Journal of Alloys and Compounds 481 (2009) 450–454

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Solvothermal growth of NiS single-crystalline nanorods

Pengfei Yang[a], B. Song[b,c], R. Wu[a], Yufeng Zheng[a], Yanfei Sun[a], J.K. Jian[a,*]

[a] *College of Physical Science and Technology, Xinjiang University, No. 14, Shengli Road, Urumqi, Xinjiang, 830046, PR China*
[b] *Institute of Physics, Chinese Academy of Sciences, Beijing 100080, PR China*
[c] *Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150080, PR China*

ARTICLE INFO

Article history:
Received 23 January 2009
Received in revised form 26 February 2009
Accepted 26 February 2009
Available online 17 March 2009

Keywords:
Nanostructures
Crystal growth
Scanning and transmission electron microscopy

ABSTRACT

Nanorods of NiS were successfully prepared by a solvothermal synthetic route using S and Ni powders as reagents in ethylenediamine (en) solvent at the temperature of 200 °C. The as prepared NiS nanorods were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). It was found that the nanorods have diameters and lengths in the region from 80 nm to 120 nm, and from 2 μm to 3 μm, respectively. The NiS nanorods are single crystals with millerite structure. On the basis of the experimental results and corresponding literatures, a possible growth mechanism of the NiS nanorods crystals is discussed.

1. Introduction

In the past few decades, inorganic nanocrystals with controlled size and shape have drawn much attention from both fields of science and technology due to their unique properties and potential applications in nanodevices [1–3]. In particular, one-dimensional nanostructures such as nanowires, nanorods, and nanotubes are currently hot focus because of their special properties [4–6].

Metal sulfides are a kind of materials with great technology-importance. Among them, nickel sulfides have been paid much attention because of their potential applications [7]. Until now, many methods have been employed to prepare novel structure of NiS. It was reported that organic-monolayer-coated NiS nanorods and triangular nanoprisms were synthesized using a solventless thermal decomposition of nickel thiolate precursors in the presence of octanoate [8]. NiS layer-rolled structures was synthesized by Jiang et al. in aqueous ammonia solution [9], and nickel sulfides was synthesized in aqueous solution by Jeong and Manthiram [10]. The solvothermal and hydrothermal methods have been also developed to prepare nickel sulfide nanocrystals with various morphologies [11–13]. Qian's group reported three-dimensional flower-like architectures of β-NiS were successfully prepared via a hydrothermal route in the presence of thisodium citrate and ammonia [14]. In addition, multiple morphologies of nickel sulfides, including hierarchical dendrites, nanobelts, could be directly grown on nickel foils [15]. Shen et al. synthesized NiS nanorods in hydrazine hydrate saturated with CO_2 [16]. Yu and Yoshimura prepared various phases of nickel sulfides through the reactions between Ni substrate or Ni^{2+} and sulfur in different solvents, and observed NiS nanowhiskers co-existing with other nickel sulfides [17]. Examining the previous reports in details, it can be found that the phases and morphologies would be affected by the form of nickel source and S source.

To the best of our knowledge, no work on the preparation of nickel sulfide using S powder and Ni powder as reagents has been reported up to now. In addition, it would be valuable to explore an additive-free solution route to prepare uniform NiS nanorods. Herein, we presented a convenient solvothermal route to prepare single-crystalline nanorods of NiS directly using S and Ni powders as starting reagents in pure en solvent, and investigated the effects of the molar ratio of Ni to S on the phases and morphologies of the products. The probable growth mechanism of the NiS nanorods was discussed too.

2. Experimental

All reagents are analytic grade and used without further purification. In a typical procedure, 0.01 mol of S (99.7%) and 0.01 mol of Ni powder (99.5%) were added into Teflon-lined stainless-steel autoclave filled with en to 80% of its total capacity (50 ml), and stirred for 15 min. Then the autoclave was sealed and maintained at 200 °C for 28 h. After cooled to room temperature naturally, there were black participates collected on the bottom of the autoclave, and were repeatedly washed with deionized water and alcohol to remove soluble inorganic and organic impurities. The final products were obtained after dried at 50 °C for 6 h in atmosphere.

The crystal structures of the products were examined by X-ray diffraction (XRD) using a Japan Mac science 18kvw X-ray diffractionmeter with Cu Kα radiation (λ = 0.1541 nm). The morphologies, microstructures of the products were characterized by a field emission scanning electron microscopy (FE-SEM, Philips XL-30) equipped with a energy dispersive X-ray spectroscopy (EDX), and a transmission electron microscopy (TEM, JEOL 2010).

---

* Corresponding author. Tel.: +86 991 8583183; fax: +86 991 8582405.
E-mail address: jikangjian@gmail.com (J.K. Jian).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.02.154

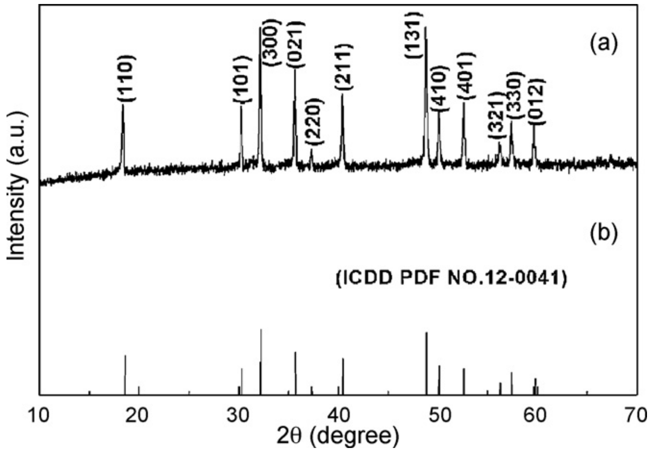

Fig. 1. XRD pattern of the product prepared at 200 °C in en with 0.01 mol S and 0.01 mol Ni for 28 h.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of the products prepared at 200 °C for 28 h with the molecule ratio of Ni:S = 1. All peaks can be well indexed to rhombohedral structured NiS with space group of $R3m$ and the cell parameters $a = 9.61$ Å, $c = 3.16$ Å, which shows a good agreement with the literature data displayed in the lower pattern of Fig. 1(b) (ICDD PDF No. 12-0041). No obvious diffraction peaks from other nickel sulfides such as Ni_2S_3, Ni_3S_4, Ni_3S_2 and Ni_9S_8, were observed in the XRD pattern. Fig. 2(a) and (b) are low and high magnification SEM images of the products revealing its morphological feature. It can be seen that the products consist of lots of nanorods which are self-assembled to form flower-like morphology. The nanorods are straight with smooth surfaces, and have diameters in the region from 80 nm to 120 nm, and lengths are from 2 μm to 3 μm. EDX (Fig. 2(c)) analysis was employed to determine the chemical compositions of the products. Nickel and sulfide elements were detected with a molar ratio of about 1:1 (Ni:S), which further confirms that the products are NiS. The trace amount of C element in the EDX spectrum originates is from the carbonous holder which is used to support the product in the test. TEM was employed to further examine the morphology and the microstructures of the products. Fig. 3(a) and (b) are TEM morphological image and the corresponding HRTEM image of an individual nanorod. The TEM bright field image (Fig. 3(a)) clearly reveals the nanorod is straight and smooth again. The HRTEM image (Fig. 3(b)) presents clear lattice strings with spacing of 0.295 nm corresponding to millerite NiS (1 0 1) plane, indicating the single crystal nature of the nanorod.

It was found that the molar ratio of Ni to S (noted as $M_{Ni}:M_S$) affected the phases and morphology of the products greatly. Fig. 4(a–d) shows the XRD pattern and the SEM images of the products prepared at 200 °C for 28 h with the molecule ratio of $M_{Ni}:M_S = 1:3$. The XRD pattern shown in Fig. 4(a) can be indexed to the cubic NiS_2 based on the reported data (ICDD PDF No. 65–3325). It should be noted that all the peaks have slight shift (about 0.03–0.08°) to low angle compared with the corresponding standard data, which implies the lattice deformation of the NiS_2

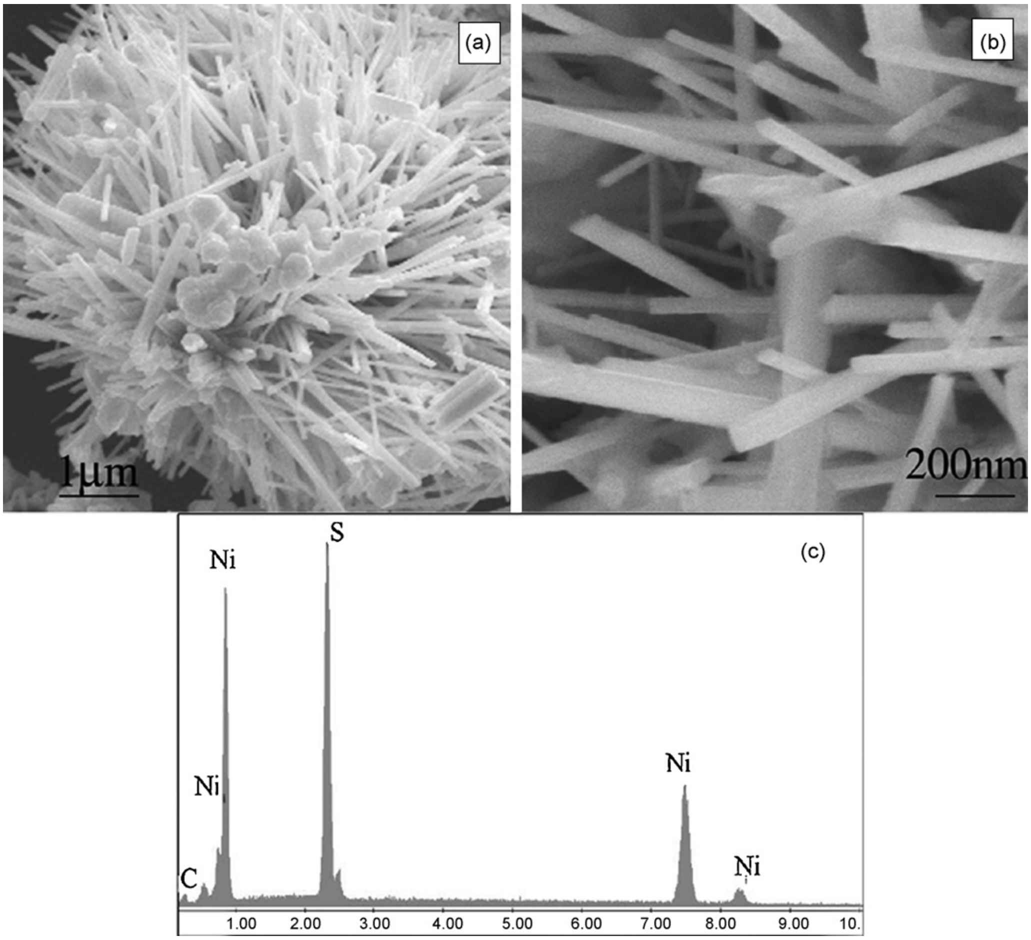

Fig. 2. SEM images (a and b) and EDX pattern (c) of the products prepared with 0.01 mol S.

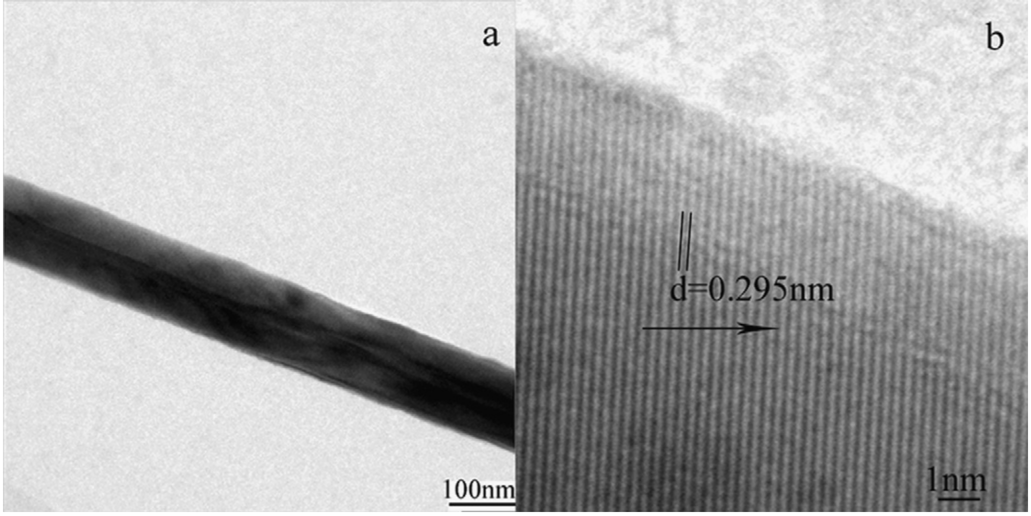

Fig. 3. TEM (a) and HRTEM (b) image of the products prepared at 200 °C for 28 h with 0.01 mol S and 0.01 mol Ni in en.

prepared here. In addition, there is a very weak peak at 48.79°, which may be due to other nickel sulfides with trace amount. The XRD analysis indicates that the main phase of the product is cubic NiS_2. SEM observations reveal that the sample is composed of NiS_2 particles with diameter of 400–500 nm (Fig. 4(c)) and few big well-faceted crystals with lateral size of about 4 μm (Fig. 4(d)).

As shown above, single crystal NiS nanorods were prepared with 0.01 mol S and 0.01 mol Ni in en at 200 °C, while cubic NiS_2 parti-

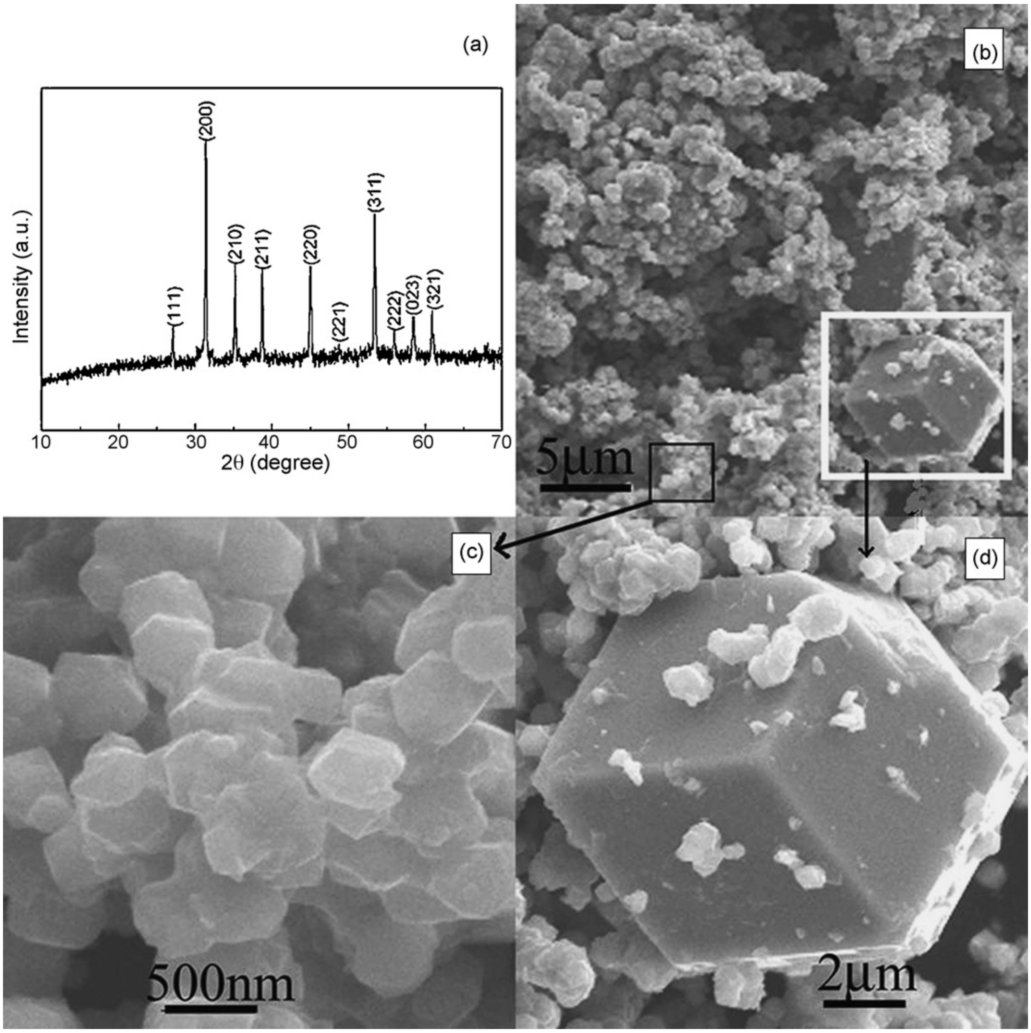

Fig. 4. XRD pattern (a) and SEM images (b–d) of the NiS_2 prepared at 200 °C for 28 h when M_{Ni}:M_S decrease to 1:3 in en.

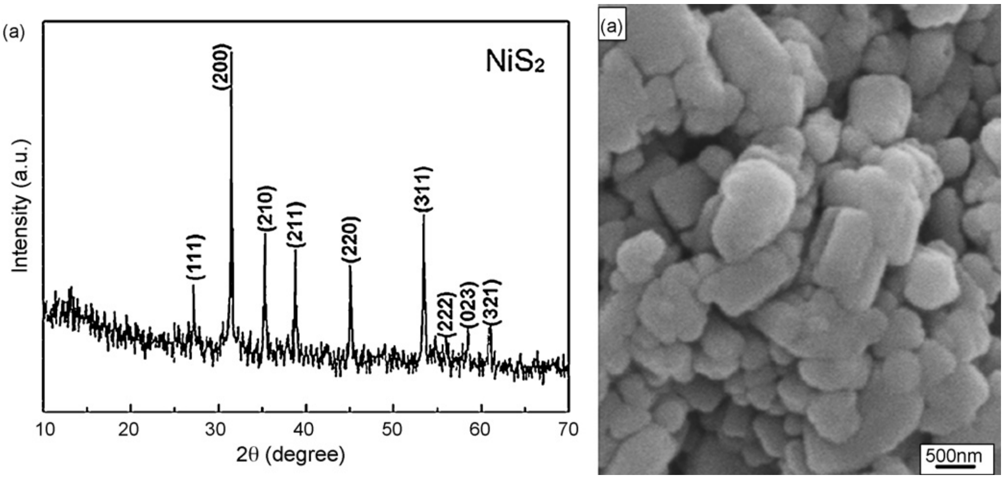

Fig. 5. XRD pattern (a) and SEM image (b) of NiS_2 prepared by the reaction between 0.01 mol NiS and 0.01 mol S in en at 200 °C for 20 h.

cles were synthesized When M_{Ni}:M_S decreased to 1:3 with other experimental parameters fixed.

The formation of sulfides under solvothermal growth has been extensively studied [18–19]. In the solvothermal reaction of sulfur with metal powder in organic solvents, it is believed that the solvent acts as a structure-directing molecule that is incorporated into the inorganic framework first and then escapes from it to form nanocrystallites with desired morphologies [20].

Up to now, en, as an important molecule precursor, has been successfully applied to grow nanorods of some important materials such as ZnS [21], CdS [22], etc. In our work, Ni^{2+} ions produced from Ni powder at the elevated temperature prefer to coordinate with en molecules to form a relatively complex $[Ni(en)_3]^{2+}$ (the stability constants $\log \beta_3 = 18.33$) as follows [17].

$$Ni \rightarrow Ni + 2e^- \quad (1)$$

$$Ni^{2+} + 3en \rightarrow [Ni(en)_3]^{2+} \quad (2)$$

$[Ni(en)_3]^{2+}$ have three coupling rings, and the stability of the complexes is expected to decrease with the increase of the temperature. At a proper temperature, sulfur may coordinate to the complex, and formed the inorganic–organic compounds [17]. With rising of temperature and prolonging of reaction time, en molecules were released from the inorganic–organic compounds, and then NiS was formed as follows.

$$[Ni(en)_3]^{2+} + S^{2-} \rightarrow NiS + 3en \quad (3)$$

According the previous study on the growth of CdS nanorods in en solvent [22], the formation of NiS nanorods prepared here may undergo the following stages: (1) the formation of chain-like $[Ni(en)_3]^{2+}$ complex through the coordination of en to Ni^{2+}; (2) S^{2+} react with the chain-like $[Ni(en)_3]^{2+}$ complex to form the inorganic–organic compounds; (3) en molecules were released from the compounds, and then NiS nanorods were left. The result presented here demonstrates that en could provide a template for NiS one-dimensional structure and make the crystals grow preferentially in a certain direction. So it can be concluded that en is favorable to the formation of NiS nanorods.

If S is excessive, NiS_2 crystals would be obtained through the following reaction.

$$NiS + S \rightarrow NiS_2 \quad (4)$$

To validate the above process, we carried out the growth experiment using 1 mmol NiS nanorods prepared in the foregoing experiment and 1 mmol S as raw materials at 200 °C for 20 h in en solvent. The XRD pattern (Fig. 5(a)) shows that the phase of the products is cubic NiS_2 and the SEM image (Fig. 5(b)) shows the morphological feature of the products is sub-micron particles. The results demonstrate that the starting NiS nanorods have been all converted into cubic NiS_2 particles, and both of their phase and morphology changed. In the process, the excessive S^{2-} ions first reacted with the NiS nanorods surface constantly and NiS_2 species was produced accordingly in local location of the NiS nanorod. Because of the different crystal structure between rhombohedral NiS and cubic NiS_2, those NiS_2 species would divorce from the surface of NiS nanorods, which destroyed the one-dimensional structure of NiS nanorods. The NiS species went into en solvent, nucleated and grew, leading to the formation of NiS_2 particles. Thus, NiS_2 particles are the final stable product when S is excessive.

4. Conclusions

In summary, NiS nanorods were prepared directly by a solvothermal route using S powder and Ni powder as starting materials in en at 200 °C for 28 h. The X-ray diffraction (XRD) analysis indicated that the products were rhombohedral structured NiS. SEM and TEM characterizations revealed that the products were composed of a large amount of nanorods with high crystallinity. It was found that the molar ratio of Ni to S affected the phases and morphology of the products greatly. The en molecules played a structure-directing role for the growth of the nanorods.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (grant No. 50862008), the National Basic Research Program of China (973 Program) with grant No. 2007CB936300, and Xinjiang University starting fund (No. BS060110).

References

[1] G. Schmid, Chem. Rev. 92 (1992) 1709.
[2] N. Herron, Y. Wang, H. Eckert, J. Am. Chem. Soc. 112 (1990) 1322.
[3] L. Motte, F. Billoudet, E. Laxaze, J. Douin, M.P. Pileni, J. Phys. Chem. B 101 (1997) 138.
[4] Q.T. Zhao, L.S. Hou, R.A. Huang, Inorg. Chem. Commun. 6 (2003) 971.
[5] Z.P. Qian, G. Xie, J. Tao, Z.Y. Nie, Y.Z. Lin, X.M. Chen, J. Solid. State. Chem. 166 (2002) 49.
[6] B. Messer, J.H. Song, P. Yang, J. Am. Chem. Soc. 122 (2000) 10232.
[7] S.C. Han, K.W. Kim, H.J. Ahn, J.H. Ahn, J.Y. Lee, J. Alloys Compd. 361 (2003) 247.
[8] A. GHezelbash, M.B. Sigman, B.A. Korgel, Nano Lett. 4 (2004) 537.
[9] X.C. Jiang, Y. Xie, J. Lu, L.Y. Zhu, W. He, Y.T. Qian, Adv. Mater. 13 (2001) 165.
[10] Y.U. Jeong, A. Manthiram, Inorg. Chem. 40 (2001) 73.
[11] N. Chen, W.Q. Zhang, W.C. Yu, Y.T. Qian, Mater. lett. 55 (2002) 230.
[12] X.C. Jiang, Y. Xie, J. Lu, L.J. Zhu, W. He, Y.T. Qian, Adv. Mater. 3 (2001) 1278.

[13] X.H. Liu, Mater. Sci. Eng. B 119 (2005) 19.
[14] H.B. Li, L.L. Chai, X.Q. Wang, X.Y. Wu, G.C. Xi, Y.K. Liu, Y.T. Qian, Cryst. Growth Des. 7 (2007) 1918.
[15] L. Zhang, J.C. Yu, M. Mo, L. Wu, Q. Li, K.W. Kwong, J. Am. Chem. Soc. 126 (2004) 8116.
[16] G.Z. Shen, D. Chen, K.B. Tang, C.G. An, Q. Yang, Y.T. Qian, J. Solid State Chem. 173 (2003) 227.
[17] S.H. Yu, M. Yoshimura, Adv. Funct. Mater. 12 (2002) 277.
[18] C.W. Chen, G.Y. Xu, H.Q. Zhang, J.M. Cao, P.P. Jiao, X.X. Wang, Mater. Lett. 60 (2006) 3561.
[19] Y.C. Li, X.H. Li, C.H. Yang, Y.F. Li, J. Phys. Chem. B 108 (2004) 16002.
[20] Y.D. Li, H.W. Liao, Y. Ding, Y. Fan, Y. Zhang, Y.T. Qian, Inorg. Chem. 38 (1999) 1382.
[21] X.J. Chen, H.F. Xu, N.S. Xu, F.H. Zhao, W.J. Lin, G. Lin, Y.L. Fu, Z.L. Huang, H.Z. Wang, M.M. Wu, Inorg. Chem. 42 (2003) 3100.
[22] Y.D. Li, H.W. Liao, Y. Ding, Y.T. Qian, L. Yang, G.E. Zhou, Chem. Mater. 10 (1998) 2301.