Journal of Solid State Chemistry **165**, 209–213 (2002)
doi:10.1006/jssc.2001.9489, available online at http://www/idealibrary.com on IDEAL®

Hydrothermal Synthesis and Crystal Structure of the First Ammonium Indium(III) Phosphate $NH_4In(OH)PO_4$ with Spiral Chains of $InO_4(OH)_2$

S.-Y. Mao, M.-R. Li, Y.-X. Huang, J.-X. Mi, H.-H. Chen, Z.-B. Wei, and J.-T. Zhao[1]

Department of Chemistry and Department of Materials Science, Xiamen University, Xiamen 361005, People's Republic of China
E-mail: itzhao@mail.sic.ac.cn

Received July 18, 2001; in revised form November 27, 2001; accepted December 21, 2001; published online March 27, 2002

An ammonium indium hydrogen phosphate, $NH_4In(OH)PO_4$, was synthesized under mild hydrothermal conditions, and the crystal structure was characterized by single-crystal X-ray diffraction method. The compound crystallizes with the $RbIn(OH)PO_4$ type with the following data: $M_r = 244.84$, tetragonal, $tP104$, $P4_32_12$ (No.96), $a = 9.416(2)$ Å, $c = 11.159(3)$ Å, $V = 989.9(3)$ Å^3, $Z = 8$, $D_x = 3.288\ \mathrm{g\,cm^{-3}}$, $\lambda = 0.71073$ Å, $\mu = 50.34\ \mathrm{cm^{-1}}$, $F(000) = 928$, $T = 293$ K, $R1 = 0.0606$, $wR2 = 0.1472$ for 91 variables and 1813 contributing unique reflections. The structure is characterized by chiral $InO_4(OH)_2$ chains along the *c* axis formed by sharing OH corners. The chains are isolated by PO_4 tetrahedra leading to a three-dimensional framework structure with channels occupied by NH_4^+ ions. The framework structure is similar to that of $KIn(OH)PO_4$ and γ-$NaTiOPO_4$. The hydrogen bonds formed by NH_4^+ with the polyhedral oxygen atoms play an important role in the anisotropic changes of the lattice with respect to its alkali metal analogues. The topological construction of the title structure can be considered as an augmented 4,6-net with larger porosity. © 2002 Elsevier Science (USA)

Key Words: **ammonium indium hydrogen phosphate; hydrothermal synthesis; crystal structure.**

INTRODUCTION

Metal phosphates with open-framework structure are of great interest to materials scientists as well as to chemists due to their diverse industrial uses and rich structural chemistry. Besides the conventional transition metals the main group element incorporations into the frameworks of these materials have been widely explored in recent years with success (1). The majority of the new microporous compounds has been synthesized in the presence of an organic template molecule, and in many cases the removal of the organic template molecule lead to the collapse of the structure during calcination. Furthermore the organic template molecules are often costly. Therefore it has great practical importance to synthesize those materials that only involve inexpensive and easy-to-remove species, such as alkali metal cations. Among the main group element systems, indium represents an interesting case since only octahedral coordination is expected. The increasing number of reports on the indium phosphate shows the richness of these systems in the senses of both structural chemistry and physical properties (2–19). Most of the compounds reported have been synthesized by either hydrothermal or solid reactions with alkali metal or alkaline earth metal as counter cation or organic molecule as templates. Surprisingly there has been ammonium-containing compounds reported until now albeit its similarity to the alkali cations. In many cases, the organic bases (in most cases some form of an organic amine) were added as templates. The porous architecture will be built around them and the final structure of the inorganic framework depends, in most cases, on the size and shape of the amine molecules added. It shows that the hydrogen-bonded interactions between the inorganic and organic moieties are very important in directing the crystallization of the inorganic framework through multipoint hydrogen bonding. The ammonium cation, which is expected to exhibit similar features, is also an obvious choice as template (20). Here we report our synthesis and characterizations of the first ammonium indium(III) phosphate with spiral chains synthesized by mild hydrothermal methods, i.e., with lower temperature and pressure.

EXPERIMENTAL

Synthesis

A sample of the title compound was synthesized as a by-product during our systematic investigations on the main group metal borophosphates by mild hydrothermal method. Starting materials were of analytical grade and used

---

[1] To whom correspondence should be addressed. Fax: +49-351-46463002.

without further purification. A mixture of 0.155 g of H_3BO_3, 1 mL of H_3PO_4, 1 mL of 38% NH_3 aqua solution, and 0.115 g of indium metal dissolved in 1 mL of 18% HCl (molar ratio of In : B : P = 1 : 2.5 : 8) was added to 1.0 mL of distilled water. The mixture was sealed in glass tubes of about 20 cm in length. The filling of the solution was about 30% of the tube volume. The glass tubes were placed in an oven and the temperature was increased slowly to 135°C and reacted for 10 days before cooling to room temperature. The reaction was under the autogeneous pressure. The colorless ball-shaped crystals were grown from the solution in the glass tube and easily separated from the borophosphate $NH_4In[BP_2O_8(OH)]$ (21). The morphology of the compound was not observed for other compounds and no reasonable explanation can be given. The synthesis is reproducible under similar reaction conditions. The elemental analysis by EDX of the selected crystals shows the atomic ratio of In and P being 1 : 1, and ICP-MS analysis gives the In : P : B atomic ratio of 1 : 1.1 : 0.04, which shows the nonexistence of boron in the structure. The traces of boron may just come from the boron source residues absorbed on the crystal surfaces.

Structure Determination

A single crystal with ball-shape (radius about 0.30 mm) was mounted on an Enraf-Nonius CAD4 automatic four-circle diffractometer, Mo$K\alpha$ radiation with graphite monochromator. Crystallographic data for the title compound are summarized in Table 1. The unit cell parameters were refined from 2θ values of 25 randomly located reflections (Mo$K\alpha$, $\lambda = 0.71073$ Å, $30° < 2\theta < 35°$). A total of 2164 reflections were collected out to $(\sin \theta/\lambda) = 0.700$ ($-15 \leq h \leq 0$, $-15 \leq k \leq 0$, $-17 \leq l \leq 0$) in the ω–2θ scan mode, yielding 1813 unique observed reflections. Two standard reflections 6 1 −6 and 4 2 −7 were measured 12 times with maximum variations of less than 0.1%, showing no detectable decay during the data collection. The intensity data were corrected for Lorentz and polarization effects, and absorption correction was made according to eight Ψ-scan reflections. The anomalous-dispersion coefficients were taken into account in the data processing. From the systematic absences of the reflections, the following space groups are possible: $P4_12_12$ and $P4_32_12$ ("International Tables for Crystallography," Vol. A, 1983). The $P4_12_12$ was initially chosen and the basic structure model was obtained using the SDP program package (22). The subsequent refinement led to the negative unity Flack parameter, which indicates the correct space group should be its enantiomorphic one, $P4_32_12$. The final space group and the structure was confirmed by the full-matrix least-squares structure refinement, based on F^2 values using the program package SHELXL-97 (23). The nonhydrogen atoms were located by direct method, and the remaining atoms were found from the successive difference Fourier maps. A total of 91 variables including anisotropic displacement parameters for nonhydrogen atoms were refined to $R1 = 0.0606$ and $wR2 = 0.1472$ [$w = 1/\sigma^2(|F|)$, $S = 1.029$] considering 1813 contributing unique reflections

TABLE 1
Crystallographic Data for $NH_4In(OH)PO_4$

Formula	$NH_4In(OH)PO_4$
Formula weight (g/mol)	244.84
Space group	$P4_32_12$ (No. 96)
Z	8
a (Å)	9.416(2)
c (Å)	11.159(3)
V (Å^3)	989.3(4)
D_x (gcm^{-3})	3.288
Linear absorption coefficient μ (cm^{-1})	50.34
Temperature (K)	293(2)
Radiation, monochromator	Mo$K\alpha$, graphite
Crystal shape, color	Ball, colorless
2θ range (°)	5.66–69.86
Total number of observed reflections	2164
Number of unique reflections	1813
hkl range	$-15 \leq h \leq 0$, $-15 \leq k \leq 0$, $-17 \leq l \leq 0$
Number of parameters	91
$F(000)$	928
$^aR1$, $^bwR2$ ($I > 2\sigma(I)$)	0.0606, 0.1472
$^aR1$, $^bwR2$ (all data)	0.0773, 0.1571
GooF	1.029
Residual peaks (hole) (eÅ^3)	+3.85(−2.50)
Software	SHELXL-97

[a] $R1 = \sum||F_o|-|F_c||/\sum|F_o|$.

[b] $wR2 = \{\sum w((F_o)^2-(F_c)^2)^2]/\sum w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$.

TABLE 2
Atomic Positional and Displacement Parameters for $NH_4In(OH)PO_4$ with Space Group $P4_32_12$

Atom	WP[a]	x	y	z	U_{eq}(100 Å^2)[b]
In1	4a	0.09939(5)	0.09939(5)	0	0.974(16)
In2	4a	0.34691(5)	0.34691(5)	−0.5	1.004(16)
P3	8b	0.1639(2)	0.3104(2)	−0.2447(2)	0.92(3)
O1	8b	0.2266(7)	0.2481(7)	−0.3606(6)	1.46(12)
O2	8b	0.5028(6)	0.1771(6)	−0.4941(7)	1.43(11)
O3	8b	0.2045(9)	0.2116(6)	−0.1413(6)	1.71(11)
O4	8b	−0.0431(7)	0.2753(6)	0.0325(6)	1.58(12)
O5	8b	−0.0456(8)	0.0203(10)	−0.1243(6)	2.03(13)
N1	8b	0.1648(17)	0.4837(9)	0.0437(10)	4.0(3)
H1	8b	0.219(12)	0.483(14)	−0.014(9)	4.8[c]
H2	8b	−0.10(2)	−0.04(2)	−0.118(14)	6.0[c]
H3	8b	0.167(15)	0.407(9)	0.077(11)	4.8[c]
H4	8b	0.084(9)	0.499(15)	0.020(12)	4.8[c]
H5	8b	0.189(14)	0.546(11)	0.091(10)	4.8[c]

[a] Wyckoff positions.

[b] U_{eq} were defined as one-third of the trace of the orthogonal U_{ij} tensor.

[c] The atomic positional and displacement parameters for the H atoms are fixed in the refinements.

TABLE 3

Selected Important Interatomic Distances (Å), Angles, and Bond Valence Sums (Σs) for $NH_4In(OH)PO_4$ with Space Group $P4_32_12$

NH4–O9 polyhedra,	$\Sigma s(NH_4–O) = 1.18$		
NH4–O4	2.774(7)	–O5	3.266(7)
–O1	2.793(6)	–O2	3.269(6)
–O3	2.879(6)	–O3	3.322(6)
–O4	2.980(7)	–O2	3.534(7)
–O3	3.002(6)		
InO6 octahedra,	Σs(In1–O) = 3.26		
In1–O5 (2 ×)	2.084(7)	< O4–In1–O4	168.2(4)
–O3 (2 ×)	2.141(6)	< O5–In1–O3(2 ×)	168.2(3)
–O4 (2 ×)	2.162(6)	< In2–In1–In2	138.0(4)
InO6 octahedra,	Σs(In2–O) = 3.09		
In2–O5 (2 ×)	2.134(7)	< O2–In2–O2	175.1(3)
–O1 (2 ×)	2.137(6)	< O5–In2–O1(2 ×)	169.9(9)
–O2 (2 ×)	2.171(6)	< In1–In2–In1	113.1(4)
PO4 tetrahedra,	Σs(P–O) = 4.89		
P1–O4	1.524(7)	– O3	1.530(7)
–O2	1.527(6)	– O1	1.539(7)
		< In1–P–In2	65.2(5)
Possible hydrogen bonds			
N1···O4	2.980	< N1–H1···O4	142.42
N1···O3	3.002	< N1–H1···O3	120.47
N1···O3	2.879	< N1–H3···O3	167.80
N1···O4	2.774	< N1–H3···O4	110.16
N1···O2	3.269	< N1–H4···O2	163.60
N1···O1	2.793	< N1–H5···O1	146.04
N1···O5	3.266	< N1–H3···O5	108.6
N1···O3	3.322	< N1–H1···O3	146.5
N1···O2	3.534	< N1 – H5···O2	117.7
O5···O1	3.011	< O5 – H2···O1	168.86

with $I > 2\sigma(I)$ ($R1 = 0.0773$, $wR2 = 0.1571$ for all data). The maximum shift/e.s.d. in the last cycle was 0.006. The final residual electron density was $+3.83(-2.50)\,e\text{Å}^{-3}$; all are very close to the In positions (0.69 Å from In(1) and 0.87 Å from In(1), respectively). The atomic positional and displacement parameters are given in Table 2 and the selected important interatomic distances and bond angles in Table 3.

RESULTS AND DISCUSSION

Structure Description

Two compounds with the same stoichiometry but with two different structure types have been reported (6,9), with the Rb compound possessing the tetragonal structure while the K compound has the orthorhombic symmetry. The title compound is isotypic of the former type.

The coordination tetrahedra around the P atoms in the title compound are quite regular with an average interatomic distance of 1.530 Å. The average bond angle is 109.5° (range from 107.8° to 111.6°). All the average P–O bond distances and bond angles are consistent with those typical values observed in phosphates. On the basis of bond strength calculations (24), the bond valence sums for P atoms are all close to + 5 and listed in Table 3. The coordination environments around the P and In atoms are shown in Fig. 1.

The coordination environments around the ammonium cations are shown in Fig. 2. The coordination number of each NH_4^+ cation was determined on the basis of the clear coordination gap (3.534 to 3.960 Å) in the N–O distance distribution histogram. The NH_4^+ cation has a clear separation of inner and outer coordination sphere. The inner coordination sphere consists of five oxygen atoms (distance ranging from 2.774 to 3.002 Å), the outer shell four oxygen atoms (distances ranging from 3.266 to 3.534 Å). Therefore, the ammonium cation is coordinated by nine oxygen atoms. The N–H···O bond angles from the inner circle range from 110.16° to 167.8°, and the N–O distances range from 2.774 to 3.002 Å, which are normal, or slightly larger than, values for hydrogen bonds. These can be reasonably considered as hydrogen bonds. The outer circle with longer distances may also form hydrogen bonds due to their appropriate angles (ranging from 108.6 to 163.6), although no direct evidence has been observed. The relatively stronger hydrogen bonds have been arranged in such a way that four have larger contributions along the *c* direction and two with larger contributions on the *ab* plane. This might be the reason for the anisotropic changes of the lattice parameters by comparing with the K and Rb compounds; i.e., *c* is smaller than that of both K and Rb while *a* is larger than that of the K and Rb compounds. The larger volume for the NH_4 than for the Rb compound may indicate some effect comes from the high-pressure synthesis of the Rb compound. As expected, the

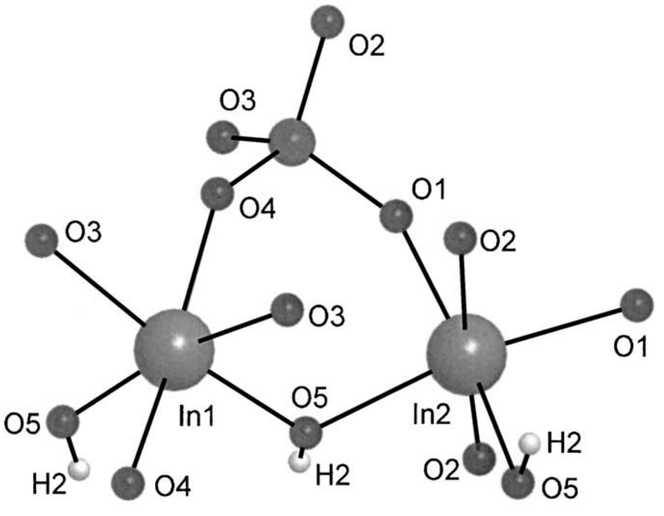

FIG. 1. Coordination environments of the In(1), In(2), and P atoms.

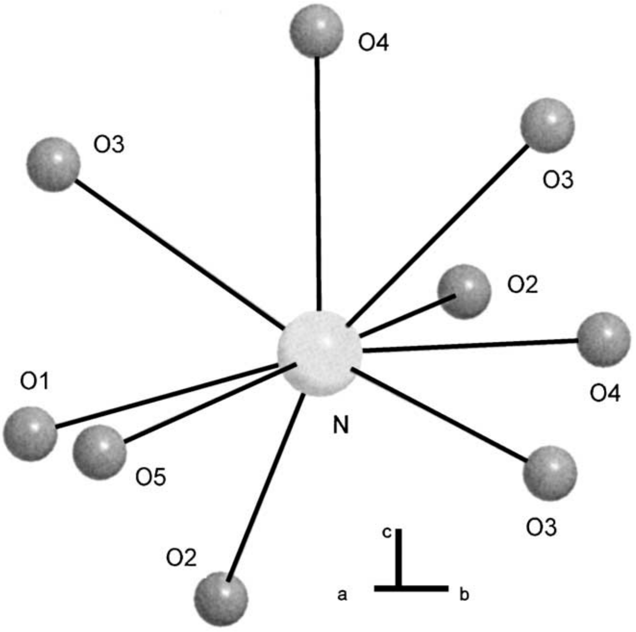

FIG. 2. The coordination environments of the ammonium cation in $NH_4In(OH)PO_4$.

ammonium compound is similar to the Rb compound by considering that they have the same type while the K compound possesses a lower symmetry modification, although the structural features for these three compounds are the same. It is also very clear that the hydrogen-bond effects introduced by ammonium ion are very well pronounced in the title compound. The obtaining of the new compound under very mild reaction conditions rather than under the high-temperature and high-pressure synthetic conditions used for the Rb and K compounds may also indicate the higher flexibility of the ammonium cation by considering its higher possibility of anisotropic deformation. The bond valence parameter of the NH_4^+ ion was not given in the reference. The parameter of Rb^+ ion, 2.26 Å, was used as an approximation by considering that the radius of NH_4^+ and that of Rb^+ are claimed to have the same value of 1.48 Å (25). The calculated bond valence sum for NH_4^+–O is very close to unity, which indicates the reasonable choice of the bond valence parameter. The coordination environment for the NH_4^+ cation is so asymmetric that no easy polyhedral descriptions could be rationalized.

The indium atoms occupying two special positions have octahedral coordination, as expected, with some deformation, as shown in Fig. 1. For $In(1)O_6$, the In–O bond distances range from 2.084 to 2.162 Å with an average value of 2.129 Å. For $In(2)O_6$, the In–O bond distances range from 2.134 to 2.171 Å with an average value of 2.147 Å. Both average In–O bond distances are close to the single bond value of 2.150 Å (21) and also close to values observed in its alkali metal Rb and K analogues, e.g., the corresponding two In–O distances are 2.133, 2.158 Å and 2.129, 2.144 Å, respectively. All these corresponding values for the three compounds should be considered as no different by considering the errors. The difference between In(1)–O and In(2)–O is 0.50 Å, which is even smaller than that in the Rb compound of 0.59 Å. The average difference in the K compound is 0.43 Å, which did not lead to a second harmonic generation (SHG) effect. The ammonium compound is not expected to show considerable SHG effect larger than that of the Rb compound if we consider only the possible polarization of the In octahedral chain. The observable difference between this compound and the Rb compound may be seen from the bond angles. The *cis* ∠ O–In(1)–O bond angles range from 80.1° to 99.7° for the ammonium compound, which is comparable with those of the Rb compound of 80.4° to 99.8°. The three *trans* ∠ O – In(1) – O angles along the pseudo-tetragonal axis have a value of 168.2° while the corresponding angles in the Rb compound are 169.9°, 169.9°, and 165.1°. The *cis* ∠O–In(2)–O bond angles range from 82.9° to 97.5° compared to the values of 82.0° to 100.8° for the Rb compound. The *trans* ∠ O–In(2)–O angles of 169.9°, 169.9°, and 175.1° are also larger than the corresponding values of 167.7°, 167.7°, and 171.4° for the Rb phase. From the above observations, one might conclude that the degree of irregularity of the InO_6 octahedra in the ammonium compound is smaller than that in the Rb compound. The bond valence sum calculations show both indium atoms are trivalent, although the values obtained are slightly larger than 3, which is also observed in other indium phosphate structures. The calculated valence sums are listed in Table 3.

A polyhedral representation of the $NH_4In(OH)PO_4$ structure along the [110] direction is shown in Fig. 3. From the figure, one can see the corner-sharing $In_4(OH)_2$ octahedra chains are well isolated by PO_4 groups. This arrangement led to corrugated channels along the *c* axis, also seen in Fig. 4, in which NH_4^+ cations reside. The hydroxyl hydrogen atoms are pointed into the channels. From the O5···O1 distance of 3.011 Å and <O5–H2···O1 of 168.9°, one may conclude that the hydroxyl hydrogen participated in the hydrogen bond. The framework of the structure is, as pointed out in (9), essentially the same as that of γ-$NaTiOPO_4$ (26). The major difference is the positions of the alkali metal or ammonium ions.

The topology of the connection, shown in Fig. 4, of the $InO_4(OH)_2$ and PO_4 groups forms a 4,6-net, the resemblance of which to other simple structures has not been identified. It should be noted that the motifs in Fig. 4 represent both the $InO_4(OH)_2$ and PO_4 groups instead of a single atom. Because of the corner-sharing octahedra, it is obviously different from another 4,6-net, $Na_2In_2[PO_3(OH)]_4 \cdot H_2O$, which contains only isolated InO_6

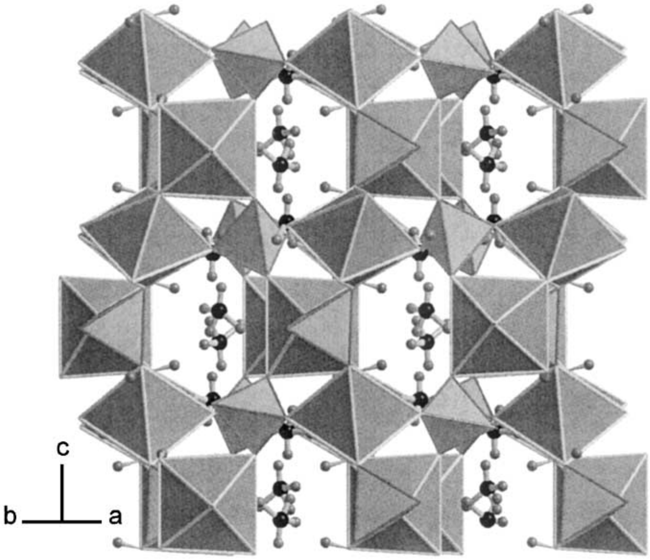

FIG. 3. Polyhedral representation of the $NH_4In(OH)PO_4$ structure along the [110] direction, showing $InO_4(OH)_2$ chiral chains and channels with ammonium cations.

octahedra and PO_4 tetrahedra with an augmented corundum form of Al_2O_3 topology (19). The augmentation of the 4,6-net in the structure led to the formation of channels in which the ammonium cations reside. The methods of producing open-framework structures by decoration and expansion of simple networks have drawn much attention recently (27).

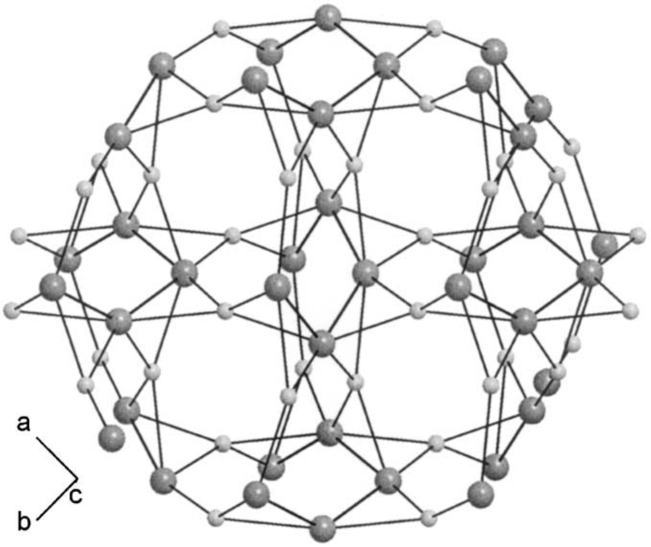

FIG. 4. Topological connectivity of $NH_4In(OH)PO_4$ with a 4,6-net; large and small balls represent the $InO_4(OH)_2$ and PO_4 groups, respectively.

ACKNOWLEDGMENTS

This study was supported by the National Science Fund for Distinguished Young Scholars from the NNSF of China, the Fund for University Key Teachers from MOE of China, the NSF of Fujian province, and the fund from the State Key Laboratory for Materials Synthesis and Processing at Wuhan University. J.T.Z. is indebted to the technical support of graph-making, word-processing, printing, and copying provided by the MPI-CPfS at Dresden.

REFERENCES

1. A. K. Cheetham, G. Férey, and T. Loiseau, *Angew. Chem. Int. Ed.* **38,** 3269 (1999).
2. E. A. Genkina, L. A. Muradyan, B. A. Maksimov, B. V. Merinov, and S. E. Sigarev, *Kristallografiya* **32,** 74 (1987).
3. T. Q. Duc, S. Hamdoune, and Y. Le Page, *Acta Crystallogr. Sect. C* **43,** 201 (1987).
4. D. Antenucci, G. Miehe, P. Tarte, W. W. Schmahl, and A.-M. Fransolet, *Eur. J. Miner.* **5,** 207 (1993).
5. S. S. Dhingra and R. C. Haushalter, *J. Solid State Chem.* **112,** 96 (1994).
6. K.-H. Lii, *J. Chem. Soc. Dalton Trans.* 815 (1996).
7. K.-H. Lii, *Eur. J. Solid State Inorg. Chem.* **33,** 519 (1996).
8. M. G. Zhizhin, V. A. Morozov, A. P. Bobylev, A. M. Popov, F. M. Spiridonov, L. N. Komissarova, and B. I. Lazoryak, *J. Solid State Chem.* **149,** 99 (2000).
9. J. A. Hriljac, C. P. Grey, A. K. Cheetham, P. D. VerNooy, and C. C. Torardi, *J. Solid State Chem.* **123,** 243 (1996).
10. X.-J. Tang and A. Lackgar, *Z. Anorg. Allg. Chem.* **622,** 513 (1996).
11. K.-H. Lii and J. Ye, *J. Solid State Chem.* **131,** 131 (1997).
12. S. S. Dhingra and R. C. Haushalter, *J. Chem. Soc., Chem. Commun.* 1665 (1993).
13. A. M. Chippindale, S. J. Brech, A. R. Cowley, and W. M. Simpson, *Chem. Mater.* **8,** 2259 (1996).
14. A. M. Chippindale and S. J. Brech, *J. Chem. Soc., Chem. Commun.* 2781 (1996).
15. K.-H. Lii and Y.-F. Huang, *Inorg. Chem.* **38,** 1348 (1999).
16. X. Tang, A. Jones, A. Lachgar, B. J. Gross, and J. L. Yarger, *Inorg. Chem.* **38,** 6032 (1999).
17. X. Tang, M. J. Gentiletti, A. Lachgar, V. A. Morozov, and B. I. Lazoryak, *Solid State Sci.* **3,** 143 (2000).
18. E. R. Losilla, M. A. G. Aranda, S. Bruque, J. Sanz, M. A. Paris, J. Campo, and A. R. West, *Chem. Mater.* **12,** 2134 (2000).
19. J.-X. Mi, Y.-X. Huang, S.-Y. Mao, X.-D. Huang, Z.-B. Wei, Z. L. Huang, and J.-T. Zhao, *J. Solid State Chem.* **157,** 213 (2000).
20. S. Natarajan and A. K. Cheetham, *J. Solid State Chem.* **134,** 207 (1997), and references therein.
21. J.-X. Mi, M.-R. Li, S.-Y. Mao, Y.-X. Huang, Z.-B. Wei, J.-T. Zhao, and R. Kniep, *Z. Krist. NCS* **217** (2000), online CSD-No.409584.
22. B. A. Frenz and Associates, Inc., "SDP User's Guide," College Station, TX 77840, and Enraf-Nonius, Delft, Holland, 1985.
23. G. M. Sheldrick, "SHELXL-97, Program for Refining Crystal Structures." University of Göttingen, Germany 1997.
24. N. E. Brese and M. O'Keeffe, *Acta Crystallogr.* Sect. *B* **47,** 192 (1991).
25. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 5th ed., p. 315. Wiley, New York, 1988.
26. M. L. F. Phillips, W. T. A. Harrison, G. D. Stucky, E. M. McCarron, J. C. Calabrese, and T. E. Gier, *Chem. Mater.* **4,** 222 (1992).
27. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke, and O. M. Yaghi, *J. Solid State Chem.* **152,** 3 (2000), and references therein.