Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Solid State Chemistry 174 (2003) 381–385
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

Synthesis and structure of organically templated lanthanum sulfate $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$

Yan Xing, Yunling Liu, Zhan Shi, He Meng, and Wenqin Pang*

College of Chemistry, State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jinlin University, Changchun 130023, People's Republic of China

Received 23 January 2003; received in revised form 18 April 2003; accepted 6 May 2003

Abstract

The first organically templated one-dimensional lanthanum sulfate $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$ has been prepared employing hydrothermal methods in the presence of diethylenetriamine (DETA). The structure was determined by single-crystal X-ray diffraction (XRD). The title compound crystallizes in the triclinic system, space group P-1 (No.2) with cell parameters $M = 551.30$, $a = 8.2773(7)$ Å, $b = 9.5660(6)$ Å, $c = 10.4363(6)$ Å, $\alpha = 105.661(2)^\circ$, $\beta = 102.849(3)^\circ$, $\gamma = 104.376(3)^\circ$, $V = 732.72(9)$ Å^3, $Z = 2$, $R = 0.0285$, w$R = 0.0778$. The structure consists of infinite linear chains. The chains are held together by hydrogen bond interactions involving the hydrogens of the amine and the framework oxygens. The as-synthesized product is characterized by powder XRD, inductive couple plasma analysis and thermogravimetric analysis.

Keywords: Hydrothermal methods; Lanthanum sulfate; Diethylenetriamine; Chain

1. Introduction

Since the pioneering works of Rao et al. [1,2] on the preparation of organically templated open-framework cadmium sulfates, there has been growing interest in the study of open-framework architectures containing oxo-anion of sulfur. Paul et al. recently reported several organically templated iron sulfates possessing Kagome and other types of layered networks [3,4]. O'Hare et al. have synthesized several organically templated uranium sulfates [5,6]. Moreover, an organically templated 3-D metal sulfate was recently reported by Wright et al. [7], which contains scandium and an azamacrocycle as the template.

Research activities in the area of lanthanide sulfates have aroused of interest due to their applications in the separation of rare earth elements. Even though many complexes and salts have been described in the literature, the report of structural information of lanthanide sulfates is comparatively limited [8]. In particular with anhydrous sulfates, only few structures have been reported only because of the difficulties in obtaining single crystals for the structure determination [9,10]. The known crystal structures of the rare earth sulfates are mainly restricted to two groups of compounds. One is inorganic sulfate hydrates with different water contents, such as $La_2(SO_4)_3\cdot 9H_2O$, $Ln_2(SO_4)_3\cdot 8H_2O$ (Ln = Ce, Dy, Yb) [11] and $(H_5O_2)M(SO_4)_2$ (M = Ho, Er, Y) [12]. The other group refers to ternary rare earth sulfates with alkaline metal ions or NH_4^+ as the third component [11,13–15]. Recently, Jacobson et al. synthesized the Yttrium-transition metal sulfates $YM(OH)_3(SO_4)$ (M = Ni, Cu) hydrothermally at high temperature and high pressure [16]. However, to our knowledge, lanthanide sulfates templated by organic amine are rarely reported hitherto [17–19]. In this paper, we report on the hydrothermal synthesis and X-ray structural characterization of one-dimensional lanthanum sulfate containing organic template, $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$.

2. Experimental

2.1. Synthesis and characterization

The title compound was prepared from a mixture of Lanthanum oxide (99.9%, Beijing Xinhua Chemical Reagent Factory), sulfuric acid (95–98 wt%, Beijing

*Corresponding author. Fax: +86-431-5671974.
E-mail address: wqpang@mail.jlu.edu.cn (W. Pang).

0022-4596/03/$ - see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/S0022-4596(03)00255-X

Chemical Plant), diethylenetriamine (DETA) (99%, Shenyang Chemical Plant), and deionized water. In a typical synthesis, solution **I** was prepared by dissolving 0.3 g of La_2O_3 into 10.0 mL diluted sulfuric acid (1.0 mL H_2SO_4/10.0 mL H_2O) under constant stirring, 0.52 mL DETA was added to 10.0 mL diluted sulfuric acid (0.3 mL H_2SO_4/10.0 mL H_2O) under stirring to make solution **II**. Then solution **I** was mixed with solution **II** under constant stirring. The resulting mixture with a molar ratio of 1.0 La_2O_3:24.4 H_2SO_4:4.8 DETA:1100 H_2O was transferred into a 30 mL Teflon-lined stainless-steel autoclave and heated at 373 K for 24 h. The product consisting of large cubic colorless single crystals (average dimensions: $1 \times 1 \times 0.5\,mm^3$) was recovered by filtration, washed with ethanol, and dried at room temperature (yield 70%, with respect to La).

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The step size was 0.02° and the count time was 4 s. The element analyses were performed on a Perkin-Elmer 2400 element analyzer and the inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer optima 3300 DV ICP spectrometer. The infrared (IR) spectrum was recorded within the 400–4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. A NETZSCH STA 449C unit was used to carry out the TGA and DTA analyses under nitrogen atmosphere with a heating rate of 10°C/min.

Table 1
Crystal data and structure refinement for $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$

Empirical formula	C4 H18 La N3 O13 S3	
Formula weight	551.30	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit-cell dimensions	$a = 8.2773(7)$ Å	$\alpha = 105.661(2)^\circ$
	$b = 9.5660(6)$ Å	$\beta = 102.849(3)^\circ$
	$c = 10.4363(6)$ Å	$\gamma = 104.376(3)^\circ$
Volume	732.72(9) $Å^3$	
Z	2	
Density (calculated)	2.499 Mg/m^3	
Absorption coefficient	3.421 mm^{-1}	
F(000)	544	
Crystal size $0.20 \times 0.2 \times 0.16\,mm^3$		
θ range for data collection	2.13–23.34°	
Limiting indices	$-8 \leqslant h \leqslant 9$, $-9 \leqslant k \leqslant 10$, $-11 \leqslant l \leqslant 11$	
Reflections collected/unique	3579/2058 [$R_{int} = 0.0425$]	
Completeness to $\theta = 23.34$	97.2%	
Absorption correction	Empirical	
Max. and min. transmission	0.6105 and 0.5478	
Refinement method	full-matrix least-squares on F^2	
Data/restraints/parameters	2058/3/229	
Goodness-of-fit on F^2	1.068	
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0285$, $wR_2 = 0.0778$	
R indices (all data)	$R_1 = 0.0287$, $wR_2 = 0.0780$	
Largest diff. peak and hole	1.180 and $-1.096\,e/Å^{-3}$	

2.2. Determination of crystal structure

A cubic crystal was selected from the batch and incised into a crystal of approximate dimensions, $0.20 \times 0.20 \times 0.16\,mm^3$, which was then mounted on a glass fiber. The intensity data were collected on a Siemens Smart CCD diffractometer. The numbers of collected reflections and independent reflections were 3579 and 2058, respectively. Data processing was accomplished with the SAINT processing program [20]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL Version 5.1 [21]. The lanthanum and sulfur atoms were first located and the carbon, nitrogen, oxygen atoms were found in difference Fourier maps. The hydrogen atoms of the amine molecule were placed geometrically. Crystal data, details of data collection, and refinement are given in Table 1.

3. Results and discussion

3.1. Charaterization

The ICP analysis shows that the compound contains 25.45 wt% La and 16.73 wt% S, in good agreement with the values (25.19 wt% La, 17.41 wt% S) based on the single-crystal structure analysis. The element analysis shows that the C, H, and N contents are 8.87, 3.22, and 7.61 wt%, respectively (calculated: C, 8.71 wt%; H, 3.26 wt%; N, 7.62 wt%), corresponding to an empirical molar ratio of C:H:N = 4.08:17.76:3.00. These results are in accordance with the formula $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$ obtained from the single-crystal analysis.

The powder XRD pattern of the as-synthesized $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$ and the pattern simulated on the basis of the single-crystal structure are presented in Fig. 1. The diffraction peaks on both patterns correspond well in position, indicating the phase purity of the as-synthesized sample.

Thermogravimetric analysis shows that the weight loss of the compound is ca. 3.58% from 100°C to 250°C corresponding to the loss of the guest water molecule (calc. 3.27%). There are two periods of sharp weight loss in the range 300–900°C (obs = 63.80%, calc. = 60.45%) due to the loss of amine molecules and SO_3. The structure collapses and converts into an amorphous phase after calcinations at 500°C for 2 h. The powder

XRD pattern of the sample heated at 900°C corresponds to $La_2O_2(SO_4)$ (JCPDS file card No. 16-0501).

3.2. Description of the structure

The selected bond lengths are listed in Table 2.

The asymmetric unit of $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$ contains 25 non-hydrogen atoms, 17 of which belong to the framework, including two non-equivalent lanthanum (La1, La2 with an occupancy of 0.5, respectively) atoms, 3 sulfate groups, and 8 to the guest (one Ow, three nitrogen and four carbon atoms) (Fig. 2). Both La atoms are 12-coordinated by oxygen atoms from the sulfate groups, each La site in the chain resembles the 12-coordinated site of $La_2(SO_4)_3\cdot 9H_2O$ [11]. They have typical geometrical parameters, with d_{av}[La(1)–O] = 2.716 Å and d_{av}[La(2)–O] = 2.696 Å. The values are in good agreement with those reported earlier [11]. All three S atoms form the centers of tetrahedral sulfate groups. The S–O bond distances in the SO_4 tetrahedron are in the range 1.448(3)–1.513(3) Å [$(S(1)–O)_{av}$ = 1.472 Å, $(S(2)–O)_{av}$ = 1.479 Å and $(S(3)–O)_{av}$ = 1.476 Å], with the O–S–O bond angles in the range 105.06(15)–112.74(18)°, [$(O–S(1)–O)_{av}$ = 109.40°, $(O–S(2)–O)_{av}$ = 109.41°, $(O–S(3)–O)_{av}$ = 109.40°]. The three independent S atoms represent the same chemically distinct types of sites. Each S atom makes four S–O–La linkages through two 2-coordinated oxygen

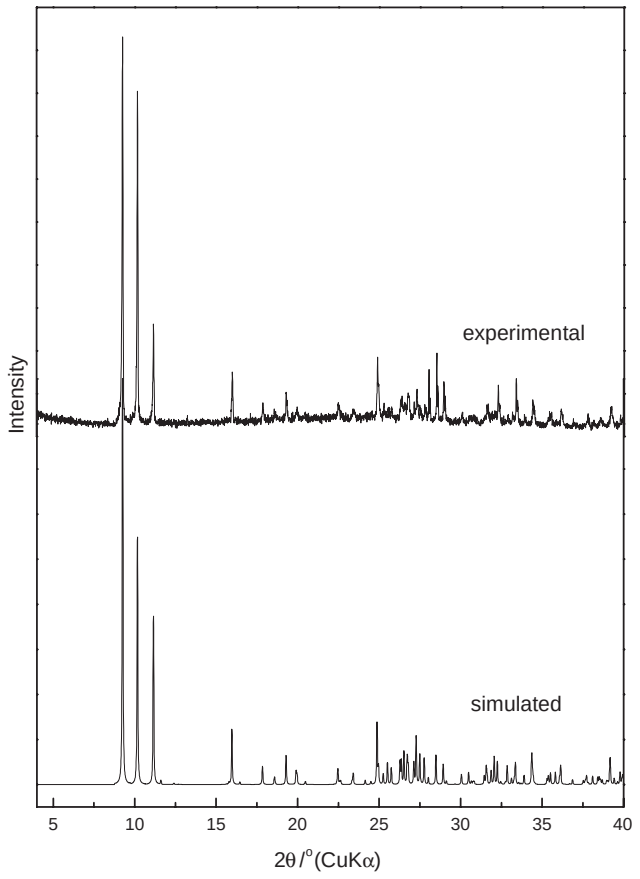

Fig. 1. Experimental and simulated powder XRD patterns of $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$.

Table 2
Selected bond lengths (Å) for $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$

La(1)–O(1)#1	2.589(2)	La(2)–O(6)	2.752(3)
La(1)–O(1)	2.589(2)	La(2)–O(2)	2.779(3)
La(1)–O(9)#1	2.599(3)	La(2)–O(2)#2	2.779(3)
La(1)–O(9)	2.599(3)	S(1)–O(4)	1.449(3)
La(1)–O(8)#1	2.728(3)	S(1)–O(2)	1.464(3)
La(1)–O(8)	2.728(3)	S(1)–O(3)	1.471(3)
La(1)–O(3)#1	2.734(3)	S(1)–O(1)	1.502(3)
La(1)–O(3)	2.734(3)	S(2)–O(7)	1.448(3)
La(1)–O(5)#1	2.810(3)	S(2)–O(5)	1.466(3)
La(1)–O(5)	2.810(3)	S(2)–O(6)	1.489(3)
La(1)–O(12)	2.839(3)	S(2)–O(8)	1.513(3)
La(1)–O(12)#1	2.839(3)	S(3)–O(10)	1.448(3)
La(2)–O(8)#2	2.609(3)	S(3)–O(11)	1.475(3)
La(2)–O(8)	2.609(3)	S(3)–O(12)	1.480(3)
La(2)–O(1)#2	2.632(3)	S(3)–O(9)	1.502(3)
La(2)–O(1)	2.632(3)	N(1)–C(1)	1.479(6)
La(2)–O(9)	2.671(3)	N(2)–C(3)	1.494(5)
La(2)–O(9)#2	2.671(3)	N(2)–C(2)	1.496(5)
La(2)–O(11)	2.736(3)	N(3)–C(4)	1.484(6)
La(2)–O(11)#2	2.736(3)	C(1)–C(2)	1.500(6)
La(2)–O(6)#2	2.752(3)	C(3)–C(4)	1.500(6)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z+1$; #2 $-x+1$, $-y$, $-z+1$.

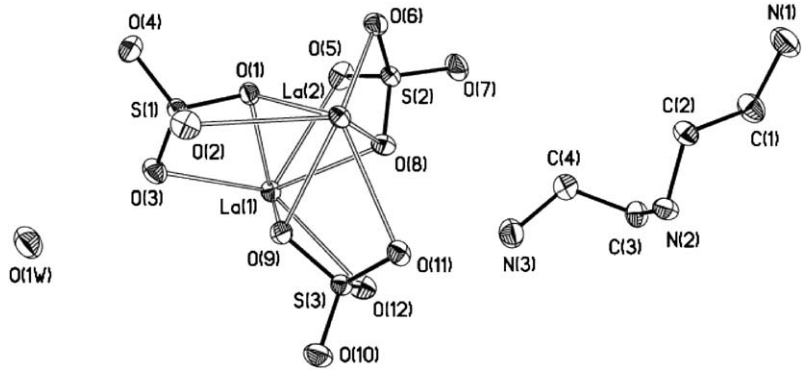

Fig. 2. ORTEP view of the $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$ structure showing the atom labeling scheme (50% thermal ellipsoids).

atoms [La–O–S bridges] and one 3-coordinated oxygen atom [S–(μ_3–O)–La_2 bridge]. The forth O atom of the sulfate group is an "unsaturated" =O atom. These three different types of S–O bonds show their expected differences in bond lengths: d_{av}[S–O] = 1.474 Å, d_{av}[S=O] = 1.448 Å, the longest S–O bond ($d_{av(\mu 3-O)}$ [S–O] = 1.506 Å) in SO_4 tetrahedron are associated with the three-coordinated oxygen atoms.

Among the 12 oxygens in the framework, three oxygens are in three-coordination [O(1), O(8) and O(9)]. The La–O–La linkages are accompanied by three-coordinated bridging oxygen atoms and the third coordination is to a sulfur. Furthermore, the three-coordinated oxygen atoms result in the formation of three-membered rings in the material. Such examples with three-coordinated oxygen atoms have been reported in organically templated metal phosphate [22,23].

The edge linkage of LaO_{12} polyhedra and SO_4 tetrahedra form the building unit, which are connected each other by sharing La atoms, in an alternating up–down manner, to give the isolated infinite chains of $[La(SO_4)_3]_n^{3-}$ running along the *a*-axis (Fig. 3). In the $[La(SO_4)_3]_n^{3-}$ chain, LaO_{12} polyhedra share faces via their three-coordinated oxygen atoms (O1, O8 and O9), and the SO_4 tetrahedra are grafted onto the chain via corner sharing and edge sharing. There are three infinite zigzag {–La–μ-O–La–μ-O–La–} chains, the angle between them is 120° and the La–La distance is 4.193 Å. The fully protonated triamine molecules and the water molecules are located in the inter-chain space. The amine and water molecules interact with the inorganic framework through N–H···O and O–H···O hydrogen bonding to hold the chains together (Fig. 4).

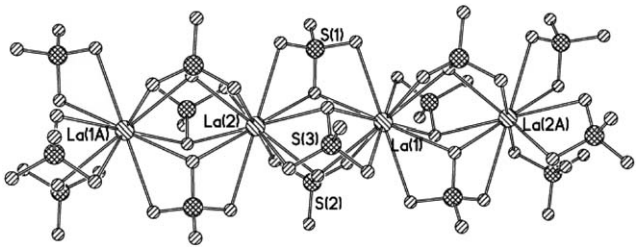

Fig. 3. Section of the $[La(SO_4)_3]_n^{3-}$ chain in $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$ running along the *a*-axis.

There are a few organically templated inorganic hosts with infinite-chain structures reported in the literature such as aluminophosphates [24], iron phosphates [25], gallium phosphates [26], zinc phosphates [27], titanium phosphates [28], nickel phosphate [29], cobalt phosphates [30], chromium phosphite [31], cadmium sulfate [1], and zinc oxalate [32]. In these chain structures, some of them occur as edge-shared ladders while some as corner-shared linear chains, made up of four-membered rings. In one-dimensional linear chain cadmium sulfate $[C_4N_2H_{12}][CdCl_2SO_4]\cdot H_2O$ [1], $CdCl_4O_2$ octahedra share edges in *trans*-fashion via their Cl atoms, and the SO_4 tetrahedra are grafted on to the chain in a symmetrical bridge. To our knowledge, the title compound is the first organically templated rare earth sulfate with chain structure in which the LaO_{12} polyhedra linked together by sharing face.

In conclusion, a new linear chain lanthanum sulfate in the presence of DETA as structure-directing agent has been synthesized and characterized. The exploratory synthesis of the new lanthanide sulfate by variation of template agent and crystallization conditions is in progress. The preliminary results will be reported soon.

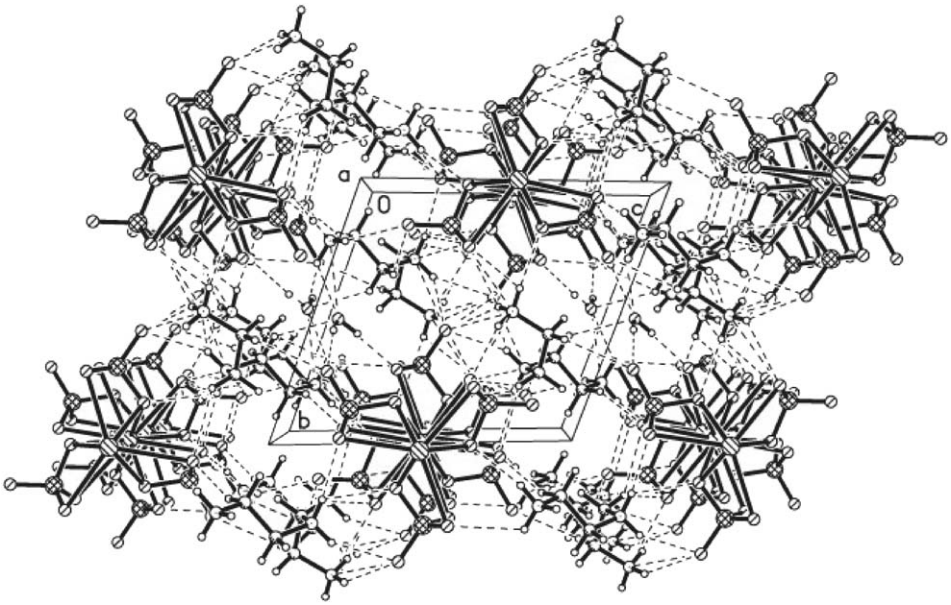

Fig. 4. The structure of $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$ viewed along the *a*-axis. Dotted lines represent hydrogen bonding.

Acknowledgments

The authors acknowledge the financial support of the State Basic Research Project of China (G200077507), the National Natural Science Foundation of China (20233030), and the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University.

References

[1] A. Choudhury, J. Krishnamoorthy, C.N.R. Rao, Chem. Commun. (2001) 2610.
[2] G. Paul, A. Choudhury, C.N.R. Rao, J. Chem. Soc. Dalton Trans. (2002) 3859.
[3] G. Paul, A. Choudhury, C.N.R. Rao, Chem. Commun. (2002) 1904.
[4] G. Paul, A. Choudhury, E.V. Sampathkumaran, C.N.R. Rao, Angew. Chem. Int. Ed. 41 (2002) 4297.
[5] A.J. Norquist, P.M. Thomas, M. Doran, D. O'Hare, Chem. Mater. 14 (2002) 5179.
[6] M. Doran, A.J. Norquist, D. O'Hare, Chem. Commun. (2002) 2946.
[7] I. Bull, P.S. Wheatley, P. Lightfoot, R.E. Morris, E. Sastre, P.A. Wright, Chem. Commun. (2002) 1180.
[8] M.S. Wickleder, Chem. Rev. 102 (2002) 2011.
[9] M.S. Wickleder, Z. Anorg. Allg. Chem. 625 (1999) 1548.
[10] M.S. Wickleder, Z. Anorg. Allg. Chem. 626 (2000) 1468.
[11] P.C. Junk, C.J. Kepert, B.W. Skelton, A.H. White, Aust. J. Chem. 52 (1999) 601.
[12] M.S. Wickleder, Chem. Mater. 10 (1998) 3212.
[13] J.C. Barnes, Acta Crystallogr. C 51 (1995) 2466.
[14] L.D. Iskhakova, V.A. Efremov, V.K. Trunov, Coord. Chem. (USSR) 7 (1981) 1417.
[15] S. Govindarajan, K.C. Patil, H. Manohar, P.E. Werner, J. Chem. Soc. Dalton. Trans. (1986) 119.
[16] X.Q. Wang, L.M. Liu, A.J. Jacobson, J. Solid State Chem. 147 (1999) 641.
[17] T. Bataille, D. Louer, J. Mater. Chem. 12 (2002) 3487.
[18] D. Wang, R. Yu, Y. Xu, S. Feng, R. Xu, N. Kumada, N. Kinomura, Y. Matsummura, M. Takano, Chem. Lett. 11 (2002) 1120.
[19] Y. Xing, Z. Shi, G.H. Li, W.Q. Pang, J. Chem. Soc. Dalton. Trans. (2003) 940.
[20] Software packages SMART and SAINT, Simens Analytical X-ray Instruments Inc., Madison, WI, 1996.
[21] G.M. Sheldrick, SHELXTL-NT, Version 5.1, Bruker AXS Inc., Madison, WI, 1997.
[22] T.Y. Song, M.B. Hursthouse, J.S. Chen, R.R. Xu, J.M. Thomas, Adv. Mater. 6 (1994) 679.
[23] R.K. Chiang, C.C. Huang, C.R. Lin, J. Solid State Chem. 156 (2001) 242.
[24] W. Yan, J. Yu, Z. Shi, R. Xu, Inorg. Chem. 40 (2001) 379;
S. Olive, A. Kuperman, A. Lough, G.A. Ozin, Inorg. Chem. 35 (1996) 6373;
Q.M. Gao, J.S. Chen, S.G. Li, R.R. Xu, J.M. Thomas, M. Light, M.B. Hursthouse, J. Solid State Chem. 127 (1996) 145.
[25] K.-H. Lii, Y.-F. Huang, V. Zima, C.-Y. Huang, H.-M. Lin, Y.-C. Jiang, F.-L. Liao, S.-L. Wang, Chem. Mater. 10 (1998) 2599;
S. Mahesh, M.A. Green, S. Natarajan, J. Solid State Chem. 165 (2002) 334.
[26] R.I. Walton, F. Millange, D. O'Hare, C. Paulet, T. Loiseau, G. Férey, Chem. Mater. 12 (2000) 1977;
R.I. Walton, F. Millange, A. Lebail, T. Loiseau, C. Serre, D. O'Hare, G. Férey, Chem. Commun. (2000) 203;
H.-M. Lin, K.-H. Lii, Inorg. Chem. 37 (1998) 4220.
[27] C.N.R. Rao, S. Natarajan, A. Choudhury, S. Neeraj, A.A. Ayi, Acc. Chem. Res. 34 (2001) 80;
A. Choudhury, S. Natarajan, C.N.R. Rao, Inorg. Chem. 39 (2000) 4295;
S. Natarajan, Solid State Sci. 4 (2002) 1331;
S. Natarajan, Inorg. Chem. 41 (2002) 5530.
[28] Y. Guo, Z. Shi, J. Yu, J. Wang, Y. Liu, N. Bai, W. Pang, Chem. Mater. 13 (2001) 203.
[29] Y. Liu, L. Zhang, Z. Shi, H. Yuan, W. Pang, J. Solid State Chem. 158 (2001) 68.
[30] A. Choudhury, S. Natarajan, C.N.R. Rao, J. Chem. Soc. Dalton Trans. (2000) 2595;
Ray-Kuang Chiang, J. Solid State Chem. 153 (2000) 180.
[31] S. Fernandez, J.L. Mesa, J.L. Pizarro, L. Lezama, M.I. Arriortua, T. Rojo, Angew. Chem. Int. Ed. 41 (2002) 3683.
[32] R. Vaidhyanathan, S. Natarajan, C.N.R. Rao, J. Chem. Soc. Dalton Trans. (2001) 699.