JOURNAL OF
Materials
CHEMISTRY

Hydrothermal synthesis and crystal structure of two novel aluminophosphites containing infinite Al–O–Al chains†

Niu Li and Shouhe Xiang*

Institute of Chemistry, University of Nankai, Tianjin 300071, P. R. China

Received 15th January 2002, Accepted 14th February 2002
First published as an Advance Article on the web 21st March 2002

Two novel aluminophosphites, $[NH_2(CH_2)_6NH_2][Al(OH)(H(HPO_3))_2]$ and $[Al(OH)(H(HPO_3))_2]\cdot 2H_2O$ (denoted as NKX-1 and NKX-4, respectively), with a molar ratio P : Al = 2, have been synthesized for the first time using a hydrothermal technique. Single crystals of these compounds have also been prepared. Structure refinement from single crystal X-ray diffraction data shows NKX-1 with composition $[NH_2(CH_2)_6NH_2][Al(OH)(H(HPO_3))_2]$ crystallizes in the monolinic space group *C*2/*c*, with $a = 29.123(17)$ Å, $b = 6.772(4)$ Å, $c = 6.851(4)$ Å, $V = 1349.3(14)$ Å^3, $Z = 4$, and NKX-4 with composition $[Al(OH)(H(HPO_3))_2]\cdot 2H_2O$ crystallizes in the orthorhombic space group *Cmma*, with $a = 6.949(2)$ Å, $b = 17.398(6)$ Å and $c = 7.903(3)$ Å, $V = 955.4(6)$ Å^3, $Z = 4$. Both compounds contain AlO_6 octahedra and HPO_2 (OH) tetrahedra in their structure. Each AlO_6 octahedron shares two hydroxide group corners with two adjacent AlO_6 octahedra to form infinite Al–O–Al chains.

1 Introduction

Since the 1980s, with the first report of the synthesis of microporous aluminophosphate ($AlPO_4$-*n*)[1,2] molecular sieves by using hydrothermal synthesis techniques, there has been a continuing growth in the number of aluminophosphates. $AlPO_4$-based molecular sieves have become comparable with silicate-based zeolites in their diversity of structure types. Recently, the synthesis of new Al–P-based materials such as aluminium phosphonates and aluminium diphosphonates has attracted considerable interest.[3–9] These materials have been synthesized by using phosphonic acid $[RPO(OH)_2]$ or diphosphonic acid $[(OH)_2OPRPO(OH)_2]$ (where R represents an organic group) as the source of phosphorus. They show a wide range of structural architectures including chain, layered and microporous structures. There are also a few reports describing the syntheses and structures of transition-metal phosphites.[10–14] Metal-phosphite contains the phosphite ion $(HPO_3)^{2-}$ rather than phosphate $(PO_4)^{3-}$ or phosphonate $(RPO_3)^{2-}$ in the structures. They are of interest because the phosphite ion, $(HPO_3)^{2-}$, is structurally similar to phosphate $[(PO_4)^{3-}]$, having a tetrahedral geometry. It might be anticipated that aluminophosphites would exhibit a similar structural chemistry, but with an important difference due to the smaller charge and smaller number of oxygens on the phosphite group. On the other hand, the terminal P–H groups may lead to materials in which the channels or cavities are lined by hydrogen, rather than oxygen as is found in zeolites and aluminophosphates.

Usually, most of the known metal-phosphite compounds have been prepared by various solvent-volatilizing methods.[13] Recently, Harrison *et al.* reported the hydrothermal synthesis of zinc phosphites.[15,16] In our present work, two novel aluminophosphites (denoted as NKX-1 and NKX-4) containing infinite Al–O–Al chains, being closely related to the tancoite structure, have been synthesized using a hydrothermal method and their crystal structures have been resolved.

2 Experimental section

2.1 Synthesis and initial characterization

Two compounds were synthesized under hydrothermal conditions. In a typical synthesis, 2.48 g of pseudoboehmite (water loss at 600 °C: 31.5 wt.%) were dispersed in a mixture containing 2.75 g H_3PO_3 and 29.2 g of water. Subsequently, 1.94 g of 1,6-hexamethylenediamine (HAD) were added to this solution to synthesize NKX-1. (As to the synthesis of NKX-4, in place of HAD, ammonia was added dropwise into the solution to adjust the pH value of the mixture to 9). The final mixture was stirred for 30 min, then transferred to a stainless steel autoclave and heated at 160 °C for 4 days. The gel composition for NKX-1 was $2.0\,Al(OH)_3 : ca.\ 2.0\text{–}3.0\,H_3PO_3 : 1.0\,HAD : 100\,H_2O$, and for NKX-4 was $2.0\,Al(OH)_3 : ca.\ 2.0\text{–}2.4\,H_3PO_3 : m\,NH_3\cdot H_2O : ca.\ 40\text{–}100\,H_2O$, where *m* is the amount of ammonia needed to adjust the solution pH to 7.5–9.5. The crystallization product was recovered and washed with distilled water, followed by centrifuging and drying at 80 °C. The initial characterization was carried out using powder X-ray diffraction (XRD). Infrared absorption spectra were obtained on a Bruker Vector 22 FTIR spectrometer (with KBr wafers).

2.2. Single-crystal structure analysis

A suitable single crystal of NKX-1 with dimensions 0.10 × 0.10 × 0.05 mm and of NKX-4 with dimensions 0.40 × 0.02 × 0.02 mm were carefully selected and glued to a thin glass fiber with superglue adhesive. The intensity data by X-ray diffraction were collected on a Bruker SMART 1000 CCD diffractometer equipped with a normal focus, 2.4-kW sealed-tube X-ray source using monochromated MoKα ($\lambda = 0.71073$ Å) radiation at a temperature of 25 °C. The final unit cell constants were determined by a least-squares fit of 2325 (NKX-1) and 1645 (NKX-4) reflections in θ ranges of 2.80–25.03° (NKX-1) and 3.48–25.01 (NKX-4). The lattice parameters are as follows: $[NH_2(CH_2)_6NH_2][Al(OH)(H(HPO_3))_2]$ crystallizes in the monolinic space group *C*2/*c*, with $a = 29.123(17)$ Å, $b = 6.772(4)$ Å and $c = 6.851(4)$ Å, $V = 1349.3(14)$ Å^3; and $[Al(OH)(H(HPO_3))_2]\cdot 2H_2O$ crystallizes in the orthorhombic space group *Cmma*, with $a = 6.949(2)$ Å, $b = 17.398(6)$ Å and

---

†Electronic supplementary information (ESI) available: XRD patterns and views of NKX-1 and NKX-4. See http://www.rsc.org/suppdata/jm/b2/b200507g/

DOI: 10.1039/b200507g

Table 1 Crystal data and structure refinement for NKX-1 and NKX-4

Identification code	NKX-1	NKX-4
Empirical formula	$C_6H_{21}AlN_2O_7P_2$	$AlP_2O_9H_9$
Formula weight	322.17	241.99
T/K	293(2)	298(2)
λ/Å	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$Cmma$
a/Å	29.123(17)	6.949(2)
b/Å	6.772(4)	17.398(6)
c/Å	6.851(4)	7.903(3)
α/°	90	90
β/°	92.991(1)	90
γ/°	90	90
V/Å^3	1349.3(14)	955.4(6)
Z	4	4
D_c/Mg m^{-3}	1.586	1.683
Absorption coefficient/mm^{-1}	0.414	0.578
F(000)	680	536
Crystal size/mm	0.10 × 0.10 × 0.05	0.40 × 0.02 × 0.02
θ Range for data collection/°	2.80–25.03	3.48–25.01
Limiting indices	$-34 \leqslant h \leqslant 34, -7 \leqslant k \leqslant 8, -8 \leqslant l \leqslant 4$	$-7 \leqslant h \leqslant 8, -20 \leqslant k \leqslant 20, -7 \leqslant l \leqslant 9$
Reflections collected/unique	2410/1085 ($R_{\text{int}} = 0.0607$)	1714/432 ($R_{\text{int}} = 0.0680$)
Completeness to $\theta = 25.03$ (%)	91.0	89.4
Refinement method	Full-matrix, least-squares on $\|F\|^2$	Full-matrix, least-squares on $\|F\|^2$
Data/restraints/parameters	1085/0/84	432/2/51
Goodness-of-fit on F^2	0.965	0.960
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0583$, $wR_2 = 0.1325$	$R_1 = 0.0397$, $wR_2 = 0.0850$
R indices (all data)	$R_1 = 0.0881$, $wR_2 = 0.1461$	$R_1 = 0.0626$, $wR_2 = 0.0918$
Largest diff. peak and hole/e Å^{-3}	0.990 and −0.389	0.336 and −0.409

$c = 7.903(3)$ Å, $V = 955.4(6)$ Å^3. A total of 2410 (1714 for NKX-4) reflections were collected, and these were merged to give 1085 (432) unique reflections [$R_{\text{merge}} = 0.0607$ (0.068)]. The structure was solved in the space group $C2/c$ (NKX-1) and $Cmma$ (NKX-4) by direct methods and refined on $|F|^2$ by full-matrix, least-squares using the SHELXTL97 program system.[17] The crystallographic data are summarized in Table 1.

CCDC reference numbers 181566 and 162456. See http://www.rsc.org/suppdata/jm/b2/b200507g/ for crystallographic data in CIF or other electronic format.

3 Results and discussion

The existence of template HAD (1,6-hexamethylenediamine) in the starting mixture has a great influence on the preparation of NKX-1 (Table 2). When the template is replaced by ammonia, NKX-4 is obtained as the pure product (Fig. 1) under the same conditions. Neither NKX-1 nor NKX-4 is obtained when the $H_3PO_3 : Al(OH)_3$ ratio is below 1. In general, NKX-1 has been prepared at an $H_3PO_3 : Al(OH)_3$ ratio range from 1 to 2. NKX-4 is synthesized in the $H_3PO_3 : Al(OH)_3$ ratio range from 1.0 to 1.5. With an increase of the water content, the crystallization time and reaction temperature decrease.

FTIR spectra of NKX-1 and NKX-4 in Fig. 2 show a strong vibration at about 2400 cm^{-1}. This frequency is characteristic of P–H stretching and indicates the existence of only one environment for the phosphite group.[10] Undergoing the hydrothermal synthesis procedure, P in NKX-1 and NKX-4 retains its P(III) oxidation state. The bands due to the PO_3 group or hydrogen bonded PO_3 group vibrations are seen in the region *ca.* 1000–1400 cm^{-1}.

Table 2 Synthesis conditions for NKX-1 and NKX-4

Run	$Al(OH)_3$	H_3PO_3	H_2O	HDA[a]	pH	T/°C	Time/d	Product
1	4.0	2.0	100	1.0	5	145	8	Unknown phase[d]
	2.0	4.0	100	1.0	4	145	3	NKX-1(p)
2	2.0	2.0	100	1.0	5	145	4	NKX-1[c](p)
3	2.0	2.0	200		6[b]	145	1	NKX-4(p)
4	2.0	2.0	100		9[b]	130	1	NKX-4[c](p)
5	2.0	3.0	50		9[b]	160	5	NKX-4(p)
6	1.54	2.0	45		9[b]	160	7	NKX-4(p)
7	3.0	2.0	45		9[b]	160	15	Gel

[a] 1,6-Hexamethylenediamine. [b] Adjusted with ammonia. [c] Single crystal. [d] XRD patterns in the ESI†; p = pure phase.

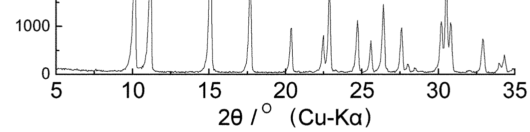

Fig. 1 XRD patterns of as-synthesized NKX-1 and NKX-4.

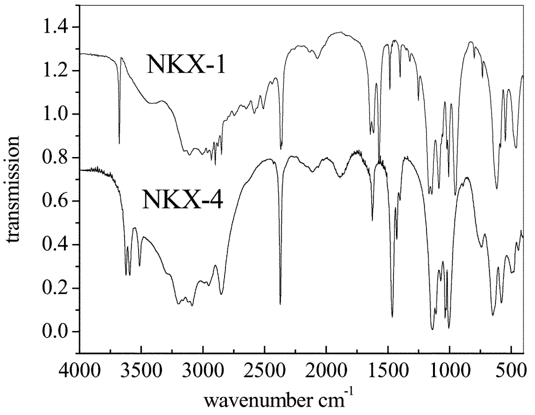

Fig. 2 IR spectra of NKX-1 and NKX-4.

Table 3 Selected bond lengths (Å) and angles (°) for NKX-1 and NKX-4

NKX-1		NKX-4	
P(1)–O(3)	1.485(4)	P(1)–O(3)	1.496(4)
P(1)–O(2)	1.512(3)	P(1)–O(1)#1	1.520(2)
P(1)–O(4)	1.521(3)	P(1)–O(1)	1.520(2)
Al(1)–O(1)	1.868(2)	Al(1)–O(2)	1.879(2)
Al(1)–O(2)	1.879(3)	Al(1)–O(1)#2	1.912(2)
Al(1)–O(4)#2	1.925(3)	Al(1)–O(1)	1.912(2)
O(1)–Al(1)#3	1.868(2)	O(2)–Al(1)#5	1.879(2)
O(4)–Al(1)#3	1.925(3)		
		O(3)–P(1)–O(1)#1	112.26(13)
O(3)–P(1)–O(2)	114.1(2)	O(3)–P(1)–O(1)	112.26(13)
O(3)–P(1)–O(4)	112.74(19)	O(1)#3–Al(1)–O(1)	90.47(15)
O(2)–P(1)–O(4)	110.90(19)	O(1)#1–P(1)–O(1)	111.43(19)
O(1)–Al(1)–O(1)#1	180.0	O(2)–Al(1)–O(1)#2	91.17(12)
O(1)–Al(1)–O(2)	91.15(14)	O(2)–Al(1)–O(1)#3	91.17(12)
O(1)–Al(1)–O(2)#1	88.85(14)	O(1)#2–Al(1)–O(1)#3	89.53(15)
O(2)–Al(1)–O(2)#1	180.0(2)	O(2)–Al(1)–O(1)	88.83(12)
O(1)–Al(1)–O(4)#2	89.55(12)	O(2)#2–Al(1)–O(1)	91.17(12)
O(1)#1–Al(1)–O(4)#2	90.45(12	O(1)#2–Al(1)–O(1)	180.00(9)
O(2)–Al(1)–O(4)#2	88.24(16)	O(2)–Al(1)–O(2)#2	180.0
O(2)#1–Al(1)–O(4)#2	91.76(16)	O(2)#2–Al(1)–O(1)#4	91.17(12)
O(1)–Al(1)–O(4)#3	90.45(12)	O(1)#2–Al(1)–O(1)#4	90.47(15)
O(4)#2–Al(1)–O(4)#3	180.000(1)	O(1)#3–Al(1)–O(1)#4	180.00(9)
Al(1)–O(1)–Al(1)#3	132.9(3)	O(1)–Al(1)–O(1)#4	89.53(15)
P(1)–O(2)–Al(1)	141.4(2)	P(1)–O(1)–Al(1)	128.64(16)
P(1)–O(4)–Al(1)#3	127.8(2)	Al(1)–O(2)–Al(1)#5	135.1(3)

Symmetry transformations used to generate equivalent atoms. NKX-1: #1 $-x + 1, -y + 1, -z + 1$; #2 $x, -y + 1, z - 1/2$; #3 $-x + 1, y, -z + 3/2$; #4 $-x + 1/2, -y + 1/2, -z$. NKX-4: #1 $-x, y, z$; #2 $-x + 1/2, -y + 1/2, -z$; #3 $-x + 1/2, y + 0, -z$; #4 $x, -y + 1/2, z$; #5 $-x + 1, -y + 1/2, z$; #6 $-x, -y + 3/2, z$; #7 $-x + 1/2, -y + 3/2, -z + 1$.

The atomic coordinates and selected bond lengths and angle data of NKX-1 are listed in the single crystal data (Tables 3 and 4). Each Al atom is six coordinated as shown in Fig. 3. Four of the oxygens bound to aluminium originate from four different phosphite groups, the bond lengths for Al–O2 and Al–O4 are 1.879 and 1.925 Å, respectively. The other two oxygens are from two opposite Al–O1–Al bridges with an Al–O1 bond length of 1.868 Å. Each AlO_6 octahedron shares two opposite hydroxy groups[18] with two adjacent AlO_6 octahedra to construct an infinite Al–O–Al chain running along the [100] direction. There is only one type of phosphite group in the structure. The P atom shares its two corners (P–O2 = 1.512 Å, P–O4 = 1.521 Å) with two adjacent AlO_6 octahedra in the Al–O–Al chain. There are also two terminal corners in each HPO_3 tetrahedron. The existence of P–H can be confirmed from the IR-spectra in Fig. 2. Another terminal corner is the P–O3 with a bond length of 1.496(4) Å. The HPO_3 tetrahedra cross – likely coordinating around the Al–O–Al chains (Fig. 3). The unit-cell structure (Fig. 4) displays a clear image of NKX-1. Aluminophosphite chains arrayed along [100] and stretched along the [001] directions assemble a net-like structure by the interactions of hydrogen bonds among the NH_2 groups and O2, O4 and O3 atoms of the aluminophosphite chains.

Table 4 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for NKX-1 and NKX-4

	x	y	z	U_{eq}
NKX-1				
P(1)	4386(1)	2122(2)	7502(2)	18(1)
Al(1)	5000	5000	5000	12(1)
O(1)	5000	6102(7)	7500	18(1)
O(2)	4611(1)	2946(5)	5738(4)	28(1)
O(4)	4459(1)	3488(5)	9253(4)	29(1)
O(3)	3896(1)	1562(5)	7125(5)	28(1)
N(1)	3913(1)	2508(6)	2472(6)	24(1)
C(1)	3439(2)	3301(9)	2463(9)	34(1)
C(3)	2651(2)	3016(9)	771(9)	40(1)
C(2)	3141(2)	2235(9)	907(8)	35(1)
NKX-4				
P(1)	0	3765(1)	1664(2)	14(1)
Al(1)	2500	2500	0	11(1)
O(1)	1807(3)	3274(1)	1606(3)	20(1)
O(2)	5000	2500	907(6)	14(1)
O(3)	0	4308(2)	3132(5)	21(1)
O(4)	0	5901(2)	3377(7)	41(1)
O(5)	1244(12)	7500	4707(11)	39(2)

The atomic coordinates and selected bond length and angle data of NKX-4 are also listed in Tables 3 and 4. The inorganic part of the symmetric unit of NKX-4 is just the same as that of NKX-1 (Fig. 3), composed of HPO_3 tetrahedra and AlO_6 octahedra. With respect to the crystallographic axis, examination of the lattice parameters reveals that there exists a close structural similarity between NKX-4 and NKX-1. In the structure of NKX-4, each AlO_6 octahedron shares two opposite hydroxy group corners (Al–O2 bond length 1.879 Å) with two adjacent AlO_6 octahedra to form infinite chains, with HPO_3 tetrahedra coordinated around with them. There are four chains per unit-cell. Each chain bonds with four other chains through hydrogen bonds (Fig. 5). There are water

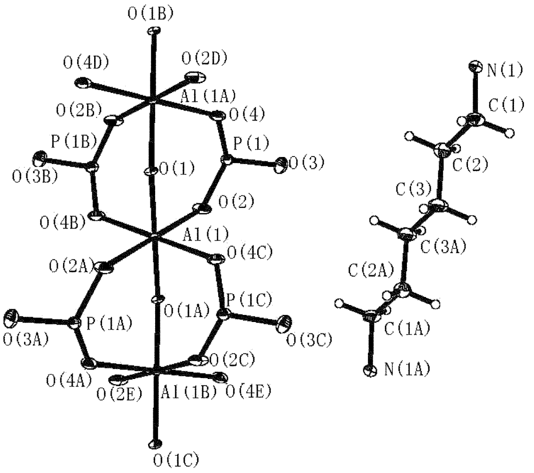

Fig. 3 Bonding environment of the Al and P atoms in NKX-1.

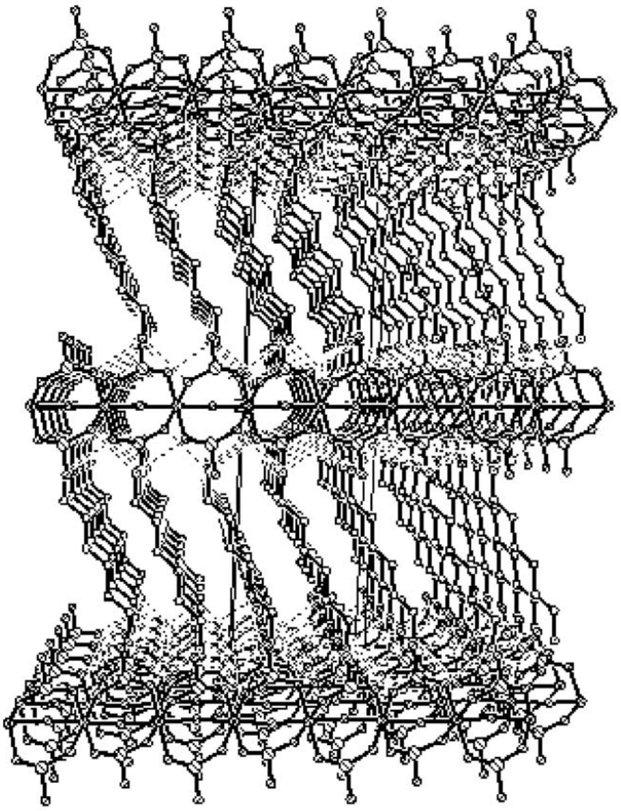

Fig. 4 View of NKX-1 along [010] showing the net-like layer.

molecules (O4, O5) encapsulated in the space formed by two adjacent chains along the [001] direction.

The structure of NKX-4 collapsed after it was heated in air at 200 °C for two hours. When calcined in air at 550 °C for two hours, both NKX-1 and NKX-4 transformed to dense aluminophosphate (the XRD patterns of the result can be seen in the supplementary information†).

Acknowledgements

We thank the National Natural Science Foundation of China (Grant No. 29733070) and China Petroleum & Chemical Corporation (X501024) for financial support. Also we thank Engineers H.G. Wang and X.H. Zhou for their assistance in obtaining single crystal X-ray diffraction data and powder X-ray diffraction patterns, respectively.

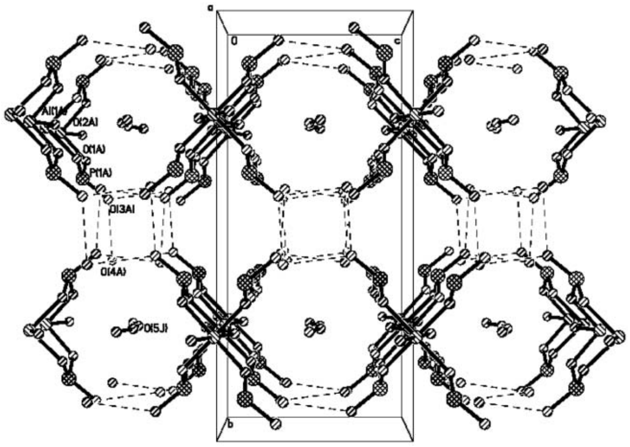

Fig. 5 Cell structure of NKX-4. Al (⊘), P (⊗) and O atoms (⦸).

References

1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.

2 B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan and M. Flanigen Edith, *J. Am. Chem. Soc.*, 1984, **106**, 6092.

3 G. B. Hix, V. J. Carter, D. S. Wragg, R. E. Morris and P. A. Wright, *J. Mater. Chem.*, 1999, **9**, 179.

4 H. G. Harvey, S. J. Teat and M. P. Attfield, *J. Mater. Chem*, 2000, **10**, 2632.

5 V. J. Carter, P. A. Wright, J. D. Gale, R. E. Morris, E. Sastre and J. Perez-Pariente, *J. Mater. Chem.*, 1997, **7**, 2287.

6 K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, *J. Chem. Soc., Chem.Commun.*, 1995, 1033.

7 K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, *Stud. Surf. Sci. Catal.*, 1997, **105**, 197.

8 K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2335.

9 K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1199.

10 D. M. Poojary, Y. Zhang, D. E. Cox, P. R. Rudolf, S. Cheng and A. Clearfield, *J. Chem. Crystallogr.*, 1994, **24**, 155.

11 R. E. Morris, W. T. A. Harrison, J. M. Nicol, A. P. Wilkinson and A. K. Cheetham, *Nature*, 1992, **359**, 519.

12 C. Y. Ortiz-Avila, P. J. Squattrito, M. Shieh and A. Clearfield, *Inorg. Chem.*, 1989, **28**, 2608.

13 Y. P. Zhang, H. L. Hu and A. Clearfield, *Inorg. Chim. Acta*, 1992, **193**, 35.

14 M. H. Shieh, K. J. Martin, P. J. Squattrito and A. Clearfield, *Inorg. Chem.*, 1990, **29**, 958.

15 W. T. A. Harrison, M. L. F. Phillips and T. M. Nenoff, *J. Chem. Soc., Dalton Trans.*, 2001, 2459.

16 J. A. Rodgers and W. T. A. Harrison, *Chem. Commun.*, 2000, 2385.

17 G. M. Sheldrick, SHELXL97, University of Gottingen, Germany, 1997.

18 J. B. Parise, *J. Chem. Soc., Chem. Commun.*, 1985, 606.