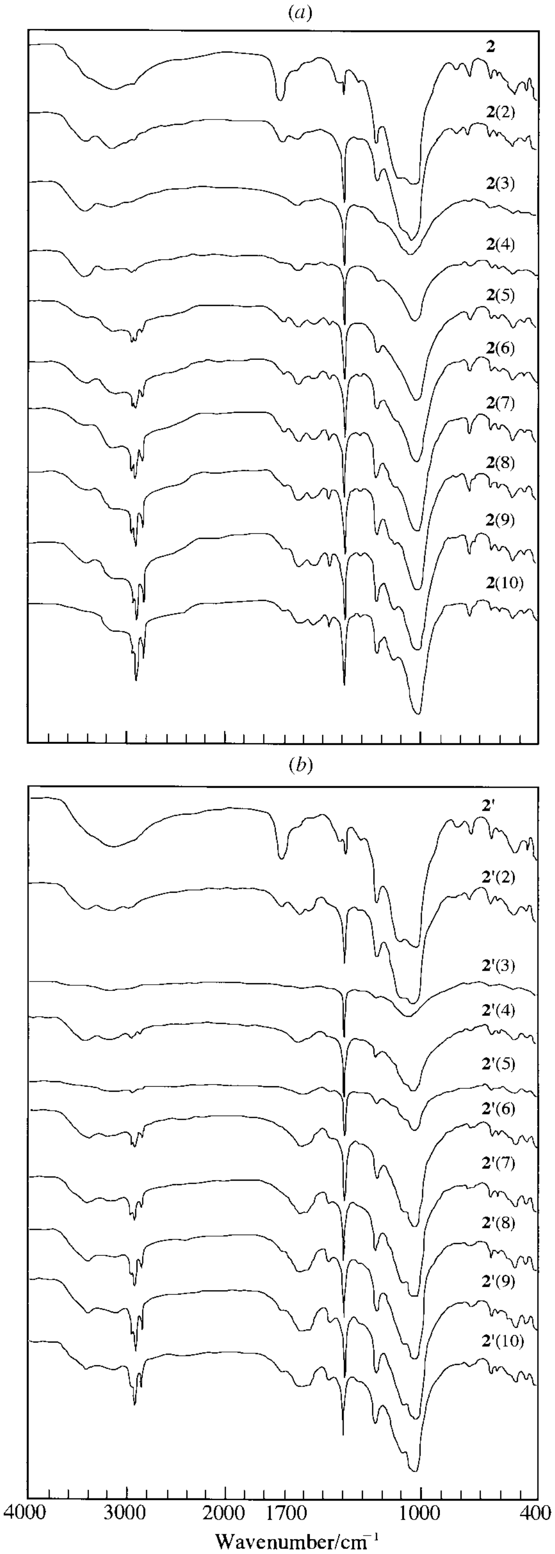

Fig. 2 Infrared absorption spectra of (*a*) compounds **2** and **2(*n*)** and (*b*) **2′** and **2′(*n*)**. Compounds **2′** and **2′(*n*)** were obtained upon heating **2** and **2(*n*)**, respectively, at 220 °C for 0.5 h

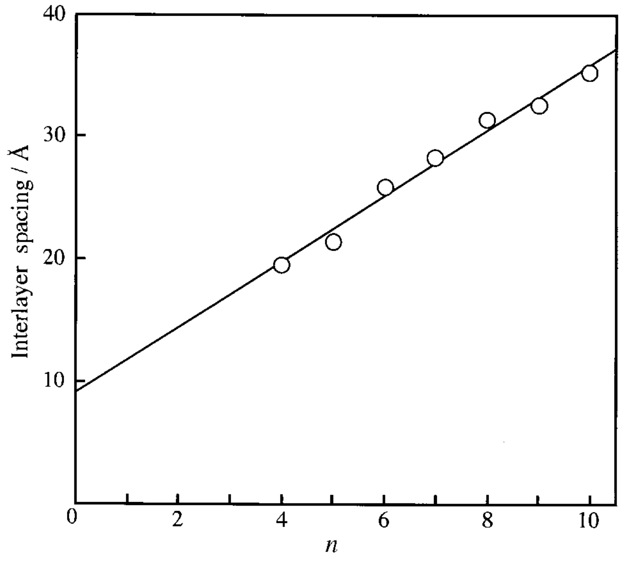

Fig. 3 Interlayer spacing of compounds **2**(*n*) as a function of the carbon number of the alkyl chain

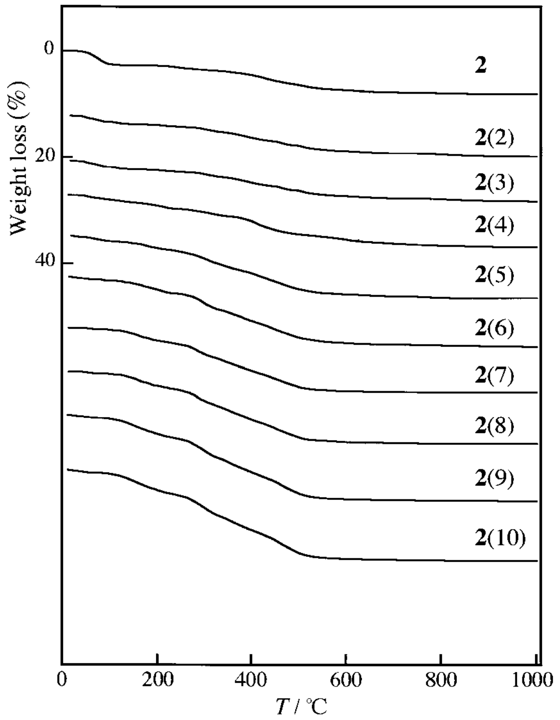

Fig. 4 Thermogravimetric curves for compounds **2** and **2**(*n*) obtained with a heating rate of 10 °C min^{-1} in air. The vertical scales for **2**(*n*) are shifted by an arbitrary percentage

6.39 and 2.53% (w/w), within an error of ±0.5%, respectively, yielding the composition $ZrPO_4(H_2PO_4)_{0.36}(HO_3PCH_2CH_2CO_2H\text{-}2)_{0.64}\cdot 2.3H_2O$.

Intercalation and interlayer amidation properties

The products of reaction of compound **2** with *n*-alkylmonoamines, **2**(*n*), were primarily characterized by their X-ray diffraction patterns shown in Fig. 1. The X-ray data indicate that alkylamines with $n \geqslant 4$ form one intercalated phase having an interlayer spacing longer than 15.4 Å for the host phase, whereas amines with $n = 2$ and 3 form a disordered or degraded product with nearly the same or decreased spacing. The interlayer spacings of the reaction products were determined from the first and/or second maximum *d* value in the X-ray diffraction patterns (Table 1). A plot of the interlayer spacing (*d*) against the number of CH_2 units (*n*) is shown in Fig. 3.

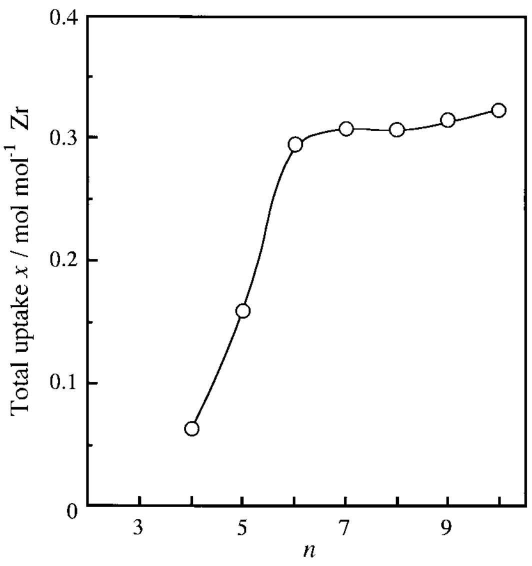

Fig. 5 Alkylamine uptake by compound **2** as a function of the carbon number of the alkyl chain

Table 1 Interlayer spacing and composition of the solids formed from γ-zirconium (2-carboxyethyl)phosphonate phosphate **2** and *n*-alkylmonoamines as a function of the carbon number, *n*

n	Interlayer spacing/Å	Composition, *x**
2	14.5	—
3	15.8	—
4	19.2	0.07
5	22.1	0.15
6	24.5	0.30
7	26.8	0.29
8	29.4	0.31
9	32.7	0.31
10	35.3	0.33

* *x* in $ZrPO_4(H_2PO_4)_{0.36}(HO_3PCH_2CH_2CO_2H\text{-}2)_{0.64}\cdot xC_nH_{2n+1}NH_2\cdot yH_2O$.

The thermogravimetric curves for the reaction solids **2**(*n*) indicated three or four steps over the temperature range 20–700 °C, as shown in Fig. 4. The first weight loss at below 100 °C is due to desorption of interlayer water. The weight losses at higher temperatures are primarily due to loss of the interlayer organic moiety and partly to condensation of the hydrogenphosphate groups. On heating at 1000 °C for 1 h the solids with $n = 2$ and 3 were totally converted into a mixture of ZrP_2O_7 and ZrO_2. This is consistent with the X-ray observations for both unpyrolysed solids indicating partial decomposition of the host phase with loss of phosphorus. The solids with $n \geqslant 4$, on the other hand, were totally converted into a single phase of ZrP_2O_7 by the same heat treatment. The amine contents of the solids were determined from a combination of the thermogravimetric data for these solids and for their host phase **2** (Table 1). The uptakes of amine in moles per mol of host are plotted against the number of CH_2 (*n*) in Fig. 5. The amine uptake increases with increasing carbon number to reach a constant value of $x = 0.32$ mol mol^{-1} for the amines with $n \geqslant 6$. The carbon-number dependence of amine uptake in the present system is in striking contrast to the extremely preferential uptake of heptylamine by α-zirconium (2-carboxyethyl)-phosphonate.[8]

The IR absorption spectra of the amine-intercalated solids are shown in Fig. 2(*a*). On addition of alkylmonoamine a new broad band near 1680 cm^{-1} due to the $CO_2^-NH_3^+$ group

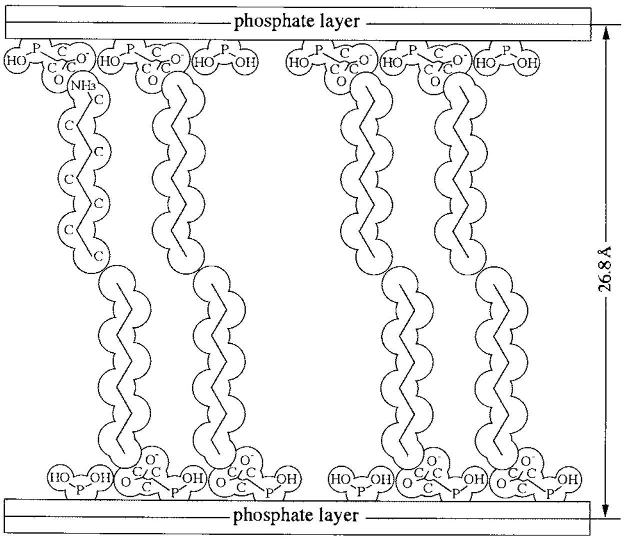

Fig. 6 Model for the arrangement of heptylammonium molecules in the interlayer space of compound **2**

appears along with the CH stretching band near 2900 cm^{-1}, while the absorption band near 1710 cm^{-1} attributable to the C=O stretching of the CO_2H group appreciably decreases in intensity; the sharp peak at 1380 cm^{-1} observed for all the samples is due to nitrate contaminants in KBr. This finding suggests that the intercalation of alkylmonoamine molecules takes place by a mode in which the ammoniated cations replace primarily the protons of the interlayer CO_2H groups to yield an ionically bonded $CO_2^-NH_3^+$ group. Quantitatively, 0.32 mol or more of CO_2H group per mol of the host phosphate would remain unchanged, as expected from the difference between the total amount of CO_2H group (0.64 mol) and the maximum amine uptake (0.32 mol). Thus the considerable decrease in intensity of the peak at 1710 cm^{-1} as a result of the amine intercalation might be attributable to a lowering of the structural order of the remaining CO_2H groups.

The d *vs.* n data for the fully loaded phases with $n = 6$–10 give a straight line with a slope of 2.6 Å per CH_2 and this value is in good agreement with twice the typical methylene repeat distance of 1.27 Å per CH_2 for an all-*trans* extended chain conformer or 2.54 Å per CH_2. The intercept of 9.2 Å for the straight line is close to 9.4 Å for the interlayer spacing of the anhydrous form of γ-zirconium phosphate. On the basis of the above X-ray, IR and analytical observations, we can propose a molecular packing model in which the intercalated alkylamine molecules having $n \geqslant 6$ are bonded through their ammonium termini to the ionized carboxyl groups to form a bilayer with their molecular axes perpendicular to the inorganic layer, as exemplified for the heptylammonium-exchanged solid in Fig. 6. It should be noted that the perpendicular arrangement of amine molecules in the present system is in striking contrast to the chain-tilt form observed for the alkylamine intercalates of α-carboxyethylated zirconium phosphonates[7b,8,9] and those of many other layered compounds including α-zirconium phosphate[21] and zirconium phosphate phosphite.[22] It is also likely that the amine guests with $n = 2$ and 3 cannot be stably held as a mono- or bi-layer, due to their short chain length.

Heating of the ammonium-exchanged solids at 220 °C for 0.5 h resulted in total conversion of the band at 1680 cm^{-1} due to the $CO_2^-NH_3^+$ group into so-called amide-I and -II bands at 1655 and 1560 cm^{-1}, respectively, as shown in Fig. 2(*b*). The IR observations indicate that the ionically bonded $CO_2^-NH_3^+$ group in the ammonium-exchanged solids is thermally condensed into the amide CONH form. This is consistent with the thermogravimetric observations for all the ammonium-exchanged solids indicating the second weight loss in the temperature range 100–250 °C. A similar thermal amidation was observed for the α-zirconium (2-carboxyethyl)phosphonate–alkyldiamine or –heptylamine systems, with an accompanying partial recovery of the initial CO_2H absorption band indicating partial deintercalation of the diamine or heptylamine guests.[8,9] In contrast, the thermal amidation in the present system occurred without an accompanying significant regeneration of the initial CO_2H band [Fig. 2(*b*)]. This means that the $CO_2^-NH_3^+$ groups formed in the present γ-phosphonate would be much more stably held than those in the α-phosphonate, leading to their full amidation without deintercalation of the intercalated amine molecules.

References

1 A. Clearfield, G. H. Nancollas and R. Blessing, *Ion Exchange and Solvent Extraction*, eds. J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, 1973, vol. 5, ch. 1.

2 G. Alberti, U. Costantino, S. Alluilli and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1113.

3 G. Alberti, U. Costantino and M. L. L. Giovagnotti, *J. Chromatogr.*, 1979, **180**, 45; G. Alberti, U. Costantino, J. Kornyei and M. L. L. Giovagnotti, *React. Polym.*, 1985, **4**, 1; L. Maya, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 297; M. B. Dines and P. M. Digiacomo, *Inorg. Chem.*, 1981, **20**, 92; P. M. Digiacomo and M. B. Dines, *Polyhedron*, 1982, **1**, 61; M. B. Dines, R. E. Cookey, P. C. Griffith and R. H. Lane, *Inorg. Chem.*, 1983, **22**, 1003.

4 G. Alberti, M. Casciola, U. Costantino and D. Fabarani, *Membranes and Membrane Processes*, eds. E. Drioli and M. Nakagaki, Plenum, New York, 1986; A. Clearfield, *Chem. Rev.*, 1988, **88**, 125.

5 G. Alberti, U. Costantino, M. Casciola and R. Vivani, *Solid State Ionics*, 1991, **46**, 61; M. Casciola, S. Chieli, U. Costantino and A. Peraio, *Solid State Ionics*, 1991, **46**, 53.

6 G. Alberti and U. Costantino, *J. Mol. Catal.*, 1994, **27**, 235; L. Vermeulen and M. E. Thompson, *Nature (London)*, 1992, **358**, 656.

7 D. A. Burwell and M. E. Thompson, *Chem. Mater.*, 1991, **3** (*a*) 14; (*b*) 730.

8 T. Kijima, Y. Kawgoe, E. Mihara and M. Machida, *J. Chem. Soc., Dalton Trans.*, 1993, 3827; T. Kijima, S. Watanabe and M. Machida, *Inorg. Chem.*, 1994, **33**, 2586.

9 T. Kijima, S. Watanabe, K. Ohe and M. Machida, *J. Chem. Soc., Chem. Commun.*, 1995, 75.

10 Y. Ding, D. J. Jones, P. Maireles-Torres and J. Roziere, *Chem. Mater.*, 1995, **7**, 562.

11 C. Kato, K. Kuroda and M. Misawa, *Clay Clay Miner.*, 1979, **27**, 129.

12 S. Yamanaka, *Inorg. Chem.*, 1976, **15**, 2811.

13 N. C. Clayden, *J. Chem. Soc., Dalton Trans.*, 1987, 1877; G. Alberti, M. G. Bernasconi and M. Casciola, *React. Polym.*, 1989, **11**, 245; A. Christensen, E. K. Andersen, I. G. K. Andersen, G. Alberti, N. Nielsen and M. S. Lehmann, *Acta Chem. Scand.*, 1990, **44**, 865; D. M. Poojary, B. Speizer and A. Clearfield, *J. Chem. Soc., Dalton Trans.*, 1995, 111.

14 G. Alberti, M. Casciola and R. Vivani, *Inorg. Chem.*, 1993, **32**, 4601.

15 (*a*) S. Yamanaka, Y. Horibe and M. Tanaka, *J. Inorg. Nucl. Chem.*, 1976, **38**, 323; (*b*) T. Kijima, *Thermochim. Acta*, 1982, **59**, 95.

16 T. Kijima, *Nippon Kagakukaishi*, 1986, 1145; U. Costantino, M. A. Massucci, A. L. Ginrsytra, A. M. Talora and L. Zampa, *J. Inclusion Phenom.*, 1986, **4**, 147.

17 T. Kijima, S. Ueno and M. Goto, *J. Chem. Soc., Dalton Trans.*, 1982, 2499; T. Kijima and S. Ueno, *J. Chem. Soc., Dalton Trans.*, 1986, 61.

18 T. Kijima and Y. Matsui, *Nature (London)*, 1986, **322**, 533; T. Kijima, *J. Chem. Soc., Dalton Trans.*, 1990, 425; 1992, 2877.

19 A. Clearfield, R. Blessing and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2249.

20 S. Yamanaka and M. Hattori, *Chem. Lett.*, 1979, 1073.

21 A. Clearfield and B. M. Tindwa, *J. Inorg. Nucl. Chem.*, 1979, **41**, 871.

22 G. Alberti, U. Costantino and F. Marmottini, *J. Inclusion Phenomen. Mol. Recogn.*, 1989, **7**, 549.

Received 25*th November* 1996; *Paper* 6/07975J