Synthesis and Structure of an Open-Framework Zincophosphate $[C_6N_4H_{22}][ZnPO_4]_4$

Yongnan Zhao,*,[1] Jing Ju,† Xiangming Chen,* Xiuhong Li,* Ruji Wang,‡ and Zhenhong Mai*

*Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China;
†College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China; and ‡Department of Chemistry,
Tsinghua University, Beijing 100084, People's Republic of China
E-mail: zhaoyn@263.net

A new zincophosphate $[C_6N_4H_{22}][ZnPO_4]_4$ **1** has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction. It crystallized in the triclinic space group $P\bar{1}$ with $a = 9.784(2)$ Å, $b = 10.074(2)$ Å, $c = 8.0573(16)$ Å, $\alpha = 121.62(3)°$, $\beta = 119.20(3)°$, $\gamma = 98.37(3)°$, $V = 496.96(17)$ Å^3, $Z = 1$. Refinement gave $R_1 = 0.0651$, $wR_2 = 0.1476$ for observed data. The zinc and phosphorous atoms are tetrahedrally coordinated by oxygen atoms with a Zn to P ratio of 1. The structure of **1** is constructed by strictly alternating linking of ZnO_4 and PO_4 with four-membered rings as the secondary building units. The four-membered rings are further connected in three styles: sharing zinc atoms to form a chain structure, connected using vertices to form an undulating chain, and a 4–1 connection. These connections give a complex three-dimensional eight-membered ring channel system.　© 2002 Elsevier Science (USA)

INTRODUCTION

Synthetic materials with open-framework structures are of considerable interest for wide applications in catalysis, ion exchange, and intercalation (1). Although aluminosilicate zeolites are perhaps the best-known open-framework materials, astonishing varieties of inorganic networks templated by organic species, contain elements from virtually all groups and exhibiting more structures than those seen in zeolite chemistry, have been reported over the past decade (2). Also metal phosphates are possibly the fastest expanding group of open-framework inorganic materials (3). Since the bivalent metal phosphates ($+2$, $+5$) are associated with the same total charge as aluminosilicate zeolites ($+3$, $+4$), phosphate-based framework structures containing bivalent metals are pursued. After the discovery of the first open-framework zincopho-

sphate with zeolite topologies was reported by Gier and Stucky (4), a great deal of effort has been devoted to preparing novel open-framework structures within this system. This compound group has experienced extraordinary expansion in terms of the diversity of their structures and compositions. Also zincophosphates with zero- (monomer), one- (chain, ladder), two- (layer), and three-dimensional architectures have been isolated (5), in which two eye-catching results are the gigantic pore structure with 24-membered rings of ND-1 (6) and 20-ring channels in $H_3N(CH_2)_6NH_3 \cdot Zn_4(HPO_4)_2 \cdot 3H_2O$ (7). This variety was achieved by varying a number of factors that can influence the structure, including template, pH, solvent, reaction temperature, additives, and zinc source. Recent research has indicated that multiple amino groups, such as triamine and tetraamine, are more effective in preparing materials with open frameworks. Also a number of new topologies have been obtained by varying the ratio of phosphorous acid to amine, from one-dimensional ladder, two-dimensional layer to three-dimensional framework structures (8). Here we report on the synthesis and structure of an open-framework zincophosphate templated by triethylenetetraamine, $[C_6N_4H_{22}][ZnPO_4]_4$ (**1**), which possesses three-dimensional eight-membered ring channels.

EXPERIMENTAL

Compound **1** was synthesized by sealing a mixture of 1 g $ZnCl_2$, 2 mL H_3PO_4 (85 wt%), 1.6 mL triethylenetetraamine (TETA), and 30 mL water in a 40-mL Teflon-lined autoclave and crystallized at 160°C for four days. The colorless plate-like crystals obtained were washed with water and dried at room temperature. The experimental and simulated XRD patterns are in agreement, showing the phase purity of the product. Infrared spectra were as follows: 501.63, 586.80, 636.50, 928.37, 1010.04, and

---

[1]To whom correspondence should be addressed.

1087.05 cm^{-1} [$\nu_{(Zn–O)}$, $\nu_{(P–O)}$]; 1452.44, 1524.64, and 1639.94 cm^{-1} [$\nu_{(TETA)}$]. Thermogravimetric analysis was performed from 20 to 700°C. It shows one sharp mass loss in the range of 320–420°C. The total mass loss of 19.1% corresponds to the loss of amine, which is in agreement with the calculated value (18.5%). Compound **1** is thermally unstable. The loss of amine results in the collapse of the framework.

A plate-like crystal was mounted on a glass fiber. The data were collected on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 KW sealed tube X-ray source. Intensities were recorded in 1271 frames with ω-scan (0.3°/min). Of the total 4741 reflections measured, 1171 were unique with 1034 observed. The structure was solved by directed method. The zinc and phosphorous atoms were located first, and the carbon, nitrogen, and hydrogen atoms were found in the final difference Fourier maps. Structure solution and refinement were performed using SHELXTL (Ver. 5.01) program. Details of structure refinement are given in Table 1. The atomic positions and the bond lengths bond angles are listed in Table 2 and Table 3.

RESULTS AND DISCUSION

The crystal structure of compound **1** is determined by single-crystal X-ray diffraction, providing a detailed structural model in space group $P\bar{1}$ (No. 2). The 17 non-hydrogen atoms of the asymmetric unit consist of two zinc, two phosphorous, eight oxygen, two nitrogen, and three carbon atoms (Fig. 1), in which the nitrogen and carbon atoms belong to the guest species and the former atoms belong to the frameworks. The two zinc atoms are both tetrahedrally coordinated by four neighboring oxygen atoms with the Zn–O distances ranging from 1.906(14) to 2.112(13) Å for Zn1 and from 1.906(10) to 1.972(9) Å for Zn2. The O–Zn–O bond angles are in the range 96.8(8)°–130.8(8)° (average value of 109.4° for Zn1 and 109.5° for Zn2). Both zinc atoms make four Zn–O–P bonds to the two distinct P atom neighbors with the Zn–O–P bond angles ranging from 110.1(7)° to 153.6(9)° ((Zn–O–P)$_{av.}$ = 133.2°). The two P atoms are tetrahedrally coordinated with the geometry of mono phosphate. The P–O distances are in the range 1.461(14)–1.547(9) Å ((P1–O)$_{av}$ = 1.53 Å and (P2–O)$_{av}$ = 1.50 Å). The O–P–O bond angles range from 107.2(6)° to 110.1(6)° for P1 and from 106.0(12)° to 112.0(7)° for P2. The stoichiometry of Zn$_2$(PO$_4$)$_2$ gives a macro-anionic framework with the net charge of −2. The negative framework charges are balanced by quadruply protonated TETA molecules.

The framework structure of **1** is constructed by alternative ZnO$_4$ and PO$_4$ tetrahedra, which are linked through their vertices, giving rise to a three-dimensional architecture with channels. The connectivity of ZnO$_4$ and PO$_4$ results in four-membered rings as the secondary building unit, which are connected to each other via oxygen. Along the [100] direction, the adjacent perpendicular four-

TABLE 1
Details of Data Collection, Processing, and Structure Refinement

Molecular formula	[ZnPO$_4$]$_4 \cdot$ C$_6$H$_{22}$N$_4$
Molecular weight	791.64
Crystal size	$0.2 \times 0.06 \times 0.02$ mm^3
Diffractometer	Bruker Smart CCD
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a = 9.784(2) Å, α = 121.62(3)°
	b = 10.074(2) Å, β = 119.20(3)°
	c = 8.0573(16) Å, γ = 98.37(3)°
Volume	496.96(17) Å^3
Z, Calculated density	1, 2.645 gcm^{-3}
Absorption coefficient	5.184 mm^{-1}
Limiting indices	$-10 \leq h \leq 10$, $-9 \leq k \leq 8$, $-8 \leq l \leq 8$
Reflections collected/unique/observed	4741/1171/1034
Completeness to theta	92.9%
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.973
Final R indices (for all reflections)	R1 = 0.0699, wR2 = 0.1495
(for all reflections)	R1 = 0.0651, wR2 = 0.1476
GooF	1.088
Largest and mean Δ/σ	0.002, 0.001
Residual extrema in final difference map	−1.676 to 1.286 e Å^{-3}

Note. $R_1 = \dfrac{\sum \|F_o| - |F_c\|}{\sum |F_o|}$, $wR_2 = \sqrt{\dfrac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2}}$, GooF = S = $\sqrt{\dfrac{\sum [w(F_o^2 - F_c^2)^2]}{n - p}}$

TABLE 2
Atomic Coordinates and Equivalent Isotropic Temperature Factors^a (Å^2)

Atoms	x	y	z	U_{eq}
Zn(1)	1.0204(2)	1.4925(2)	1.2880(3)	0.0231(7)
Zn(2)	0.5390(2)	0.7603(2)	0.2804(3)	0.0314(7)
P(1)	0.7630(5)	1.2176(5)	0.6989(6)	0.0270(11)
P(2)	0.7198(5)	0.5367(5)	0.3528(6)	0.0235(11)
O(1)	0.9104(14)	1.3217(13)	0.7233(18)	0.037(3)
O(2)	0.8541(14)	1.2429(12)	0.9393(16)	0.030(3)
O(3)	0.6317(15)	1.2884(14)	0.672(2)	0.043(3)
O(4)	0.6537(18)	1.0133(13)	0.4510(18)	0.059(4)
O(5)	0.7164(17)	0.7084(14)	0.4412(18)	0.054(4)
O(6)	0.5418(13)	0.3616(13)	0.0658(16)	0.035(3)
O(7)	0.7324(17)	0.5007(15)	0.516(2)	0.049(3)
O(8)	0.888(2)	0.565(2)	0.393(3)	0.141(10)
N(1)	0.2158(17)	1.3107(16)	1.005(2)	0.036(3)
N(2)	0.4033(15)	1.1207(16)	1.141(2)	0.031(3)
C(1)	0.126(2)	1.1069(19)	0.853(3)	0.031(4)
C(2)	0.213(2)	1.076(2)	1.030(3)	0.035(4)
C(3)	0.4030(19)	0.9660(19)	0.952(3)	0.027(4)

^{a}U_{eq} defined as one-third of the trace of the orthogonalized **U** tensor.

ZHAO ET AL.

TABLE 3
Bond Lengths (Å) and Bond Angles (°)

Zn(1)–O(8)[a]	1.906(14)	P(2)–O(7)	1.494(11)
Zn(1)–O(2)	1.951(9)	P(2)–O(5)	1.499(12)
Zn(1)–O(1)[b]	1.959(11)	P(2)–O(6)	1.547(9)
Zn(1)–O(7)[c]	2.112(13)	O(1)–Zn(1)[b]	1.959(11)
Zn(2)–O(4)	1.906(10)	O(3)–Zn(2)[d]	1.937(12)
Zn(2)–O(5)	1.935(12)	O(6)–Zn(2)[e]	1.972(9)
Zn(2)–O(3)[d]	1.937(12)	O(7)–Zn(1)[c]	2.112(13)
Zn(2)–O(6)[e]	1.972(9)	O(8)–Zn(1)[f]	1.906(13)
P(1)–O(1)	1.511(11)	N(1)–C(1)	1.509(19)
P(1)–O(4)	1.528(10)	N(2)–C(2)	1.473(19)
P(1)–O(2)	1.531(10)	N(2)–C(3)	1.501(17)
P(1)–O(3)	1.537(12)	C(1)–C(2)	1.49(2)
P(2)–O(8)	1.461(14)	C(3)–C(3)[g]	1.52(3)
O(8)[a]–Zn(1)–O(2)	110.8(5)	O(8)–P(2)–O(7)	106.0(12)
O(8)[a]–Zn(1)–O(1)[b]	96.8(8)	O(8)–P(2)–O(5)	108.9(10)
O(2)–Zn(1)–O(1)[b]	111.0(4)	O(7)–P(2)–O(5)	111.1(7)
O(8)[a]–Zn(1)–O(7)[c]	130.8(8)	O(8)–P(2)–O(6)	112.0(7)
O(2)–Zn(1)–O(7)[c]	102.5(4)	O(7)–P(2)–O(6)	106.2(6)
O(1)[b]–Zn(1)–O(7)[c]	104.0(5)	O(5)–P(2)–O(6)	112.5(6)
O(4)–Zn(2)–O(5)	112.1(5)	P(1)–O(1)–Zn(1)[b]	140.4(7)
O(4)–Zn(2)–O(3)[d]	108.0(5)	P(1)–O(2)–Zn(1)	119.2(6)
O(5)–Zn(2)–O(3)[d]	105.2(5)	P(1)–O(3)–Zn(2)[d]	124.0(7)
O(4)–Zn(2)–O(6)[e]	100.5(4)	P(1)–O(4)–Zn(2)	149.0(7)
O(5)–Zn(2)–O(6)[e]	107.8(5)	P(2)–O(5)–Zn(2)	134.7(6)
O(3)[d]–Zn(2)–O(6)[e]	123.2(4)	P(2)–O(6)–Zn(2)[e]	134.8(7)
O(1)–P(1)–O(4)	107.2(6)	P(2)–O(7)–Zn(1)[c]	110.1(7)
O(1)–P(1)–O(2)	110.1(6)	P(2)–O(8)–Zn(1)[f]	153.6(9)
O(4)–P(1)–O(2)	110.1(6)	C(2)–N(2)–C(3)	111.9(10)
O(1)–P(1)–O(3)	109.7(6)	C(2)–C(1)–N(1)	111.3(12)
O(4)–P(1)–O(3)	109.6(7)	N(2)–C(2)–C(1)	114.2(13)
O(2)–P(1)–O(3)	110.1(6)	N(2)–C(3)–C(3)[g]	109.8(14)
Hydrogen bonding			
N(1)–H1C · · · O(1)[h]	0.89, 2.80(2)	N(2)–H2A · · · O(3)[j]	0.90, 2.86(2)
N(1)–H1E · · · O(3)[i]	0.89, 2.96(2)	N(2)–H2B · · · O(7)[a]	0.90, 2.99(2)
N(1)–H1D · · · O(6)[a]	0.89, 2.90(2)		

Note. Symmetry transformation codes: [a]$(x, 1+y, 1+z)$, [b]$(2-x, 3-y, 2-z)$, c $(2-x, 2-y, 2-z)$, [d]$(1-x, 2-y, 1-z)$, [e]$(1-x, 1-y, -z)$, [f]$(x, -1+y, -1+z)$, [g]$(1-x, 2-y, 2-z)$, [h]$(-1+x, y, z)$, [i]$(1-x, 3-y, 2-z)$, [j]$(x, y, 1+z)$.
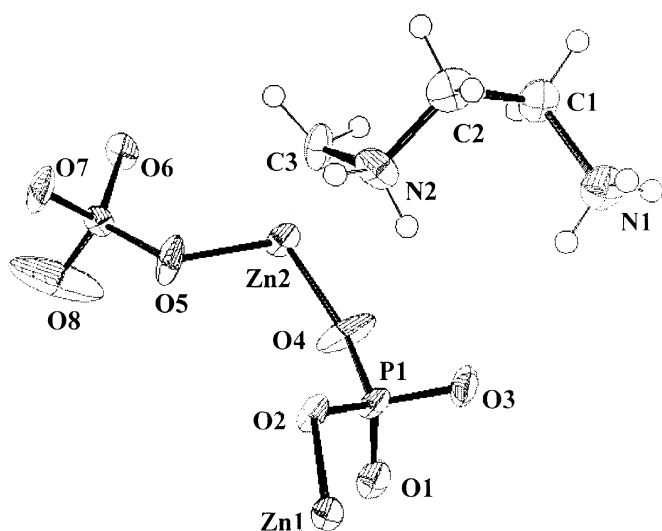

FIG. 1. ORTEP drawing for the structure of **1**, showing the asymmetric unit with labeling scheme. Thermal ellipsoids are shown at 35% probability.

membered rings link to each other by sharing the zinc atoms, forming a chain structure. These chains are further connected by oxygen atoms to give rise to eight-membered ring channels along the [100] direction. The width of these channels is 6.19 (O4–O4) × 7.53 (O1–O1) Å^2 (Fig. 2).
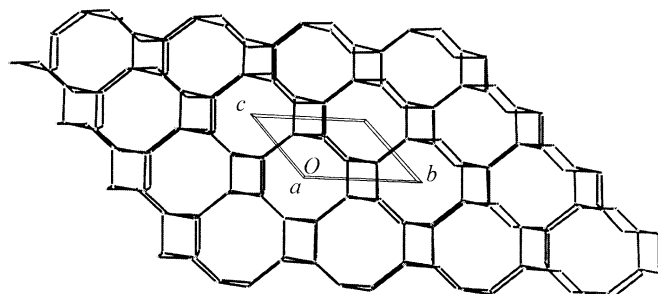

FIG. 2. The structure of **1** viewed along the [100] direction showing the eight-membered ring channels. Oxygen, carbon, and nitrogen atoms are omitted.
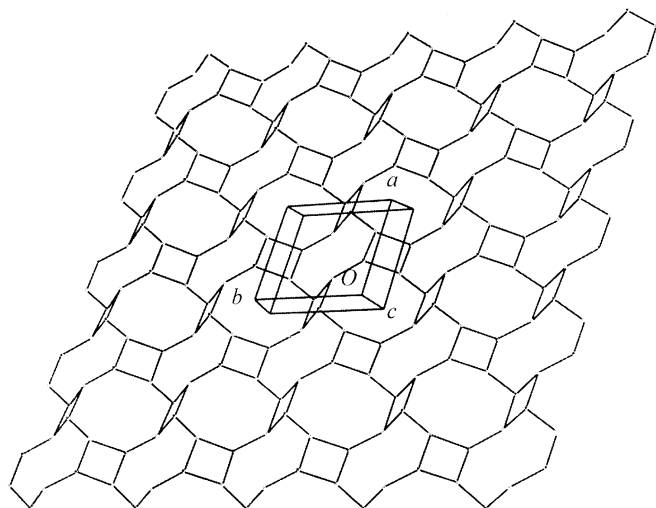
FIG. 3. The structure of **1** along the [001] direction showing the eight-membered ring channels. Oxygen, carbon, and nitrogen atoms are omitted.

FIG. 5. The structure of **1** along the [111] direction showing the eight-membered ring channels. The TETA molecules are omitted.

Along the [001] direction, the structure of **1** possesses a 4–1 connection, which also leads to eight-membered channels along the [001] direction with a width of 6.49 (O4–O4) × 7.71 (O8–O8) Å^2 (Fig. 3). Interestingly, along the [010] direction, the four-membered rings share their edges, giving rise to an undulating four-membered ring chain (Fig. 4a). These chains are further connected together, forming a terrace-like structure (Fig. 4b), which gives rise to another eight-membered channel system along the [111] direction with a width of 5.73 (O13–O13) × 8.29 (O6–O6) Å^2 (Fig. 5). Thus, compound **1** possesses a complex three-dimensional channel system.

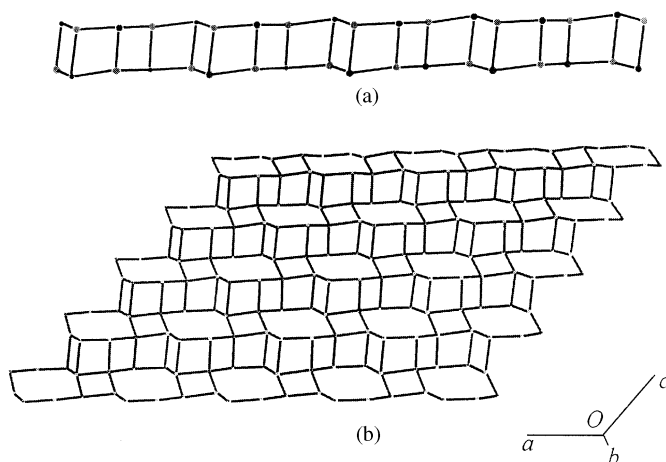The quadruply protonated TETA molecules occupy the channel spaces and interact with the framework through

N–H···O hydrogen bonds to balance the negative framework charge. All the nitrogen atoms participate in the hydrogen bonding to the acceptor oxygen species with the N–H···O distances ranging from 2.80 to 2.99 Å.

CONCLUSIONS

In conclusion, a three-dimensional zincophosphate has been hydrothermally synthesized using TETA as a structure-directing reagent. This compound is constructed by alternating ZnO$_4$ and PO$_4$ tetrahedra forming four-membered ring chains. The connectivity of these chains gives rise to three-dimensional intersecting eight-membered ring apertures. The successful synthesis of this open-framework zincophosphate gives us more possibilities of exploring new topologies in the organic amine templated zincophsphate system.

FIG. 4. The undulating chains (a), formed by four-membered rings sharing their edges and rise to the terrace-like structure (b) viewed along the [010] direction. Oxygen atoms are omitted.
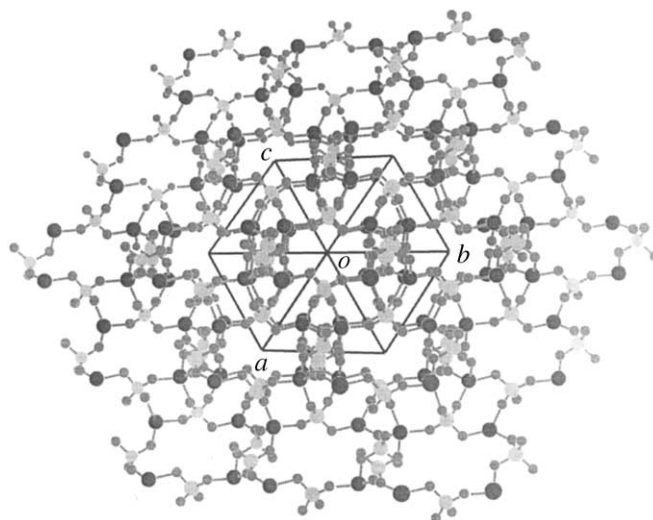
REFERENCES

1. G. Alberti, M. Casciola, U. Costantino, and R. Vivani, *Adv. Mater.* **8,** 291 (1996).
2. A. Muller, H. Renter, and S. Dillinger, *Angew. Chem. Int. Ed. Engl*, **34,** 2328 (1995).
3. A. K. Cheetham, G. Ferey, and T. Loiseau, *Angew. Chem. Int. Ed.* **39,** 3268 (1999); C. N. R. Rao, S. Natarajan, A. Choudhury, S. Neeraj and A. A. Ayi, *Acc. Chem. Res.* **34,** 80 (2001), and references therein.
4. T. E. Gier, and G. D. Stucky, *Nature* **349,** 508 (1991).
5. R. J. Francis, S. J. Price, S. O'Brien, A. M. Fogg, D. O'Hare, T. Loiseau, and G. Férey, *Chem. Commun.* 521 (1997); T. R. Jensen and R. G. Hazell, *Chem. Commun.* 371 (1999); T. R. Jenson, *J. Chem.*

Soc., Dalton Trans. 2261(1998); S. B. Harmon and S. C. Sevov, *Chem. Mater.* **10,** 3020 (1998); S. Neeraj and S. Natarajan, *Chem. Mater.* **12,** 2753 (2000); D. Chidambaram, S. Neeraj, S. Natarajan, and C. N. R. Rao, *J. Solid State Chem.* **147,** 154 (1999); S. Neeraj, S. Natarajan, and C. N. R. Rao, *Chem. Mater.* **11,** 1390 (1999); W. T. A. Harrison, Z. Bircsak, L. Hannooman, and Z. Zhang, *J. Solid State Chem.* **136,** 93 (1998); A. V. Chavze, T. M. Nenoff, L. Hannooman, and W. T. A. Harrison, *J. Solid State Chem.* **147,** 584 (1999); C. N. R. Rao, S. Natarajan, and S. Neeraj, *J. Am. Chem. Soc.* **122,** 2810 (2000).

6. G. Y. Yang, and C. C. Sevov, *J. Am. Chem. Soc.* **121,** 8389 (1999).

7. J. A. Rodgers, and W. T. A. Harrison, *J. Mater. Chem.* **10,** 2853 (2000).

8. A. Choudhury, S. Natarajan, and C. N. R. Rao, *Inorg. Chem.* **39,** 4295 (2000); W. Liu, Y. Liu, Z. Shi, and W. Pang, *J. Mater. Chem.* **10,** 1451 (2000); Y. N. Zhao, Z. Shi, X. M. Chen, Z. H. Mai, and S. H. Feng, *Chem. Lett.* 363 (2001); A. Choudhury, S. Natarajan, and C. N. R. Rao, *J. Solid State Chem.* **157,** 110 (2001).