ACADEMIC
PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 172 (2003) 252–256

JOURNAL OF
SOLID STATE
CHEMISTRY

http://elsevier.com/locate/jssc

Synthesis and characterization of organic–inorganic hybrid compounds with a pillared layer structure: $Ga_2(4,4'\text{-bpy})(XO_4)_2$ ($X=$P, As)

Ching-Yeh Chen,[a] Kwang-Hwa Lii,[a,b,*] and Allan J. Jacobson[c]

[a] *Department of Chemistry, National Central University, Chungli 320, Taiwan, ROC*
[b] *Institute of Chemistry, Academia Sinica, Nankang, Taipei 115, Taiwan, ROC*
[c] *Department of Chemistry, University of Houston, Houston, TX 77204-5003, USA*

Received 30 September 2002; received in revised form 16 December 2002; accepted 18 December 2002

Abstract

Two organic–inorganic hybrid compounds, $Ga_2(4,4'\text{-bpy})(PO_4)_2$, **1**, and $Ga_2(4,4'\text{-bpy})(AsO_4)_2$, **2**, have been synthesized under hydrothermal conditions and structurally characterized by single-crystal X-ray diffraction. The two compounds are isostructural and crystallize in the triclinic space group $P\bar{1}$ (No. 2) with $a = 4.9723(9)$ Å, $b = 5.770(1)$ Å, $c = 11.812(2)$ Å, $\alpha = 78.268(3)^\circ$, $\beta = 89.159(3)^\circ$ $\gamma = 88.344(3)^\circ$, $V = 331.7(2)$ Å^3, $Z = 1$, and $R1 = 0.0377$ for **1**, and $a = 5.1111(7)$ Å, $b = 5.9327(8)$ Å, $c = 11.788(2)$ Å, $\alpha = 79.497(2)^\circ$, $\beta = 88.870(2)^\circ$, $\gamma = 88.784(2)^\circ$, $V = 351.3(2)$ Å^3, and $R1 = 0.0264$ for **2**. The structure consists of neutral sheets of $GaXO_4$ ($X=$P or As) which are pillared through 4,4′-bipyridine ligands. Each oxide layer, which is formed only by four-membered rings, is constructed from corner-sharing GaO_4N trigonal bipyramids and XO_4 tetrahedra. The title compounds are two of the few examples in which the gallium atoms are exclusively five-coordinate.

Keywords: Gallium; Phosphate; Arsenate; Bipyridine; Structure

1. Introduction

Aluminophosphates have been extensively studied due to the diverse fields of applications as catalysts, corrosion protection, and medicine [1]. In the mid-1980s, research was extended to gallophosphates in order to discover new materials with open-framework structures [2,3]. The replacement of aluminum by gallium yields both novel structures and phases that are analogous to known aluminophosphates. Interests in gallophosphates also stems from the ability of the gallium atom to adopt four-, five- or six-coordination which enhances the probability that novel structures will be formed. Most of these materials are synthesized in the presence of an organic amine as structure-directing agents. One of the most interesting gallophosphates is cloverite [4]. The cages of cloverite have body diagonals of ~29–30 Å, the openings to which are comprised of 20 tetrahedra. The structure can be described solely in terms of Ga–O–P double four rings (D4Rs) having fluoride ions in the center. Recently, we synthesized a discrete gallophosphate D4R unit containing an occluded oxygen atom using 4-aminopyridine as a structure-directing agent [5]. In addition to organically templated metal phosphates, we have also been interested in the synthesis of organic–inorganic hybrid compounds by incorporating organic ligand such as oxalate or 4,4′-bipyridine (abbreviated as 4,4′-bpy) in the structures of metal phosphates. Several oxalate-phosphates and 4,4′-bpy-phosphates of gallium have been reported [6–9]. As part of continuing work in these systems, we synthesized a new gallophosphate, $Ga_2(4,4'\text{-bpy})(PO_4)_2$, and the arsenate analogue, $Ga_2(4,4'\text{-bpy})(AsO_4)_2$, which consist of neutral sheets of $GaXO_4$ ($X=$P or As) linked by 4,4′-bipyridine pillars. The Ga atoms in the structure are exclusively five-coordinate. In this paper, the synthesis and crystal structures of the two compounds are presented.

---

[*] Corresponding author. Department of Chemistry, National Central University, Chungli 320, Taiwan, ROC. Fax: +886-3-4227664.
E-mail address: liikh@cc.ncu.edu.tw (K.-H. Lii).

0022-4596/03/$-see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0022-4596(03)00051-3

2. Experimental

2.1. Synthesis

The hydrothermal reactions were carried out in Teflon-lined stainless-steel Parr acid digestion bombs. All chemicals were purchased from Aldrich. Arsenic acid was prepared from a reaction of As_2O_3 and H_2O_2. Hydrothermal reaction of Ga_2O_3 (0.5 mmol), 4,4′-bipyridine (10 mmol), H_3PO_4 (5 mmol), tetraethylammonium bromide (2 mmol) and H_2O (10 mL) for 3 days at 165°C followed by slow cooling at 10°C/h to room temperature yielded colorless plate-shaped crystals of Ga_2(4,4′-bpy)$(PO_4)_2$ (further denoted as **1**) in 73% yield based on Ga. A suitable plate crystal was selected for structure determination by single-crystal X-ray diffraction. The product is monophasic because its powder X-ray diffraction pattern can be completely indexed based on the unit cell from single-crystal X-ray diffraction. However, the intensities of $0\,0\,l$ reflections are considerably greater than the values simulated from single-crystal data because of preferred orientation of crystals within the powder specimen. Elemental analysis confirmed its stoichiometry (anal. found: C, 24.17%; H, 1.69%; N, 5.71%. calc.: C, 24.74%; H, 1.66%; N, 5.77%) We have also carried out retro-syntheses without tetraethylammonium bromide; the resulting product is a mixture of **1** and a small amount of unidentified acicular crystals. The arsenate analogue, Ga_2(4,4′-bpy)$(AsO_4)_2$ (further denoted as **2**), has also been synthesized under the same reaction conditions. The arsenate is indicated from single-crystal X-ray diffraction to be isotypic with **1**.

Thermogravimetric analysis of **1** was performed on a Perkin-Elmer TGA 7 thermal analyzer; the sample was heated to 900°C at 5°C/min in flowing oxygen. The TGA curve showed a broad weight loss which began at ca. 300°C, reached maximum rate at ca. 450°C and was incomplete by 900°C (Fig. 1). The decomposition products contained $GaPO_4$ (JCPDS: 31–546) and black glassy carbon, as indicated from powder X-ray diffraction and the color. The total weight loss between 30°C and 900°C is ca. 30%, which is smaller than the calculated value of 32.2% because of incomplete oxidation of the organic component.

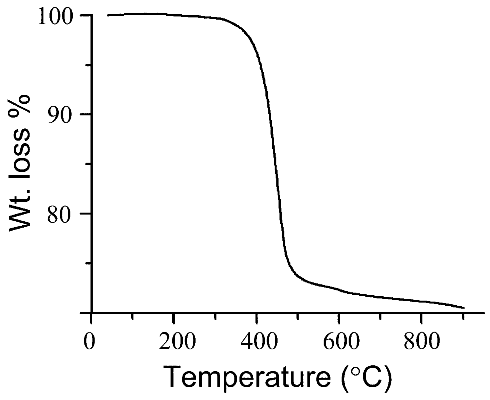

Fig. 1. TGA curve, recorded in oxygen, of **1**.

2.2. Single-crystal X-ray diffraction

A suitable crystal of each compound was selected for indexing and intensity data collection on a Siemens SMART CCD diffractometer equipped with a normal focus, 3-kW sealed tube X-ray source. The data were collected at room temperature in 1271 frames with ω scans (width 0.30° per frame). Empirical absorption corrections based on symmetry equivalents were applied. The structures were solved by direct methods and difference Fourier syntheses. All H atoms in 4,4′-bpy molecule were found in difference Fourier maps. The final cycles of least-squares refinement included atomic coordinates for all atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic

Table 1

Crystallographic data for Ga_2(4,4′-bpy)$(PO_4)_2$ (**1**) and Ga_2(4,4′-bpy)$(AsO_4)_2$ (**2**)

	1	**2**
Crystal size, mm	$0.14 \times 0.05 \times 0.01$	$0.25 \times 0.12 \times 0.08$
Color	Colorless	Colorless
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	4.9723(9)	5.1111(7)
b, Å	5.770(1)	5.9327(8)
c, Å	11.812(2)	11.788(2)
α, deg	78.268(3)	79.497(2)
β, deg	89.159(3)	88.870(2)
γ, deg	88.344(3)	88.784(2)
V, Å^3	331.7(2)	351.3(1)
Z	1	1
Fw	485.56	573.46
D_c, g cm^{-3}	2.431	2.710
T, °C	23	23
μ(Mo$K\alpha$), cm^{-1}	43.5	85.6
$T_{\text{min, max}}$	0.599, 0.942	0.316, 0.859
λ(Mo$K\alpha$), Å	0.71073	0.71073
Maximum 2θ, deg	56.2	56.6
Number of unique reflections	1483	1650
Observed unique reflections ($I > 2\sigma(I)$)	1230	1521
Number of parameters	126	126
$R1$[a], w$R2$[b]	0.0377 (0.0490), 0.0903	0.0264 (0.0294), 0.0685
Goodness of fit	1.021	1.084
$(\Delta\rho)_{\text{max, min}}$, eÅ^{-3}	1.10, −0.73	0.91, −0.83

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. The value in parentheses is for all data.

[b] $wR2 = \sum\left\{\left[w(F_o^2 - F_c^2)^2\right]/\sum\left[w(F_o^2)^2\right]\right\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (\text{Max}\,F_o^2 + 2F_c^2)/3$, where $a = 0.0518$ and $b = 0$ for **1** and $a = 0.0343$ and $b = 0.27$ for **2**.

thermal parameters for all H atoms. All calculations were performed using the SHELXTL Version 5.1 software package [10].

3. Results and discussion

The crystallographic data, atomic coordinates and selected bond lengths for **1** and **2** are given in Tables 1, 2 and 3, respectively. The two compounds are isostructural and crystallize in the triclinic space group $P\bar{1}$ with a unit cell content of one formula unit. All atoms are at general positions. Fig. 2 shows the coordination environment of the Ga atom in **1**. Each gallium is bonded to four phosphate oxygen atoms and one 4,4′-bpy nitrogen atom at an axial position to form a GaO$_4$N trigonal bipyramid. The 4,4′-bpy molecule sits on an inversion center. The bipyridine molecules are planar and parallel to each other in an offset parallel-stacked geometry. The distance between the least-squares planes of adjacent 4,4′-bpy molecules is 3.44 Å, indicative of the presence of intermolecular aromatic interaction. The 4,4′-bpy ligands extend from the inorganic layers at an angle of ca. 51°.

Table 2
Atomic coordinates and thermal parameters for Ga$_2$(4,4′-bpy)(PO$_4$)$_2$ (**1**) and Ga$_2$(4,4′-bpy)(AsO$_4$)$_2$ (**2**)[a]

Atom	*x*	*y*	*z*	U_{eq} (Å^2)[b]
Compound **1**				
Ga(1)	0.66596(9)	0.79543(8)	0.90025(4)	0.0123(2)
P(1)	0.8454(2)	0.2796(2)	0.92558(9)	0.0114(2)
O(1)	0.1402(6)	0.2808(5)	0.9581(2)	0.0162(2)
O(2)	0.6720(6)	0.2261(5)	0.0345(2)	0.0159(6)
O(3)	0.8036(6)	0.0941(5)	0.8506(2)	0.0163(6)
O(4)	0.7661(6)	0.5203(5)	0.8495(2)	0.0154(6)
N(1)	0.4446(7)	0.8806(6)	0.7383(3)	0.0170(8)
C(1)	0.2793(9)	0.7189(9)	0.7175(4)	0.025(1)
C(2)	0.103(1)	0.7584(9)	0.6253(4)	0.026(1)
C(3)	0.0921(9)	0.9755(8)	0.5502(4)	0.0203(9)
C(4)	0.264(1)	0.1446(9)	0.5738(5)	0.034(1)
C(5)	0.433(1)	0.0908(9)	0.6673(4)	0.029(1)
H(1C)	0.30(1)	0.56(1)	0.761(6)	0.07(2)
H(2C)	−0.04(1)	0.63(1)	0.613(5)	0.06(2)
H(4C)	0.56(1)	0.203(9)	0.693(4)	0.03(1)
H(5C)	0.25(1)	0.29(1)	0.528(5)	0.04(2)
Compound **2**				
Ga(1)	0.66357(6)	0.79160(5)	0.89350(3)	0.0123(1)
As(1)	0.85145(6)	0.27684(5)	0.92550(2)	0.0112(1)
O(1)	0.1654(4)	0.2926(4)	0.9600(2)	0.0164(5)
O(2)	0.6722(4)	0.2118(4)	0.0464(2)	0.0171(4)
O(3)	0.8200(4)	0.0732(4)	0.8437(2)	0.0161(4)
O(4)	0.7588(4)	0.5237(4)	0.8391(2)	0.0162(4)
N(1)	0.4490(5)	0.8747(4)	0.7305(2)	0.0176(6)
C(1)	0.2856(7)	0.7174(6)	0.7082(3)	0.0228(7)
C(2)	0.1075(7)	0.7593(6)	0.6199(3)	0.0254(8)
C(3)	0.0938(6)	0.9753(6)	0.5482(3)	0.0205(7)
C(4)	0.2633(8)	0.1390(6)	0.5736(4)	0.0312(9)
C(5)	0.4374(8)	0.0832(6)	0.6640(3)	0.0296(8)
H(1C)	0.278(7)	0.583(6)	0.761(4)	0.018(9)
H(2C)	0.279(9)	0.286(7)	0.519(4)	0.04(1)
H(4C)	0.003(8)	0.645(7)	0.604(4)	0.03(1)
H(5C)	0.57(1)	0.19(1)	0.672(6)	0.07(2)

[a] The coordinates of hydrogen atoms are given in supplementary materials.

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

Table 3
Interatomic distances (Å) for Ga$_2$(4,4′-bpy)(PO$_4$)$_2$ (**1**) and Ga$_2$(4,4′-bpy)(AsO$_4$)$_2$ (**2**)

Compound **1**			
Ga(1)–O(1)	1.909(3)	Ga(1)–O(2)	1.836(3)
Ga(1)–O(3)	1.852(3)	Ga(1)–O(4)	1.860(3)
Ga(1)–N(1)	2.182(4)	P(1)–O(1)	1.522(3)
P(1)–O(2)	1.521(3)	P(1)–O(3)	1.541(3)
P(1)–O(4)	1.537(3)	C(1)–C(2)	1.384(7)
C(2)–C(3)	1.380(6)	C(3)–C(3)	1.486(3)
C(3)–C(4)	1.387(7)	C(4)–C(5)	1.377(7)
N(1)–C(1)	1.323(6)	N(1)–C(5)	1.327(6)
C(1)–H(1C)	0.94(7)	C(2)–H(2C)	1.07(7)
C(4)–H(4C)	0.90(6)	C(5)–H(5C)	1.00(5)
Compound **2**			
Ga(1)–O(1)	1.929(3)	Ga(1)–O(2)	1.843(2)
Ga(1)–O(3)	1.859(2)	Ga(1)–O(4)	1.871(2)
Ga(1)–N(1)	2.202(3)	As(1)–O(1)	1.672(2)
As(1)–O(2)	1.668(2)	As(1)–O(3)	1.689(2)
As(1)–O(4)	1.689(2)	C(1)–C(2)	1.381(5)
C(2)–C(3)	1.402(5)	C(3)–C(3)	1.485(6)
C(3)–C(4)	1.392(5)	C(4)–C(5)	1.390(5)
N(1)–C(1)	1.331(4)	N(1)–C(5)	1.339(4)
C(1)–H(1C)	0.92(4)	C(2)–H(2C)	0.92(5)
C(4)–H(4C)	0.99(4)	C(5)–H(5C)	0.94(6)

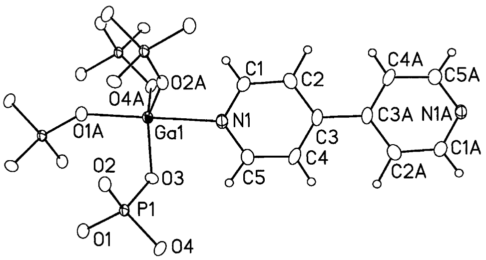

Fig. 2. The coordination environment of Ga in the structure of **1** showing atom labeling scheme. Thermal ellipsoids are shown at 50% probability. Small open circles represent hydrogen atoms.

As shown in Fig. 3a, the structure consists of gallium phosphate layers covalently linked through 4,4′-bpy pillars into a 3D framework. Thus, the structure exhibits the characteristic pattern of alternating organic/inorganic domains often observed in metal organophosphonate phases [11]. Several other members in the 4,4′-bpy-phosphate system also adopt a pillared layer structure [12–14]. The inorganic layer, shown in Fig. 3b, is constructed from corner-sharing GaO$_4$N trigonal bipyramids and PO$_4$ tetrahedra. The covalent connectivity in each layer produces two different

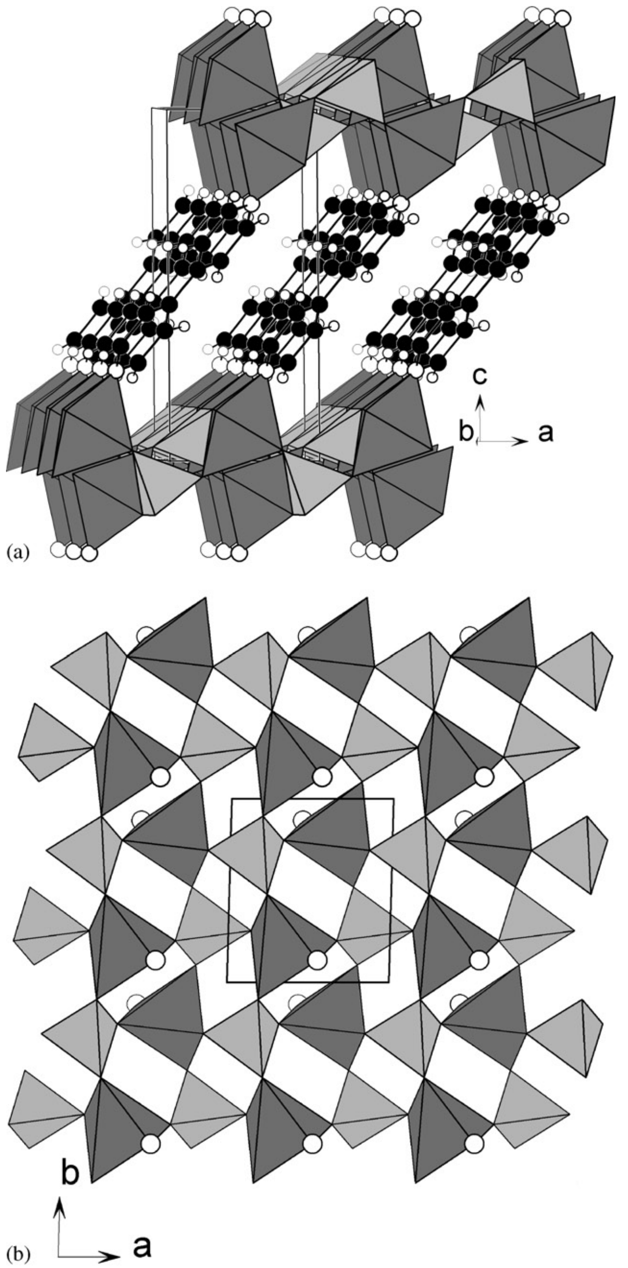

Fig. 3. (a) Structure of **1** viewed along the [010] direction. Polyhedra with darker and lighter gray patterns are GaO_4N trigonal bipyramids and PO_4 tetrahedra, respectively. Solid circles, C atoms; large open circles, N atoms; small open circles, H atoms. (b) Section of a gallium phosphate layer in **1** viewed along [001]. Open circles are N atoms.

four-membered $\{Ga_2P_2\}$ rings, which fuse to propagate the network structure. The layer structure is unusual as it is formed only by four-membered rings, which are one of the fundamental building units in solids possessing open structures. Each 4,4′-bpy ligand links two Ga atoms in adjacent layers to produce $[Ga_2(4,4'\text{-bpy})]$ as a structural unit. Each Ga is bonded to four phosphate oxygen atoms and each phosphate connects four Ga atoms to form a 3D neutral framework with the stoichiometry $Ga_2(4,4'\text{-bipy})(PO_4)_2$.

An interesting structural feature of **1** and **2** is the presence of exclusively five-coordinate gallium. The Ga atoms in most gallophosphates are found in four-, five-, and six-fold coordination, or in some combinations of the three. For example, $Ga_5(OH)_2(C_{10}H_9N_2)(C_2O_4)(PO_4)_4$, $Ga_4(PO_4)_4(OH) \cdot C_3H_{10}N \cdot 1.09H_2O$ ($GaPO_4$-14), $Rb_2[Ga_4(HPO_4)(PO_4)_4] \cdot 0.5H_2O$, and $Ga_{12}P_{12}O_{48}(OH)_4(C_6H_{18}N_2)_2 \cdot 4H_2O$ (Mu-8) consist of mixed four-, five-, and six-coordinate Ga [8, 15–17]. However, among the large number of gallophosphates that have been reported, few contain exclusively five-coordinate gallium. The cobalt-substituted gallophosphate $(NH_4)[CoGa_2P_3O_{12}(H_2O)_2]$ [18], $(4\text{-HAP})_2[Ga_4O(PO_4)_4(H_2O)_4]$ (AP = aminopyridine) [5], and $(NH_4)_3[Ga_2(PO_4)_3]$ [19] are three examples in which only five-coordinate Ga exists. Compounds **1** and **2** are the only examples in which each gallium is coordinated by one nitrogen and four oxygen atoms in a geometry of trigonal bipyramid.

The structures of the title compounds consist of metal phosphate layers pillared by 4,4′-bpy ligands. This type of structure is common and is seen in about a half of the compounds in the 4,4′-bpy-phosphate system. However, these compounds should be regarded condensed phases with little or no accessible interlayer space. It is interesting to explore the synthesis of open-framework materials in the 4,4′-bpy-phosphate system by including appropriate organic amine templates in their structures. Further research on this theme is underway.

Acknowledgments

The authors thank the National Science Council and Chinese Petroleum Corp. and the Robert A. Welch Foundation (A.J.J.) for support, and Ms. F.-L. Liao and Prof. S.-L. Wang at National Tsing Hua University for X-ray data collection.

References

[1] R. Kniep, Angew. Chem. Int. Ed. Engl. 25 (1986) 525 and references therein.
[2] A.K. Cheetham, G. Ferey, T. Loiseau, Angew. Chem. Int. Ed. Engl. 38 (1999) 3286 and references therein.
[3] F.-S. Xiao, S. Qiu, W. Pang, R. Xu, Adv. Mater. 11 (1999) 1091 and references therein.
[4] M. Estermann, L.B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, Nature 352 (1991) 320.
[5] M.-C. Hsien, H.-M. Kao, K.-H. Lii, Chem. Mater. 13 (2001) 2584.
[6] L.-C. Hung, H.-M. Kao, K.-H. Lii, Chem. Mater. 12 (2000) 2411.
[7] K.-H. Lii, C.-Y. Chen, Inorg. Chem. 39 (2000) 3374.
[8] C.-Y. Chen, P.P. Chu, K.-H. Lii, J. Chem. Soc. Chem. Commun. (1999) 1473.
[9] C.-Y. Chen, F.-R. Lo, H.-M. Kao, K.-H. Lii, Chem. Commun. (2000) 1061.
[10] G.M. Sheldrick, SHELXTL Programs, version 5.1, Bruker AXS GmbH, Karlsruhe, Germany, 1998.

[11] M.I. Kahn, J. Zubieta, Prog. Inorg. Chem. 34 (1995) 1.
[12] K.-H. Lii, Y.-F. Huang, Inorg. Chem. 38 (1999) 1348.
[13] Z. Shi, S. Feng, S. Gao, L. Zhang, G. Yang, J. Hua, Angew. Chem. Int. Ed. 39 (2000) 2325.
[14] L.-I. Hung, S.-L. Wang, H.-M. Kao, K.-H. Lii, Inorg. Chem. 41 (2002) 3929.
[15] J.B. Parise, Acta Crystallogr. C 42 (1986) 670.
[16] K.-H. Lii, Inorg. Chem. 35 (1996) 7440.
[17] P. Reinert, B. Marler, J. Patarin, Micropor. Mesopor. Mater. 39 (2000) 509.
[18] A.R. Overweg, J.W. de Hann, P.C.M.M. Magusin, R.A. van Santen, G. Sankar, J.M. Thomas, Chem. Mater. 11 (1999) 1680.
[19] F. Bonhomee, S.G. Thoma, T.M. Nenoff, Micropor. Mesopor. Mater. 53 (2002) 87.