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# Preparation of $\text{Bi}_2\text{S}_3$ nanorods by microwave irradiation

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## Abstract

$\text{Bi}_2\text{S}_3$  nanorods, with a diameter of ca. 10 nm and a length of up to ca. 300 nm, have been successfully prepared from a formaldehyde solution of bismuth nitrate and thiourea by microwave irradiation. Powder X-ray diffraction (XRD) pattern indicates that the product is pure orthorhombic  $\text{Bi}_2\text{S}_3$  phase. The product is also characterized by the techniques of transmission electron microscopy (TEM) and X-ray photoelectron spectra (XPS). © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* A. semiconductors; A. nanostructures; B. chemical synthesis; C. X-ray diffraction

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## 1. Introduction

Currently, one-dimensional (1D) nanostructured materials have been the focus of recent scientific research due to their unusual properties and potential uses in both mesoscopic research and the development of nanodevices [1–6]. Especially, synthesis of semiconductor nanorods or nanofibers and the investigation of their properties have prompted considerable interest [1–3,7–14]. Control over both nanocrystalline morphology and the crystal size is a new challenge to synthetic chemists and materials scientists [14]. Especially, soft solution processing has been proven to be a convenient, economical, less energy and material consuming, and environmentally friendly way to produce shaped/sized/oriented advanced materials in only one step [15,16].

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Main-group metal chalcogenides such as the  $A^V_2B^{VI}_3$  ( $A = \text{Sb, Bi, As}$ ;  $B = \text{S, Se, Te}$ ) group compounds are semiconductors, and have applications in television cameras with photoconducting targets, thermoelectric devices, and electronic and optoelectronic devices and in IR spectroscopy [17]. Bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) is a semiconductor material with a direct band gap  $E_g$  of 1.3 eV [18], and is useful for photodiode arrays or photovoltaics [19,20]. Conventionally, bismuth sulfide is prepared by direct element reaction in a quartz vessel at high temperature [17,21]. The chemical deposition method has been applied to prepare bismuth sulfide through a reaction of bismuth salt complexed by trethanolamine (TEA) or EDTA in an aqueous solution containing a sulfur source such as thioacetamide, thiourea, sodium thiosulphate, or gaseous  $\text{H}_2\text{S}$ . The powders obtained through this route are mostly amorphous or poorly crystallized [22–27]. Colloidal suspensions of bismuth sulfide have been prepared in water at room temperature with solution of  $\text{Bi}(\text{NO}_3)_3$  and  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  as the starting materials, but sodium hexametaphosphate is needed to stabilize  $\text{Bi}^{3+}$ , and only colloidal particles can be obtained [28]. Crystallized bismuth sulfide has been prepared by thermal decomposition of bismuth dithiocarbamate complexes [29], metal ethylxanthate [30], Bi–thiourea complex [31], and thiosulfatobismuth [32]. However, high temperature is required, and the final products contain some impurities.  $\text{Bi}_2\text{S}_3$  nanorods and  $\text{Bi}(\text{Se,S})$  nanowires have been prepared by the hydrothermal and solvothermal preparation techniques [33–35], but those techniques need longer reaction time, higher temperature, and higher pressure.

Since 1986, microwave irradiation as an efficient heating method has been found to have a number of applications in chemistry. The microwave synthesis, which is generally quite fast, simple, and very energy efficient, has been developed, and widely used to prepare zeolites and inorganic materials, etc. [36–42]. Compared with the conventional methods, the microwave synthesis has the advantages of a short reaction time, small particle size, narrow particle size distribution, and high purity. Jansen et al. suggested that these advantages could be attributed to fast homogeneous nucleation and the easy dissolution of the gel [43]. Unfortunately, the exact nature of the interaction of the microwaves with the reactants during the synthesis of materials is somewhat unclear and speculative. However, it is well known that the interaction of dielectric materials, liquids or solids, with microwaves leads to what is generally known as dielectric heating. Electric dipoles present in such materials respond to the applied electric field. In liquids, this constant reorientation leads to friction between molecules, which subsequently generates heat [44].

In this study, we report on the preparation of bismuth sulfide nanorods with a diameter of ca. 10 nm and a length of up to ca. 300 nm in a formaldehyde solution of bismuth nitrate and thiourea by microwave irradiation. The product was characterized by the techniques of transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and X-ray photoelectron spectra (XPS).

## 2. Experimental section

In a typical procedure, 0.005 mol analytical-grade  $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$  and 0.01 mol thiourea were dissolved in 100 mL formaldehyde (aqueous solution with 37.0–40.0% HCHO in it).

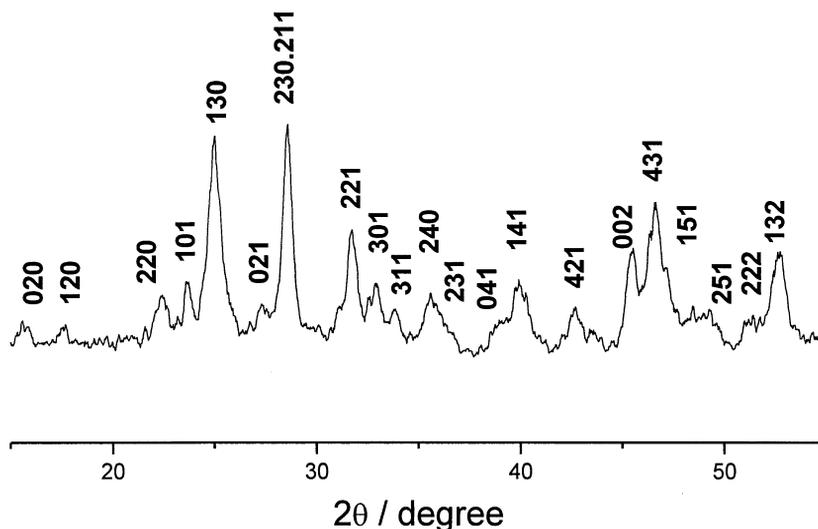


Fig. 1. X-ray diffraction (XRD) pattern of the obtained sample  $\text{Bi}_2\text{S}_3$ .

Then, the mixture solution was reacted in a microwave refluxing system for 20 min. The microwave oven followed a working cycle of 9 min on and 21 min off. (30% power) After cooling to room temperature, the precipitates were centrifuged, washed with 0.5 M HCl, distilled water, and acetone in sequence, and dried in air. The final dark brown product was collected for characterizations.

Powder X-ray diffraction (XRD) was used to characterize the sample. Data were collected on a Shimadzu XD-3A X-ray diffractometer (Cu  $K\alpha$  radiation,  $\lambda = 0.15418$  nm). Further evidence for the purity of  $\text{Bi}_2\text{S}_3$  was obtained by the X-ray photoelectron spectra (XPS) of the product. The X-ray photoelectron spectra (XPS) were recorded on an ESCALAB MK II X-ray photoelectron spectrometer, using nonmonochromatized Mg  $K\alpha$  X-ray as the excitation source. The morphology and size were determined by transmission electron microscopy (TEM). The TEM images were recorded on a JEOL-JEM 200CX transmission electron microscope, using an accelerating voltage of 200 kV. The samples used for TEM observations were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 30 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon.

### 3. Results and discussion

The XRD pattern of the product is shown in Fig. 1. All the reflections in Fig. 1 can be indexed to be a pure orthorhombic phase  $\text{Bi}_2\text{S}_3$ , which is in good agreement with literature (JCPDS File No. 17-320). Fig. 2 shows the XPS spectra of the above sample. On the wide XPS picture (Fig. 2a), the C1s peak lies at 290.0 eV, which should be corrected to 284.6 eV. All the other peaks are corrected accordingly. No peaks of other elements except C, Bi, and S are observed on the picture, indicating the high purity of the product. Fig. 2b and c are

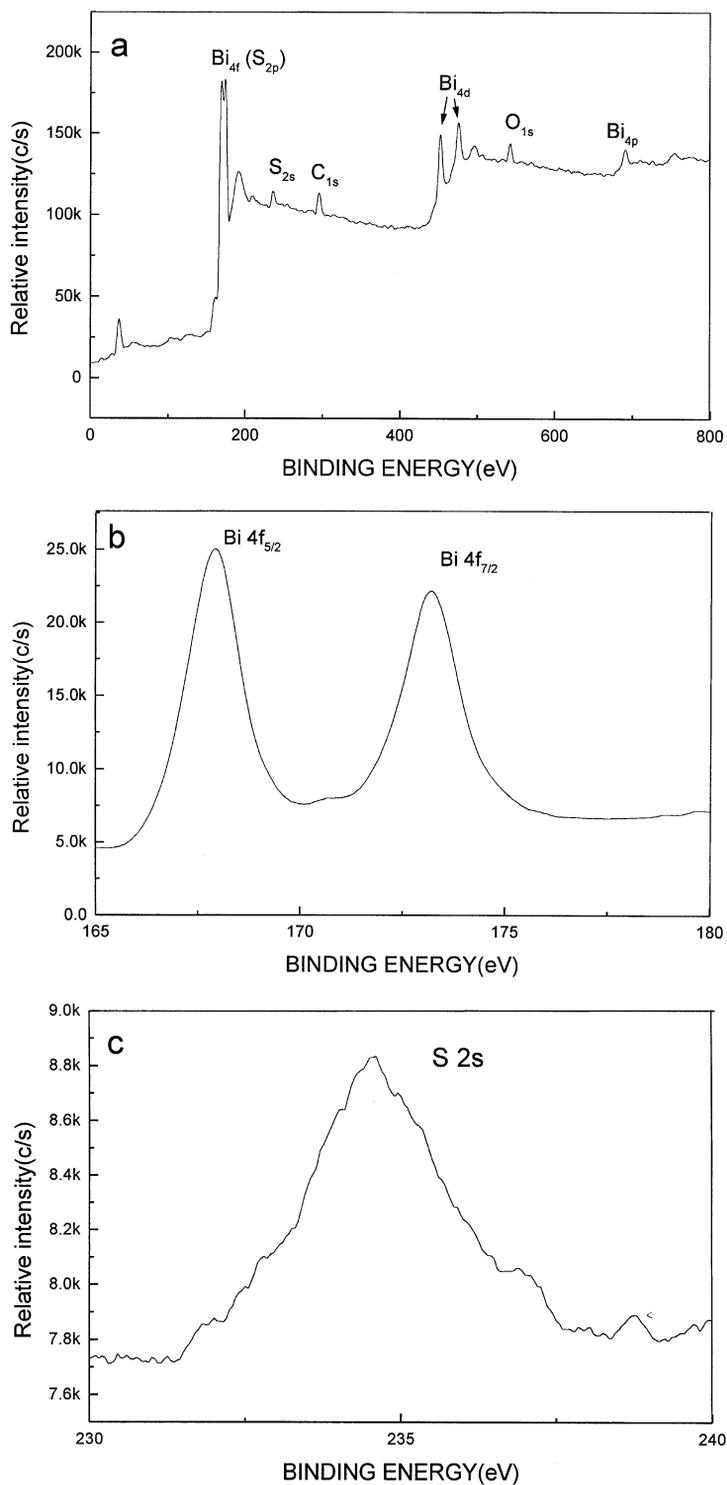


Fig. 2. XPS analysis of the sample as-prepared  $\text{Bi}_2\text{S}_3$ . (a) Survey scan, (b) Bi region, (c) S region.

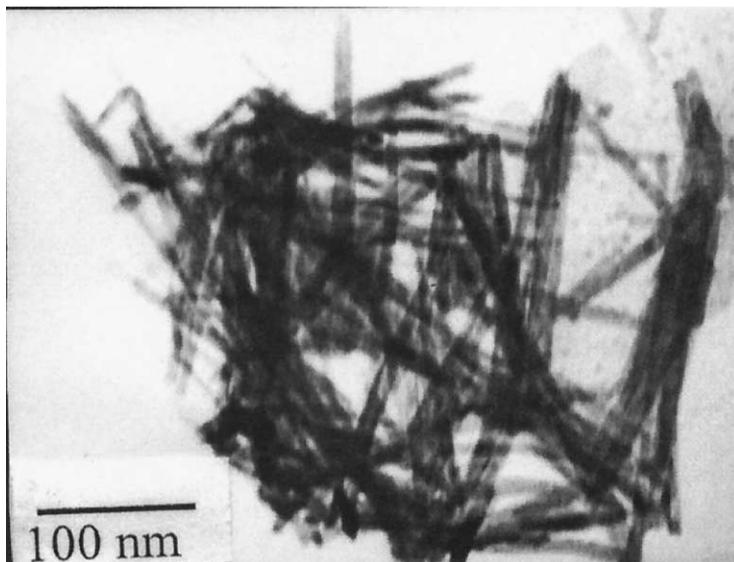


Fig. 3. TEM image of as-prepared  $\text{Bi}_2\text{S}_3$ .

high-resolution XPS spectra taken for Bi and S regions of the sample. The two strong peaks in Fig. 2b at 167.8 eV and 173.0 eV correspond to the Bi (4f) transitions, and the peak at 234.2 eV (Fig. 2c) is attributed to the S (2s) binding energy. Fig. 3 shows the TEM image of as prepared nanocrystalline  $\text{Bi}_2\text{S}_3$ . This image reveals that the product consists of uniform rods with an average diameter of ca. 10 nm and a length of up to ca. 300 nm. The particles are rod-like in shape, which is similar to those of the powders prepared by the direct reaction of bismuth and sulfur in inert atmosphere at high temperature [29]. The observed morphology of bismuth sulfide particles is possible due to its inherent chain-type structure according to the literature [17]. It is known that  $\text{Bi}_2\text{S}_3$  crystallizes with a lamellar structure with linked  $\text{Bi}_2\text{S}_3$  units forming infinite chains, which in turn, are connected via weaker van der Waals interactions. It seems that the formation of  $\text{Bi}_2\text{S}_3$  nanorods originates from the preferential directional growth of  $\text{Bi}_2\text{S}_3$  crystallites. The effects of microwave power and reaction time on the formation of  $\text{Bi}_2\text{S}_3$  nanorods were investigated. Microwave power and reaction time have influence on the formation of  $\text{Bi}_2\text{S}_3$  nanorods. The experiment shows that bumping would occur when the power was larger than 40%. When reaction time was less than 11 min the decomposition reaction would not happen, and the color did not turn to dark. The color of the solution turned deeper and deeper with the reaction time increasing. When the reaction time was over 12 min, the color of the solution become dark brown, which shows the formation of  $\text{Bi}_2\text{S}_3$ .

In this process, formaldehyde solution is selected as the solvent to obtain pure and uniform  $\text{Bi}_2\text{S}_3$  nanorods. Other solvents, such as water and ethanol, were also tested in our experiments. However, the results show that when they were selected as solvents, the products consisted of short rods in aggregated states. In our experiments, thiourea is selected as a sulfur source due to the formation of uniform and small-sized nanorods. When thioacetamide (TAA) was used as a sulfur source, we also succeeded in preparing  $\text{Bi}_2\text{S}_3$  nanorods. In this

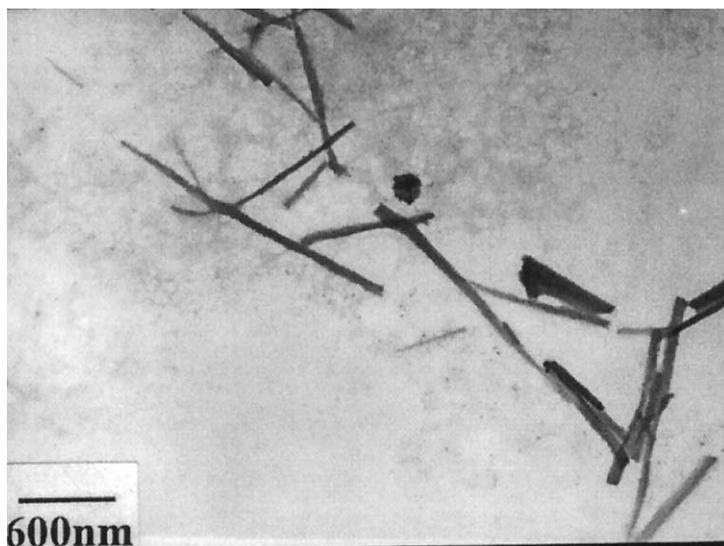
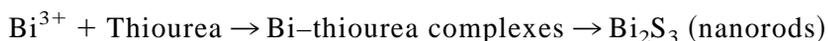


Fig. 4. The image of the Bi<sub>2</sub>S<sub>3</sub> nanorods prepared using TAA as the sulfur source.

case, the as-prepared nanorods appeared to be thicker and longer. The product had an average diameter of 50 nm and length up to 1–2  $\mu\text{m}$ .

We have also carried out experiments to investigate the influence of the reactants' concentrations on the formation of the products. When the concentration of Bi(NO<sub>3</sub>)<sub>3</sub> was in the range of 0.01–0.06 M, uniform and stable nanorods were obtained. When the concentration decreased to 0.005 M, the products consisted of aggregated unstable nanorods that decomposed under the electron beam of TEM. When the concentration increased to over 0.1 M, the experiments were unsuccessful because the reactants could not solubilize completely in the formaldehyde solution.

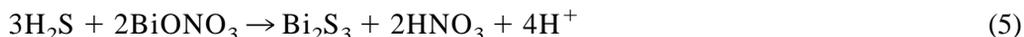
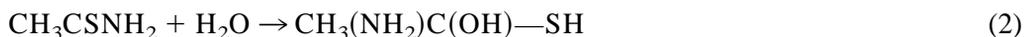
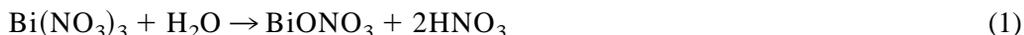
The proposed mechanism of microwave synthesis of Bi<sub>2</sub>S<sub>3</sub> nanorods may be as follow: first, the strong complex action between Bi<sup>3+</sup> and thiourea leads to the formation of Bi–thiourea complexes in the microwave synthesis, which prevent the production of a large number of free S<sup>2-</sup> in the solution, and will be favorable for the formation of the nanorods. Our observation confirms that Bi(NO<sub>3</sub>)<sub>3</sub> and thiourea can easily dissolve in formaldehyde solution to form a yellow solution, indicating the formation of Bi–thiourea complexes. Second, the Bi–thiourea complexes undergo a decomposition process under microwave irradiation for a certain period of time to produce Bi<sub>2</sub>S<sub>3</sub> nanorods. The formation of Bi<sub>2</sub>S<sub>3</sub> nanorods can be expressed as the following [45]:



The Bi<sub>2</sub>S<sub>3</sub> nanorods synthesized in our work are uniform, and smaller than those reported before [33,34,45]. The microwave irradiation decomposition of the Bi–thiourea complexes is favorable for the oriented growth of the nanorods. In the microwave heating environment, it shows a more rapid and simultaneous nucleation than the conventional heating method due to the fast and homogeneous heating effects of microwaves. Moreover, because of the

simultaneous nucleation and homogeneous heating, uniformly small particles can be synthesized. In addition, the solvent acts as both reaction media and dispersion media so that it will prevent the aggregation of the particles and favor producing a uniform  $\text{Bi}_2\text{S}_3$  powder with good dispersivity.

In the case of using TAA as a sulfur source, the reaction process follows a different mechanism. During the whole process, HCHO does not take part in the reactions but only acts as a dispersant. The whole process can be described as below:



In aqueous environment,  $\text{Bi}(\text{NO}_3)_3$  reacts with  $\text{H}_2\text{O}$  to produce  $\text{BiONO}_3$ . Meanwhile,  $\text{H}_2\text{O}$  reacts with  $\text{CH}_3\text{CSNH}_2$  to form  $\text{CH}_3(\text{NH}_2)\text{C}(\text{OH})\text{—SH}$  by the microwave heating. Repeating this process results in the formation of  $\text{CH}_3(\text{NH}_2)\text{C}(\text{OH})_2$  and  $\text{H}_2\text{S}$ . Then  $\text{CH}_3(\text{NH}_2)\text{C}(\text{OH})_2$  immediately loses water to give  $\text{CH}_3\text{CONH}_2$ . The decomposition process of  $\text{CH}_3\text{CSNH}_2$  in aqueous solution under microwave irradiation is shown in Eqs. (2) to (4). The released  $\text{H}_2\text{S}$  reacts with  $\text{Bi}(\text{NO}_3)_3$  to yield  $\text{Bi}_2\text{S}_3$  nanorods. In this case, the  $\text{Bi}_2\text{S}_3$  nanorods are not formed via the decomposition of precursor complex but the product of the reaction between  $\text{BiONO}_3$  and free  $\text{H}_2\text{S}$ . As a result, the product has a larger diameter and length.

#### 4. Conclusions

$\text{Bi}_2\text{S}_3$  nanorods have been successfully prepared by the microwave heating method. The advantages of this process are that it is a simple, fast, and efficient method for producing nanocrystalline metal sulfides. We can foresee the upscaling of the process to form large quantities of this kind of nanomaterials.

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#### References

- [1] A.M. Morales, C.M. Lieber, *Science* 279 (1998) 208.
- [2] W.Q. Han, S.S. Fan, Q.Q. Li, Y.D. Hu, *Science* 277 (1997) 1287.

- [3] A.P. Alivisatos, *Science* 271 (1996) 933.
- [4] H. Dai, E.W. Wong, Y.Z. Lu, S. Fan, C.M. Lieber, *Nature* 375 (1995) 769.
- [5] S. Saito, *Science* 278 (1997) 77.
- [6] K. Suenaga, C. Colliex, N. Demoncey, A. Loiseau, H. Pascard, F. Willaime, *Science* 278 (1997) 653.
- [7] P.V. Braun, P. Osenar, S.I. Stupp, *Nature* 380 (1996) 325.
- [8] T.J. Trentler, K.M. Hickman, S.C. Goel, A.M. Viano, P.C. Gibbons, W.E. Buhro, *Science* 270 (1995) 1791.
- [9] T.J. Trentler, S.C. Goel, K.M. Hickman, A.M. Viano, M.Y. Chiang, A.M. Beatty, et al., *J. Am. Chem. Soc.* 119 (1997) 2172.
- [10] J.P. Yang, F.C. Meldrum, J.H. Fendler, *J. Phys. Chem.* 99 (1995) 5500.
- [11] J.D. Klein, R.D. Herrick, D. Palmer, M.J. Sailor, *Chem. Mater.* 5 (1993) 902.
- [12] C.R. Martin, *Science* 266 (1994) 1961.
- [13] D. Routkevitch, T. Bigioni, M. Moskovits, J.M. Xu, *J. Phys. Chem.* 100 (1995) 14037.
- [14] J.J. Shiang, A.V. Kadavanich, R.K. Grubbs, A.P. Alivisatos, *J. Phys. Chem.* 99 (1995) 17417.
- [15] M. Yoshimura, *J. Mater. Res.* 13 (1998) 769.
- [16] M. Yoshimura, W. Suchanek, *Solid State Ionics* 98 (1997) 197.
- [17] D. Arivuoli, F.D. Gnanam, P. Ramasamy, *J. Mater. Sci. Lett.* 7 (1988) 711.
- [18] J. Black, E.M. Conwell, L. Seigle, C.W. Spencer, *J. Phys. Chem. Solids* 2 (1957) 240.
- [19] B.B. Nayak, H.N. Acharya, G.B. Mitra, B.K. Mathur, *Thin Solid Films* 105 (1983) 17.
- [20] S.H. Pawar, P.N. Bhosale, M.D. Uplane, S. Tanhankar, *Thin Solid Films* 110 (1983) 165.
- [21] C. Kaito, Y. Saito, K. Fujita, *J. Cryst. Growth* 94 (1989) 9677.
- [22] S. Biswas, A. Mondal, D. Mukherjee, P. Pramanik, *J. Electrochem. Soc.* 33 (1986) 48.
- [23] P. Pramanik, S. Bhattacharya, *J. Mater. Sci. Lett.* 6 (1988) 1105.
- [24] C.D. Lokhande, V.S. Yermune, S.H. Pawar, *J. Electrochem. Soc.* 135 (1988) 1852.
- [25] R.D. Engelken, S. Ali, L.N. Chang, C. Brinkley, K. Turner, C. Hester, *Mater. Lett.* 10 (1990) 264.
- [26] N.S. Yesugade, C.D. Lokhande, C.H. Bhosale, *Thin Solid Films* 263 (1995) 145.
- [27] J.D. Desai, C.D. Lokhande, *J. Indian, Pure Appl. Phys.* 31 (1993) 152.
- [28] B.F. Variano, D.M. Hwang, C.S. Sandroff, P. Wiltzius, T.W. Jing, N.P. Ong et al., *J. Phys. Chem.* 91 (1987) 6455.
- [29] R. Nomura, K. Kanaya, H. Matsuda, *Bull. Chem. Soc. Jpn.* 62 (1989) 939.
- [30] S.V. Larionov, L.A. Patrino, E.M. Uskov, *Izv. Sib. Otd. Akad. Nauk SSSR. Ser. Khim. Nauk* 3 (1979) 94.
- [31] V.N. Popov, A.B. Kolodezev, V.P. Safonov, *Tezisy Dokl. Vses. Soveshch. Tekhnol., protsessy, Appar. Kach. Prom. Lyuminoforov* (1977) 98.
- [32] A. Cyganski, J. Kobylecka, *Thermochim. Acta* 45 (1981) 65.
- [33] S.H. Yu, J. Yang, Y.S. Wu, Z.H. Han, Y. Xie, Y.T. Qian, *Mater. Res. Bull.* 33 (11) (1998) 1661.
- [34] S.H. Yu, Y.T. Qian, L. Shu, Y. Xie, J. Yang, C.S. Wang, *Mater. Lett.* 35 (1998) 116.
- [35] H. Su, Y. Xie, P. Gao, H. Lu, Y. Xiong, Y.T. Qian, *Chem. Lett.* (2000) 790.
- [36] I. Girnus, K. Jancke, R. Vetter, J. Richter-Mendau, J. Caro, *Zeolites* 15 (1995) 33.
- [37] I. Girnus, K. Hoffmann, F. Marlow, J. Caro, G. Doering, *Microporous Mater.* 2 (1994) 537.
- [38] X.C. Xu, W.S. Yang, J. Liu, L.W. Lin, *Adv. Mater.* 3 (12) (2000) 195.
- [39] X.H. Liao, J.M. Zhu, J.J. Zhu, J.Z. Xu, H.Y. Chen, *Chem. Commun.* (2001) 937.
- [40] O. Palchik, J.J. Zhu, A. Gedanken, *J. Mater. Chem.* 10 (2000) 1251.
- [41] J.J. Zhu, O. Palchik, S.G. Chen, A. Gedanken, *J. Phys. Chem. B* 104 (2000) 7344.
- [42] O. Palchik, I. Felner, G. Kataby, A. Gedanken, *J. Mater. Res.* 15 (10) (2000) 2176.
- [43] J.C. Jansen, A. Arafat, A.K. Barakat, H. Van Bekkum, in: M.L. Occelli, H. Robson, Eds., *Synthesis of Microporous Materials*, Vol. 1, Van Nostrand Reinhold, New York 1992, p. 507.
- [44] K.J. Rao, B. Vaidyanathan, M. Gaguli, P.A. Ramakrishnan, *Chem. Mater.* 11 (1999) 882–895.
- [45] S.H. Yu, L. Shu, J. Yang, Z.H. Han, Y.T. Qian, Y.H. Zhang, *J. Mater. Res.* 14 (11) (1999) 4157.