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A Novel Open-Framework Cerium Phosphate Fluoride: $(NH_4)[Ce^{IV}F_2(PO_4)]$

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A novel open-framework cerium phosphate fluoride, $(NH_4)[Ce^{IV}F_2(PO_4)]$, has been synthesized under hydrothermal conditions and characterized by means of single-crystal X-ray diffraction, ion chromatography analysis, and thermal analysis. The compound crystallizes in the monoclinic space group $P2_1/m$ (No. 11), with $a = 6.660(2)$, $b = 5.875(2)$, $c = 7.177(3)$ Å, $\beta = 114.31(2)^\circ$, and $V = 255.9(2)$ Å^3 ($R = 0.039$ and $R_w = 0.045$). In this compound, the cerium-centered CeO_4F_4 polyhedra link via Ce_2F_2 rings to form corrugated chains along the b axis of the structure. These are tetrahedrally connected via PO_4 groups to create the three-dimensional network with a one-dimensional channel. NH_4^+ cations are accommodated at the intersection of the channels. © 2001 Academic Press

Key Words: **hydrothermal synthesis; open-framework structure; cerium phosphate fluoride.**

INTRODUCTION

Rare earth phosphates with potential applications as ion exchangers, moisture sensors, fluorescence materials, and ion conductors, have attracted considerable researchers (1, 2). Synthesis of open-framework rare earth phosphate is of great interest because the three-dimensional tunnels would be capable of supporting cation conductivity (3, 4). In 1950, in aqueous solution at moderate temperature, Mooney (5) obtained a metastable hexagonal phase of $RE^{III}PO_4$ (RE = La, Ce, Pr, Nd) with one-dimensional open tunnels along the c axis. Subsequently, through charge-compensating substitution on a RE site, the hexagonal compounds of $A^IB^{II}C^{III}(PO_4)_2$ (A^I = K, Rb, Cs; B^{II} = Ca, Sr, Eu; $C^{III} = RE$ and Bi) were prepared in which cations were accommodated in the tunnels (6–9). Although preparations of rare earth phosphates with tunnel structures were started early, examples of three-dimensional open-framework compounds are rather few. In the 1980s, rare earth metal scandium substituted NASICONs were obtained by using a solid-state reaction (4). Simultaneously, a mild hydrothermal method was also applied and resulted in an open-framework NASICON-type $Na_3Sc_2^{III}(PO_4)_3$ (10). Recently, hydrothermal synthesis of $M_2Ce^{IV}(PO_4)_2H_2O$ ($M = NH_4$, Na, K) powders under alkaline conditions were reported, but the structures of them were not clarified (11). In addition, active research studies have also paid attention to cerium polyphosphates (12, 13).

Since the use of fluoride ions as mineralizers was introduced by Guth *et al.* (14) into hydrothermal preparation of zeolites, a good number of metal phosphate fluorides has been obtained. In many cases, fluoride ions are incorporated into the framework, for example, ZrPOF-*n* (15, 16), ULM-*n* (17,18), and TREN-GaPO (19). However, cerium phosphate fluorides are only found in some known minerals, and almost all of them are mixed with other cations. To our knowledge, no example of synthesis of this class of compounds has been reported.

Based on previous studies, we started our research on hydrothermal synthesis of an open-framework compound in the $Ce(SO_4)_2$–H_3PO_4–$H_2N(CH_2)_2NH_2$–NH_4F–H_2O system. In the present work, the title compound, $(NH_4)[Ce^{IV}F_2(PO_4)]$, was obtained hydrothermally under acidic conditions by using NH_4F as the mineralizer and its open-framework structure was characterized. The structure of the compound contains four and six rings formed by the cerium-centered CeO_4F_4 polyhedra and PO_4 tetrahedra and six-ring channels parallel to the b axis.

EXPERIMENTAL

Synthesis

The title compound was synthesized hydrothermally from a starting composition of 1.0 $Ce(SO_4)_2$/3.5 H_3PO_4/3.0 $H_2NCH_2CH_2NH_2$/8.0NH_4F/280H_2O. The pH value of the

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starting mixture is about 3. This mixture was sealed in Teflon-lined stainless steel autoclaves and heated at 180°C for 5 days. The yellow crystalline product was filtered and washed with deionized water and ethanol and then dried in air at ambient temperature.

Characterization

X-ray powder diffraction patterns were taken on a RINT 1200 Rigaku X-ray diffractometer using Ni-filtered Cu$K\alpha$ radiation. Thermogravimetric analysis (TGA) was carried out on a Rigaku Thermoflex TAS 200 thermal analysis system with a heating rate of 10°C/min over a 20–1000°C temperature range. Infrared absorption spectra (IR) were recorded on a JASCO FT/IR-410 spectrometer using transparent KBr pellets: 1–2 mg of the sample was crushed and mixed with 300 mg of KBr.

Ion chromatography analysis of fluoride was carried out on an IC 7000 SERIES ion chromatographic analyzer equipped with a Yokogawa ICS AZG + ICS-A23 (4.6 mm × 75 mm) column by using aqueous NaF as the standard solution. The sample used for measurement was prepared as follows: ca. 0.2 g of as-synthesized product was dissolved in 10 ml of 5 N H_2SO_4 at ambient temperature. Then, the solution was further diluted with deionized water to the F^- ion concentration of 1–10 ppm.

Crystal Structure Determination

A crystal of dimensions $0.2 \times 0.2 \times 0.2$ mm^3 was isolated and mounted on a glass fiber. Single-crystal X-ray diffraction data were collected with a Rigaku AFC7R diffractometer equipped with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The systematic absence ($0k0 = 2n + 1$) was consistent with either space group $P2_1$ or $P2_1/m$. Successful solution and refinement led to the choice of the centrosymmetic space group; 2243 of the total 2364 collected reflections were unique ($R_{int} = 0.033$). The crystal structure was solved by direct methods (SAPI90) and expanded by Fourier techniques. The non-hydrogen atoms were refined anisotropically. All calculations were performed using the teXsan (20) crystallographic package. Further details of crystal data and structure refinement are summarized in Table 1. Atomic coordinates and thermal parameters are given in Table 2.

TABLE 1
Crystal Data and Structure Refinement for $[NH_4][Ce^{IV}F_2(PO_4)]$

Empirical formula	$CePO_4NH_4F_2$
Formula weight	219.13
Crystal system	Monoclinic
Space group	$P2_1/m$ (No. 11)
Lattice parameters	
a (Å)	6.660(2)
b (Å)	5.875(2)
c (Å)	7.177(3)
β (°)	114.31(2)
V (Å^3)	255.9(2)
Z	2
D_{calc} (g/cm^3)	3.777
Radiation	Mo$K\alpha$ ($\lambda = 0.71069$ Å)
Number of reflections measured	Total: 2364
	Unique: 2243 ($R_{int} = 0.033$)
Number of observations	
($I > 3.00\sigma(I)$)	1810
Number of variables	83
Residuals: R, R_w	0.039, 0.045
Goodness of fit indicator	1.69

Note. $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.039$.
$R_w = \sqrt{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2} = 0.045$.

RESULTS AND DISCUSSION

Synthesis

The experimental results indicated that the molar ratio of the starting materials, organic amine, reaction temperature, and time influenced the crystallization of the product deeply. The synthetic conditions and products are shown in Table 3. Various starting materials molar ratios have been investigated, which indicated that the pure phase of the products could be obtained in a very narrow range. Slight change of the molar ratio would give a crystalline cerium oxyfluoride as an impurity (21). Although ethylendiamine has not been accommodated in the channel of the product, it was proved to be a structure-directing agent. Crystalline $(NH_4)[Ce^{IV}F_2(PO_4)]$ could be synthesized only by using ethylendiamine. Other organic amines such as 1,3-diaminopropane, 1,4-diaminobutane, and 2-aminoethanol would give neither the title compound nor other new material. Besides NH_4F, NaF and HF have also been used as the mineralizer; however, the title compound could not be obtained. Under higher reaction temperatures and/or longer

TABLE 2
Atomic Coordinates and B_{eq}

Atom	x	y	z	B_{eq}
Ce	0.11857(5)	$\frac{1}{4}$	0.70677(5)	0.498(4)
P	0.7261(8)	$\frac{1}{4}$	0.9562(8)	0.52(2)
F	0.1682(4)	0.0020(6)	0.4711(4)	1.30(5)
O(1)	0.5029(7)	$\frac{1}{4}$	0.7665(7)	0.85(6)
O(2)	0.2600(5)	− 0.0386(6)	0.9124(5)	1.30(5)
O(3)	− 0.0846(8)	$\frac{1}{4}$	0.8889(8)	1.36(8)
N	0.437(9)	$\frac{1}{4}$	0.3186(1)	1.43(10)

Note. $B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

TABLE 3
The Synthetic Conditions and Products

Starting materials molar ratio							
$Ce(SO_4)_2$	H_3PO_4	Organic amine	F source	H_2O	T (°C)	Time (day)	Product
1.0	3.5	3.0 EN[a]	8.0 NH_4F	280	180	5	CePOF[e]
1.0	3.5	2.0 EN	6.0 NH_4F	280	180	5	CePOF+CeOF[f]
1.0	3.5	3.0 EN	8.0 NH_4F	280	200	5	CePOF + CeF_3
1.0	3.5	3.0 EN	8.0 NH_4F	280	180	8	CeF_3
1.0	3.5	3.0 PDA[b]	8.0 NH_4F	280	180	5	Unknown phase
1.0	3.5	3.0 BDA[c]	8.0 NH_4F	280	180	5	Unknown phase
1.0	3.5	3.0 EA[d]	8.0 NH_4F	280	180	5	Unknown phase
1.0	3.5	3.0 EN	8.0 NaF	280	180	5	Unknown phase + CeF_3
1.0	3.5	3.0 EN	8.0 HF	280	180	5	Unknown phase + CeF_3

[a]EN: ethylenediamine.
[b]PDA: 1,3-diaminopropene.
[c]BDA: 1,4-diaminobutane.
[d]EA: 2-aminoethanol.
[e]CePOF: $[NH_4][Ce^{IV}F_2(PO_4)]$.
[f]CeOF: cerium oxyfluoride with yield of 20–30% (21).

reaction times a crystalline CeF_3 (JCPDS: 8-45) was easily formed.

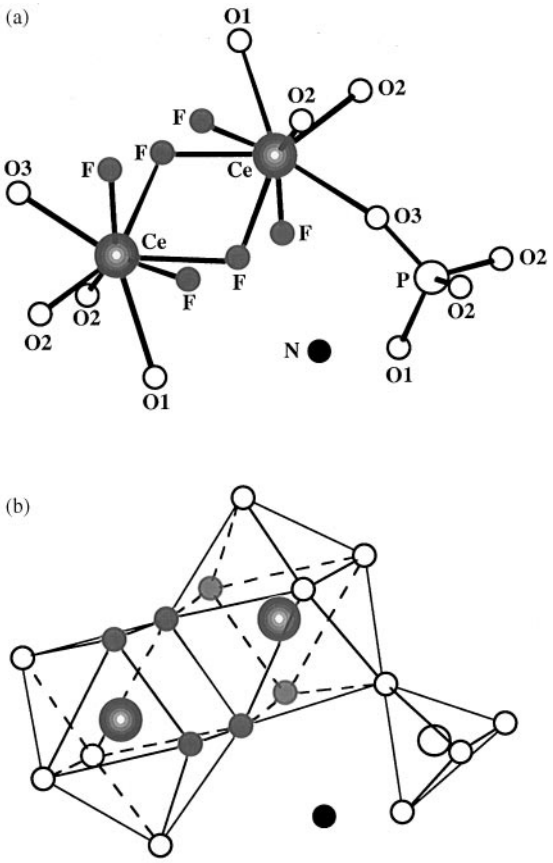

FIG. 1. Stick-ball (a) and polyhedral (b) representation of the asymmetric unit of $[NH_4][Ce^{IV}F_2(PO_4)]$.

Structure Description

The cerium fluoride phosphate material synthesized in the present study was found to contain framework fluoride atoms coordinated to cerium atoms, giving rise to the structure formula $(NH_4)[Ce^{IV}F_2(PO_4)]$. The structure of this crystal is based on a network of cerium-centered polyhedra CeO_4F_4 and phosphorus-centered tetrahedral PO_4. In the crystalline cerium oxyfluoride, which we obtained together with the title compound, cerium-centered dodecahedra CeO_6F_2 were observed (22). Along the *b* axis of the structure, there are corrugated chains linked by CeO_4F_4 polyhedra via Ce_2F_2 rings. They are further tetrahedrally connected via PO_4 groups to create the 3-D open-framework structure. Similar to many open-framework transition metal phosphate fluorides (15–19), fluoride atoms are involved in the framework. There is a six-ring channel system along the *b* axis of the structure as shown in Fig. 2. Each six-ring channel contains four CeO_4F_4 polyhedra and two PO_4 tetrahedra with the polyhedron arrangement –Ce–Ce–P–Ce–Ce–P– and has a diagonal that varies between 4.26 and 6.71 Å, which are almost the same as the dimensions of an eight-ring window in zeolite NaA (22). Three types of four-ring windows are found in the structure. In the planes vertical to the *a* axis, there are four-ring windows that contain three CeO_4F_4 polyhedra and one PO_4 tetrahedron with a diagonal that varies between 4.03 and 4.07 Å (Fig. 3). NH_4^+ cations are accommodated in the interspace of these four-ring windows as well as that of the six-ring channels to balance the framework negative charge and direct the windows structure. The presence of NH_4^+ cations is further proved by CHN elemental analysis. The other two kinds of four-ring windows vertical to the *c* and *b* axis, in which CeO_4F_4 dodecahedra and PO_4 tetrahedra are strictly alternated have diagonals of 2.95–4.47 Å and 3.31–4.17 Å, respectively.

Bond lengths and selected bond angles are listed in Table 4. The Ce–O distances vary in the range from 2.19 to 2.415 Å, which is comparable with the range of 2.188–2.407 Å for cerium atoms coordinated by eight oxygen atoms in $Ce^{IV}OSO_4(H_2O)$ (23). The average Ce–F bond length of 2.347 Å is coincident with that observed in $NH_4CeF_7(H_2O)$ (24). The P–O distances are within the range of 1.524–1.549 Å, and the average (1.538 Å) is a little longer than 1.53 Å seen in calcium–cerium phosphate, $Ca_{19}Ce^{IV}(PO_4)_{14}$ (25). NH_4^+ cations hydrogen bond to

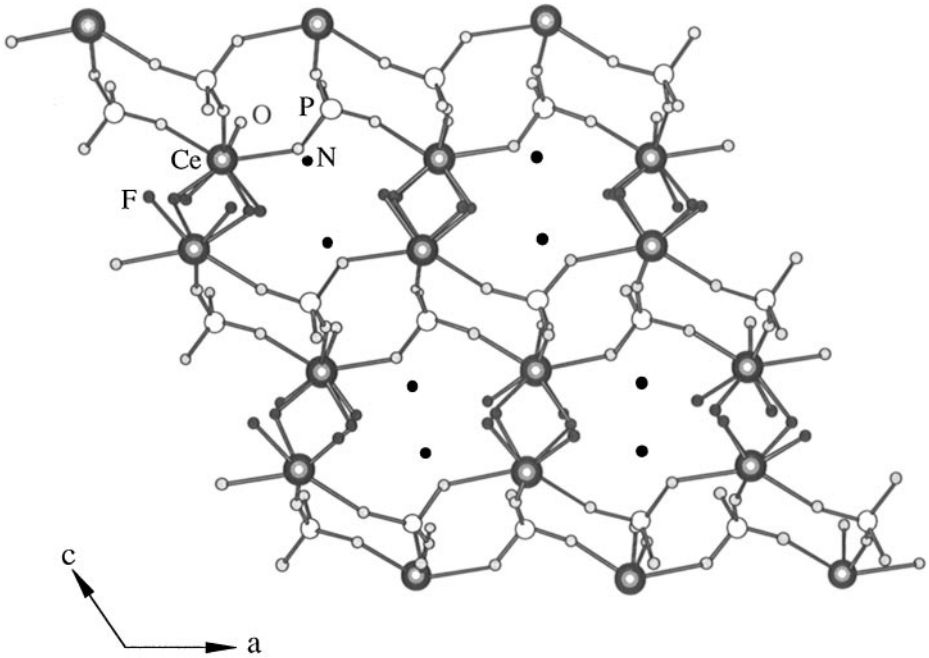

FIG. 2. Projection of the structure along the *b* axis, showing the channels with a six-ring window.

framework O(1), O(3), and F atoms with average N–H---O distance of 3.149 Å and N–H---F distance of 2.843 Å. Bond valence sum (BVS) values, calculated according to the Brese–O'Keefe formalism (26), are also characteristic: BVS[Ce] = 3.7, and BVS[P] = 4.5, BVS[F] = 0.8, BVS[O(1)] = 1.8, BVS[O(2)] = 2.2, and BVS[O(3)] = 1.8.

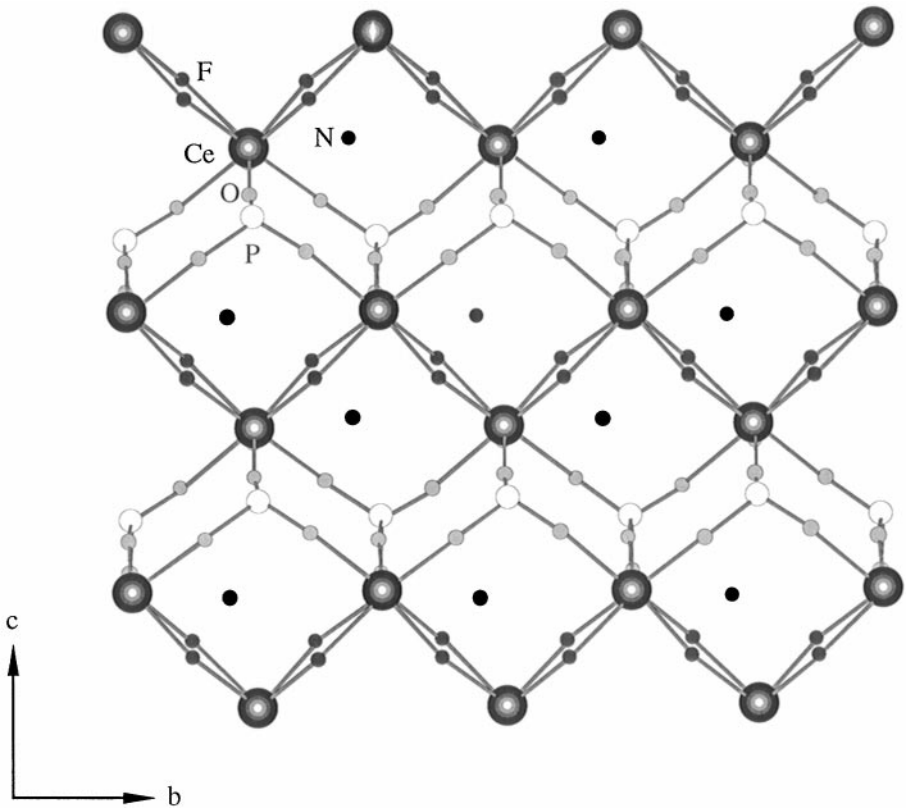

FIG. 3. Projection of the structure along the *a* axis, showing four-ring windows and the corrugated chains of CeO_4F_4 polyhedra.

TABLE 4
Bond Lengths (Å) and Selected Bond Angles (°) for $[NH_4][Ce^{IV}F_2(PO_4)]$

Ce–F	2.357(3)2×	Ce–F	2.337(3)2×
Ce–O(1)	2.415(4)	Ce–O(2)	2.190(3)2×
Ce–O(3)	2.235(5)	P–O(1)	1.549(5)
P–O(2)	1.539(3)2×	P–O(3)	1.524(5)
F–Ce–F	76.4(2)	F–Ce–F	108.92(5)
F–Ce–F	62.7(1)	F–Ce–O(1)	71.1(1)
F–Ce–O(2)	81.7(1)	F–Ce–O(2)	144.5(1)
F–Ce–O(3)	135.84(10)	F–Ce–F	78.6(2)
F–Ce–O(1)	131.69(9)	F–Ce–O(2)	152.5(1)
F–Ce–O(2)	84.6(1)	F–Ce–O(3)	76.3(1)
O(1)–Ce–O(2)	75.5(1)	O(1)–Ce–O(3)	138.5(2)
O(2)–Ce–O(2)	101.5(2)	O(2)–Ce–O(3)	78.6(1)

Ion Chromatography Analysis

Ion chromatography analysis of fluoride indicated that the content of fluoride in the compound is 12.7%, which is in good agreement with the theoretical value of 12.9% and corresponding to the Ce : P : F ratio of 1 : 1 : 2.

Thermal Analysis

Thermogravimetric analysis of the compound shows that the $(NH_4)[Ce^{IV}F_2(PO_4)]$ undergoes a exothermal redox decomposition at 320–550°C, giving a weight loss of ca. 19.51%, which agrees well with the calculated result (19.23%) according to Eq. [1]. At higher temperature, the compound converts via an amorphous into a crystalline phase of $CePO_4$ (27):

$$2(NH_4)[Ce^{IV}F_2(PO_4)] + 2O_2 \longrightarrow 2CePO_4 + 4HF + N_2 + 4H_2O. \quad [1]$$

Infrared Spectrum

On the basis of the framework vibration model for microporous aluminophosphates and transition metal phosphates (28, 29), the absorption bands for this compound are assigned as follows: 1114, 1046, and 969 cm^{-1} are associated with the stretching vibrations of PO_4 units; the bands at 593 and 547 cm^{-1} correspond to bending vibrations of PO_4 groups. Bands arising from NH_4^+ cations are also seen. The band at 1411 cm^{-1} may be due to δ_{N-H} of the NH_4^+ and the band at 3224 cm^{-1} is assigned to the stretching vibration of NH_4^+ (Fig. 4).

CONCLUSION

A novel open-framework cerium phosphate fluoride has been synthesized under hydrothermal conditions. In the compound, cerium(IV)-centered CeO_4F_4 polyhedra connect PO_4 tetrahedra to give rise to an open-framework structure with a 1-D channel system. NH_4^+ cations are accommodated in the channels to balance the negative charge of the framework and control the shape of the channels. This work illustrates the possibility of synthesis of new open-framework rare earth phosphates with F^- anions as the mineralizers. Studies on incorporating organic amines into the structure as templates are in progress.

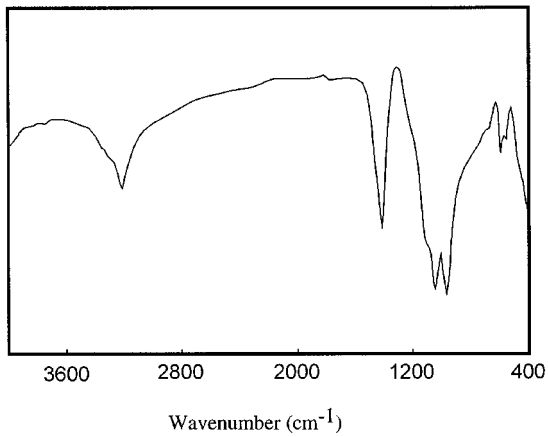

FIG. 4. IR spectrum of $[NH_4][Ce^{IV}F_2(PO_4)]$.

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REFERENCES

1. G. J. McCarthy, W. B. White, and D. E. Pfoertsch, *Mater. Res. Bull.* **13,** 1239 (1978).
2. I. Szczygiel and T. Znamierowska, *J. Solid State Chem.* **95,** 260 (1991).
3. H. Y.-P. Hong, *Mater. Res. Bull.* **11,** 173 (1976).
4. M. A. Subramanian, P. R. Rudolf, and A. Clearfield, *J. Solid State Chem.* **60,** 172 (1985).
5. R. C. L. Mooney, *Acta Crystallogr.* **3,** 337 (1950).
6. M. Vlasse, *Acta Crystallogr.* **38,** 2328 (1982).
7. C. Parent, P. Bochu, A. Daouidi, and G. Leflem, *J. Solid State Chem.* **43,** 190 (1982).
8. L. P. Keller, G. J. McCarthy, and R. G. Garvey, *Mater. Res. Bull.* **20,** 459 (1985).
9. G. Wu, M. Jansen, and K. Konigsten, *J. Solid State Chem.* **98,** 210 (1992).
10. S. Susman, C. J. Delbecq, and T. O. Brun, *Solid State Ionics* **9,** 839 (1983).
11. Y. Xu, S. Feng, W. Pang, and G. Pang, *Chem. Commun.* 1305 (1996).
12. M. Rzaigui, K. Ariguib, M. T. Averbuch-Pouchot, and A. Durif, *J. Solid State Chem.* **50,** 240 (1983).
13. V. Krasnikov, M. Vaivada, and Z. Konstants, *J. Solid State Chem.* **74,** 1 (1988).
14. J. L. Guth, H. Kessler, and R. Wey, *Stud. Surf. Sci. Catal.* **28,** 121 (1986).
15. M. Wloka, S. I. Troyanov, and E. Kemnitz, *J. Solid State Chem.* **135,** 293–301 (1998).

16. M. Wloka, S. I. Troyanov, and E. Kemnitz, *J. Solid State Chem.* **149,** 21–27 (2000).
17. T. Loiseau and G. Ferey, *J. Solid State Chem.* **111,** 403 (1994).
18. M. Cavellec, D. Riou, and G. Ferey, *J. Solid State Chem.* **112,** 441 (1994).
19. S. T. Weigel, S. C. Weston, A. K. Cheetham, and G. D. Stucky, *Chem. Mater*. **6,** 1293 (1997).
20. "teXsan: Crystal Structure Analysis Package." Molecular Structure Corporation, 1985, 1999.
21. R. Yu, D. Wang, N. Kumada, and N. Kinomura, *Chem. Mater*. **12,** 3527 (2000).
22. D. W. Breck, "Zeolite Molecular Sieves: Structure, Chemistry, and Use." Wiley-Interscience, Toronto, 1974.
23. O. Lindgren, *Acta Crystallogr. B* **32,** 3347 (1976).
24. R. R. Ryan and R. A. Penneman, *Acta Crystallogr. B* **27,** 1939 (1971).
25. B. I. Lazoryak, R. N. Kotov, and S. S. Khasanov, *Zh. Neorg. Khim.* **41,** 1281 (1996).
26. N. Brese and M. O'Keefe, *Acta Crystallogr.B* **47,** 192 (1991).
27. "Powder Diffraction File, Inorganic and Organic, Set 32, 32–199," JCSPD International Center Diffraction Data, USA.
28. M. E. Davis, P. E. Hathaway, C. Montes, and J. M. Gares, *Stud. Surf. Sci. Catal.* **49,** 199 (1989).
29. D. Wang, R. Yu, N. Kumada, and N. Kinomura, *Chem. Mater*. **12,** 956 (2000).