A water–ethanol mixed-solution hydrothermal route to silicates nanowires

Xun Wang*, Jing Zhuang, Qing Peng, Yadong Li*

Department of Chemistry and the Key Laboratory of Atomic & Molecular Nanosciences, (Ministry of Education, China), Tsinghua University, Beijing 100084, PR China

Abstract

In this manuscript, series of silicates nanowires, such as calcium silicate, strontium silicate, barium silicate, zinc silicate and cadmium silicate, etc., have been successfully prepared from a water–ethanol mixed solution system through a hydrothermal synthetic way. The formation process of these silicates nanowires has been studied in detail. Due to their rich sources and possible novel properties from reduced dimensionalities, we believe that the synthesis of these silicates nanowires may bring some new opportunity in the solid state chemistry and nanoscience and technology fields, etc.
© 2005 Elsevier Inc. All rights reserved.

Keywords: Silicates; Nanowires; Water–ethanol; Hydrothermal

1. Introduction

The development of nanoscience and nanotechnology requires precise control over crystal structures, compositions, sizes and dimensionalities of materials in nanoscale [1–4]. However, it turns out to be a challenging task to develop a general synthetic strategy towards this goal, especially for the synthesis of one-dimensional nanomaterials (1-D), the growth of which is confined in two dimensions and usually needs additional driving force to break the symmetry of the crystal structures [4]. Up to now, many novel 1-D nanostructures have been successfully synthesized, such as metal [5,6], semiconductor element [7], II–VI [8–13], III–V [14,15] nanowires/nanorods, semiconducting oxides nanobelts [16,17], WX_2 (W = W and Mo, X = S, Se) nanotubes, [18–21] based on which several methods have been developed, including vapor–liquid–solid method, thermal evaporation, solution-based routes,

hydrothermal way, etc. Usually, a specific method might be applied to the synthesis of a certain class of materials that share similar crystal structures in nature; so it seems particularly important to study the underlying principle of the growth behavior of such materials under certain conditions, aiming at the final establishment of a general methodology. Herein, we will demonstrate a water–ethanol mixed-solution hydrothermal route to prepare a series of silicates nanowires, the synthesis of which will further expand the family of 1-D nanostructures and may be suggested for the exploration of new methods to other new-type 1-D nanostructures.

The silicates are the largest, the most interesting and the most complicated class of minerals by far. Approximately 30% of all minerals are silicates and 90% of the Earth's crust is made up of silicates [22]. The basic unit of silicates is the (SiO_4) tetrahedron-shaped anionic group with a negative four charge −4, which can be linked to each other in different modes and formed as single units, double units, chains, sheets, rings and framework structures. The richness in crystal structures endows silicates affluent chemistry, physics and materials contents, including zeolites [23], mesoporous

*Corresponding authors. Fax: +86 10 6278 8765.
E-mail addresses: wangxun@mail.tsinghua.edu.cn (X. Wang), ydli@mail.tsinghua.edu.cn (Y. Li).

materials [24], and inorganic–organic composites [25], etc. Exploration upon new-type nanostructures of silicates with unexpected properties seems especially technologically and economically important, simply due to their low cost and richest resources. Recently, based on the layer structure of silicates, we have prepared silicates nanotubes via a hydrothermal route [26]. In this paper, by properly designing a water–ethanol mixed hydrothermal route, we have successfully prepared a series of silicate nanowires, the formation of which is believed to be related to the chain structure of silicates.

Although there have been many studies concerning the growth of nanowires structures, there is still the lack of a general growth mechanism. Nevertheless, recent studies show that compounds with anisotropic crystal structures may show strong growth tendency along certain direction (for example, Se, Te, MMo_3Se_3 nanowires) [4], and in these cases the crystal structures may be the inherent and decisive factors. In a similar way, the chain structure in silicates may serve as the potential driving force for the growth of silicates nanowires. Since the silicates may take quite different structures under different reaction conditions, the first task in designing the growth process of silicates nanowires may be properly tuning the crystal structure of the final products.

2. Experimental section

2.1. Chemicals

All the chemicals are of analytical grade and used as received without further purification. Deionized water was used throughout. Sodium silicate ($Na_2SiO_3 \cdot 9H_2O$), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$), cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$), barium nitrate ($Ba(NO_3)_2$), strontium nitrate ($Sr(NO_3)_2$), zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), lead nitrate ($Pb(NO_3)_2$), hexadecyltrimethyl ammonium bromide (CTAB), ethanol, acetone and triethanolamine were all supplied by Beijing Chemical Reagent Company.

2.2. Synthesis

In a typical synthesis of calcium silicate nanowires, 0.5 g $Ca(NO_3)_2 \cdot 4H_2O$ and 0.6 g $Na_2SiO_3 \cdot 9H_2O$ were dissolved into 5 mL diluted water, respectively, then the two solutions were mixed together under intense agitation to form white precipitate, to which 20 mL ethanol were added. The above mixture was transferred into a Teflon-lined autoclave and hydrothermal treated at 180 °C for about 2 days and then allowed to cool to room temperature naturally. The as-obtained white precipitates were filtered and washed with diluted water to remove ions possibly remnant in the final products and dried at 70 °C in air. As far as the preparation of zinc silicate nanowires are concerned, a slightly different condition has been adopted, and in a typical synthesis, 0.5 g $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved into 5 mL water and then precipitated and re-dissolved by aqueous ammonium to form $Zn(NH_3)_4^{2+}$, to which 30 mL ethanol were added to form clear colution. Five milliliter 0.5 mol/L $NaSiO_3$ was used to precipitate the $Zn(NH_3)_4^{2+}$ ions to form white precipitates, which were then treated at a temperature condition of 180 °C for 2 days under hydrothermal conditions. For the synthesis of cadmium silicate nanowires, 0.2 g NaOH was added to adjusted the pH of the reaction system. For details see Table 1.

In order to study the formation mechanism of these silicate nanowires, controlled experiments have been carried out in the synthesis of calcium silicate nanowires. The amount of ethanol was varied. And different solvents were used to study the formation mechanism of these silicate nanowires.

2.3. Characterization

2.3.1. Powder X-ray diffraction (XRD)

The phase purity of the products were examined by XRD using a Brucker D8-advance X-ray diffractometer with CuKα radiation ($\lambda = 1.5418$ Å), the operation voltage and current keeping at 40 kV and 40 mA, respectively. The 2θ range used was from 10° to 70° in steps of 0.02° with a count time of 2 s.

Table 1
Optimal conditions for the formation of silicate nanowires

Silicates	Experimental conditions			Phase	Morphology
	Water (mL)	Ethanol (mL)	NaOH (g)		
Ca	10	20	0	$Ca_2NaHSi_3O_9$	Nanowires
Sr	10	20	0	$SrSi_3O_9$	Nanowires
Ba	10	30	0	$BaSiO_3$	Nanorods
Cd	10	20	0.2	$Na_2Cd_3(Si_3O_{10})$	Nanowires
Zn	10 $Zn(NH_3)_4^{2+}$	30	0	Na_2ZnSiO_4	Nanowires
Pb	10	20	0	$PbSiO_3$	Nanowires (20%)

2.3.2. Transmission electron microscopy (TEM)

The size and morphology of the products were observed by using a Hitachi Model H-800 TEM, with a tungsten filament at an accelerating voltage of 200 kV. Samples were prepared by placing a drop of dilute alcohol dispersion of nanocrystals on the surface of a copper grid. Electron diffraction (ED) and energy dispersive X-ray analysis (EDAX) were also performed to study the single crystal nature or element components of the samples on H-800 TEM. Structural information of the nanocrystals was measured by high-resolution transmission electron microscopy (HRTEM) on a JEOL JEM-2010F TEM operated at 200 kV. ED was also performed on samples during HRTEM measurements.

3. Results and discussions

The synthesis of silicates nanowires was based on a hydrothermal method in a mixed solution system. Although the silicates may have chains or layer structures in nature, the direct reaction of metal ions and Na_2SiO_3 in water only results in irregular particles. As stimulated by the successful synthesis of nanotubes from layered silicates, polar solvents such as ethanol, acetone and triethanolamine, have been adopted in the experiments to adjust the growth conditions of the silicates.

Here calcium silicates have been chosen as an example to illustrate the formation process of these nanowires. Since ethanol is a much cheaper and greener solvent, it has been the first choice and finally evidenced to be effective in guiding the growth of silicates nanowires. The amounts of ethanol have been varied in the synthesis of calcium silicate nanowires.

As shown in Fig. 1a, the final products in the pure water system can be characterized to be a pure phase of triclinic (Space group C-1) phase of $CaSiO_3$ with lattice constants $a = 10.121$ Å, $b = 11.07$ Å, $c = 7.312$ Å, $\alpha = 99.51°$, $\beta = 100.51°$ and $\gamma = 83.43°$ (JCPDS 42-550). TEM images of the samples (Fig. 2a) have revealed that only irregular particles can be obtained under these ethanol-free conditions, which as an evidence show that ethanol is necessary in the formation of nanowires.

With the addition of ethanol (0–15 mL) to the reaction system, the crystal structure of the calcium silicates change from $CaSiO_3$ to a body-centered orthorhombic (space group: $Imm2$ (44)) phase of $Ca_5Si_6O_{16}(OH)_2 \cdot 8H_2O$ with lattice constants $a = 5.624$ Å, $b = 3.67$ Å and $c = 27.97$ Å (JCPDS 29-331) (Fig. 1b and c). Although nanowires have not yet been obtained, the existence of curling images of the sheet-like structures (Fig. 2b) are observed, which have been believed to be the possible intermediates in the formation process of manganese dioxides [27] and rare-earth [28] 1-D nanostructures. All these clues have provided the
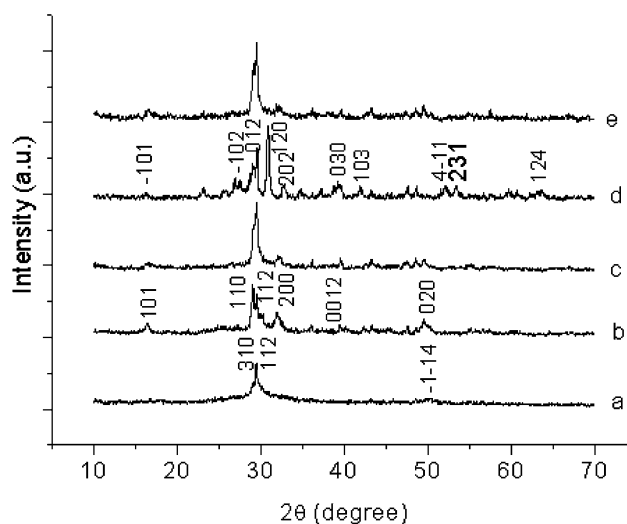

Fig. 1.

possibility of the formation of silicates nanowires. With the amount of ethanol increased to 20 mL, calcium silicate nanowires (Fig. 2c) have been successfully prepared. The obtained products have been characterized to be a pure triclinic (space group P-1(2)) phase of $Ca_2NaHSi_3O_9$ with lattice constants $a = 7.99$ Å, $b = 7.04$ Å and $c = 7.02$ Å (JCPDS 74-330) (Fig. 1d), which indicate that Na^+ ions have been incorporated into the crystal structure. Further increased ethanol will result in nanowires with smaller diameter and the same phase. All these results show that the amount of ethanol should be critical in the growth process of these nanowires.

Considering that the polarity of the solvents changes little when ethanol were increased from 15 to 20 mL, the effects of solvents on the modulation of the crystal structures of the final products are believed to be responsible for the growth of calcium silicate nanowires. Silicates have silicate-oxygen tetrahedral as their basic structural units, and different link modes will lead to the formation of different structures of silicates. One of the distinctive structures is the chain-like silicates with a Si:O = 1:3 when tetrahedrals are connected to each other in a linear way, which may be favorable for the anisotropic growth. It is believed that the formation of these nanowires is closely related to this particular link mode.

Surfactant molecules have found their application in guiding the growth direction of 1-D nanostructures, and we have adopted CTAB as anisotropic growth directing reagents in the synthesis of calcium silicate nanowires. With 1 g CTAB being introduced into the 20 mL H_2O–20 mL ethanol reaction system, nanowires were prepared with a crystal structure of $Ca_2NaHSi_3O_9$, which have shown its effect in directing the growth of these nanowires. It has also been found that the CTAB
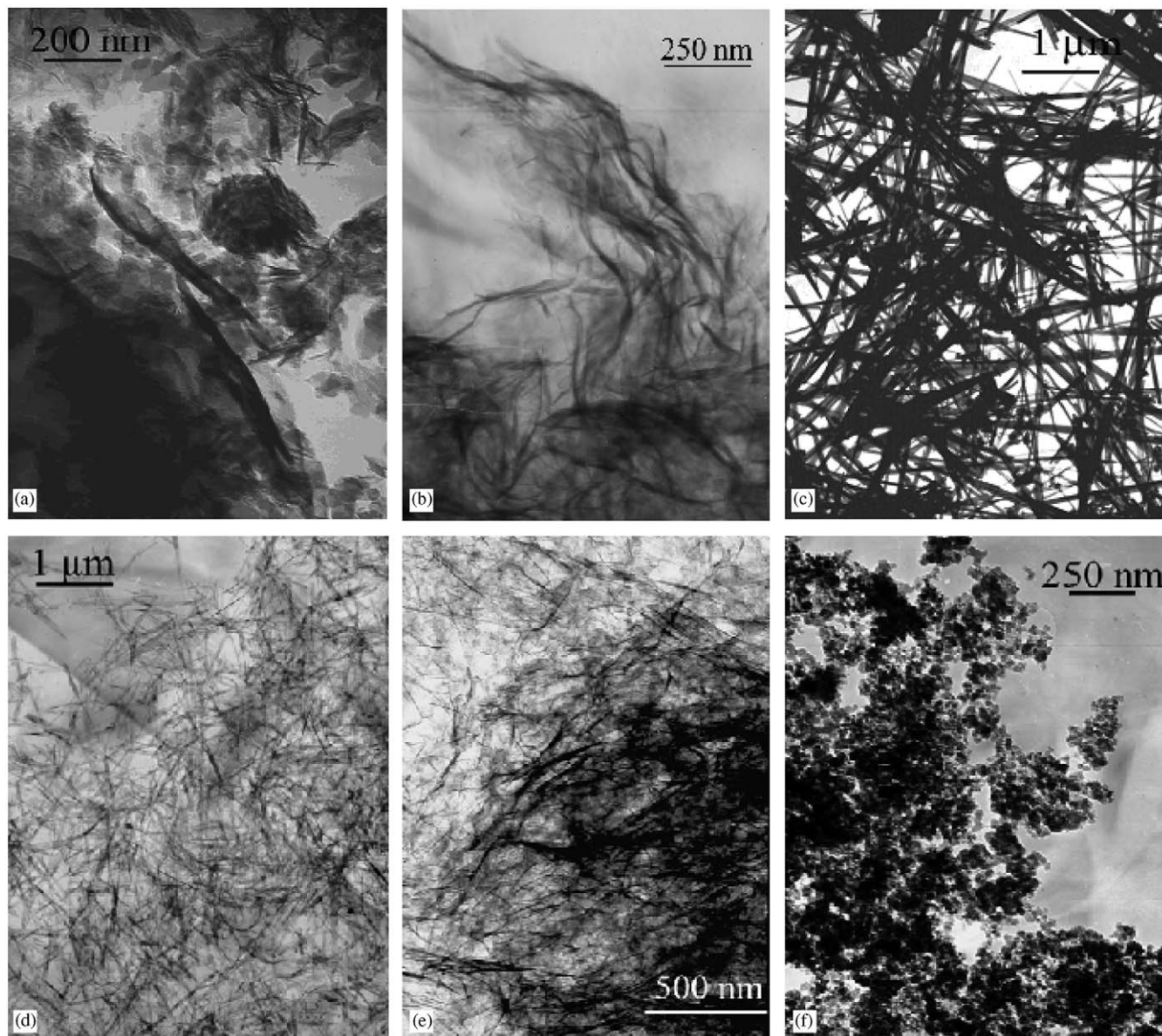
Fig. 2.

have an excellent effect in confining the diameters of these nanowires. Compared with those obtained in water–ethanol system, the nanowires always have smaller diameters 10–20 nm (Fig. 2d). However, the involvement of surfactants in the preparation process will greatly increase the production cost of these nanowires, so it has been avoided in the synthesis of other silicates nanowires.

Based on the above experimental results the amount of ethanol should be critical. Since ethanol has a different polarity from that of water, other polar solvents might do a similar work in guiding the growth of nanowires. So we have investigated the effects of different polar solvents on the growth of nanocrystals,

such as acetone and triethanolamine, etc. As shown in Fig. 2e, curling images of calcium silicates have been observed when 10 mL acetone was used to form a ternary solution (acetone:H_2O:ethanol $= 10$:20:10), indicating a possible rolling process for these nanostructures, which have been characterized to be the same $Ca_5Si_6O_{16}(OH)_2 \cdot 8H_2O$ (Fig. 1e) phase as those obtained from a water–ethanol system (0–15 mL). However, this system cannot provide enough driving force for these curing sheets to roll into nanowires or nanotubes. When triethanolamine was used, nanoparticles of calcium silicates have been obtained (Fig. 2f).

Inspired by the successful synthesis of calcium silicate nanowires, this water–ethanol hydrothermal route has

been applied to the synthesis of other silicates nanowires. By simply tuning several parameters, such as temperature, concentration, ethanol water ratios, etc., the growth behavior of nanocrystals can be easily modulated and several kinds of silicates nanowires, such as calcium silicates, strontium silicates, barium silicates, zinc silicates and cadmium silicates, etc., have been successfully prepared (Table 1).

The phase purity of the samples has been examined. Thorough XRD analysis indicates that pure phase of silicates can be obtained. However, for different salts, Na can be selectively incorporated into the crystal structure of the silicates.

As shown in Fig. 3, the reflection patterns of the samples in Fig. 3a can be readily indexed to that of the pure base-centered monoclinic (space group $C2/c(15)$) phase of $SrSi_3O_9$ with lattice constants $a = 12.323$ Å, $b = 7.139$ Å and $c = 10.873$ Å (JCPDS 77-0233), and those in Fig. 3b indexed to that of the pure hexagonal phase of $BaSiO_3$ with lattice constants $a = 7.5$ Å and $c = 10.467$ Å (JCPDS 33-0176), while the XRD patterns in Fig. 1d show that Na atoms have been incorporated into the samples of calcium silicates and result in a pure triclinic phase of $Ca_2NaHSi_3O_9$. Similar results have been obtained in the synthesis of zinc silicates ($Na_2Zn\ SiO_4$ JCPDS 74-1802, monoclinic phase, $a = 5.248$ Å, $b = 7.025$ Å and $c = 5.445$ Å) (Fig. 4a) and cadmium silicates ($Na_2Cd_3(Si_3O_{10})$), JCPDS83-2138, base-centered monoclinic phase, $a = 16.426$ Å, $b = 5.086$ Å and $c = 10.958$ Å) (Fig. 4b) nanowires. Other pure phase silicates could also be prepared from a similar mixed solution system. All the information indicates that different pure phase silicates can be obtained under current experimental conditions.

The micro/nanostructures of these nanowires have been carefully examined with TEM. As shown in Figs. 5a–d and 2c, different silicates of Ca, Sr, Ba, Cd and Zn can be prepared as uniform nanowires with diameters 30–50 nm and lengths up to 10 μm. It is
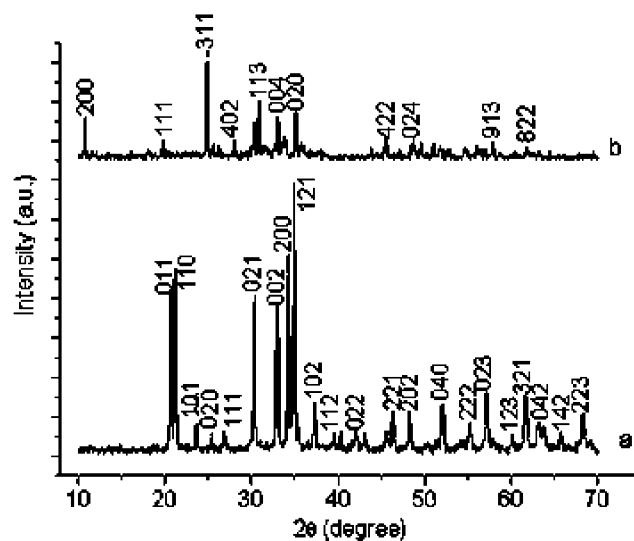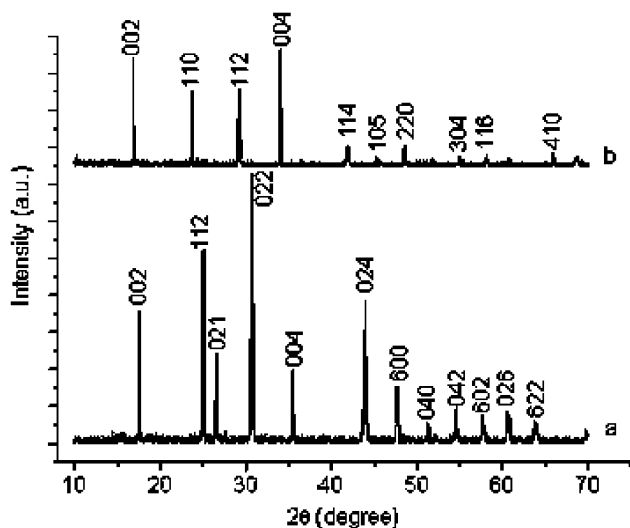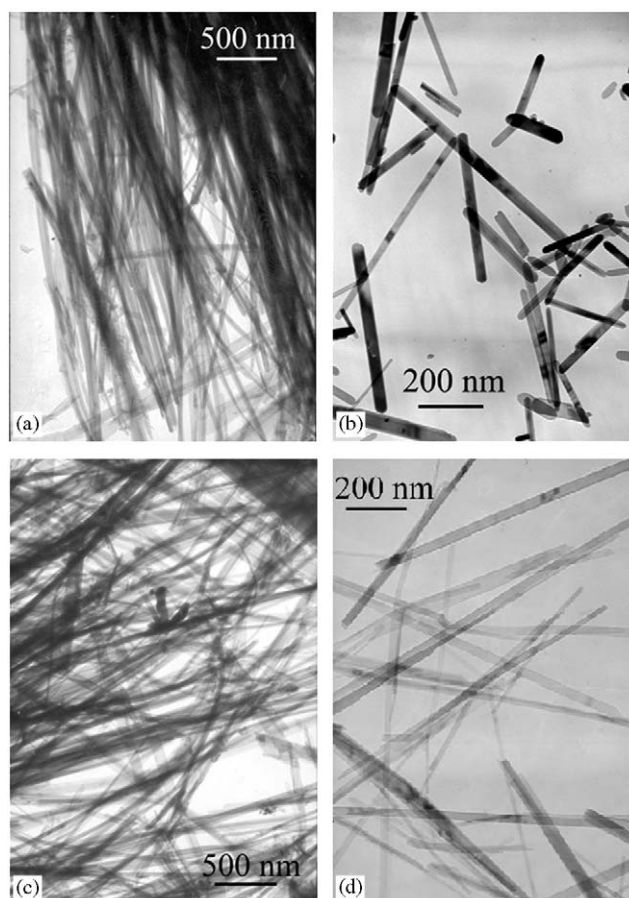

Fig. 4.

Fig. 3.

Fig. 5.

interesting to find that as a result of the slight changes of the ion radii of the corresponding metal elements, the Ba seems to have a shorter length and thus a lower aspect ratio than that of the Ca (Fig. 2c) and Sr (Fig. 5a) ones. The metal categories will also influence the growth behavior of these nanocrystals, and as shown in Fig. 5d, NaCdSiO₃ show nanobelts morphology with smooth surface and a width ~40 nm and length up to several micrometers. Electron patterns, taken from individual nanowires of corresponding silicates (Hitachi 800, TEM), have shown that the as-prepared nanowires are single crystals in nature.

The behavior of these nanowires under the bombardment of electron beams is quite different. The ED patterns are all rather stable during the bombardment process on H-800 TEM operated at an accelerating voltage of 200 kV, indicating that the samples will not be destroyed under current experimental conditions. However, when the HRTEM images were tried to be taken on F-2010 high-resolution TEM operated at an accelerating voltage of 200 kV, these nanowires usually cannot endure the strong electron beam and a different decomposing process will occur.

The calcium nanowires have shown comparatively better stability than those of Sr, Zn and Cd, and ED patterns (Fig. 6a, down inset) taken from a single nanowire have revealed its single crystal nature, and can be indexed as that of [001] zone axis of triclinic $Ca_2NaHSi_3O_9$. Under the long-time irradiation of electron beam, the nanowires tend to decompose and single crystal domains (Fig. 6a upper inset) appear in the bulk of the nanowires while the edge of the individual nanowries tend to become amorphous. For those of Sr, after long-time electron beam irradiation, these nanowires tend to decompose into amorphous nanowires and HRTEM images containing crystal lattice of the nanowires can hardly be taken due to their quick transformation. As shown in Fig. 6b–d, series of ED patterns along with time have revealed a transformation process from a single crystal into polycrystalline one. An interesting phenomenon appears when single crystal Cd nanowires (ED, Fig. 6e) were irradiated, these nanowires tend to become amorphous at first, then under further irradiation single crystal nanoparticles have been found embedded in the decomposed nanowires, and nanocluster wires were obtained in situ (Fig. 6f). The chemical and physical behavior of these nanocluster wires may be interesting since the individual nanoparticles may behave as quantum dots in the coherent nanowires.
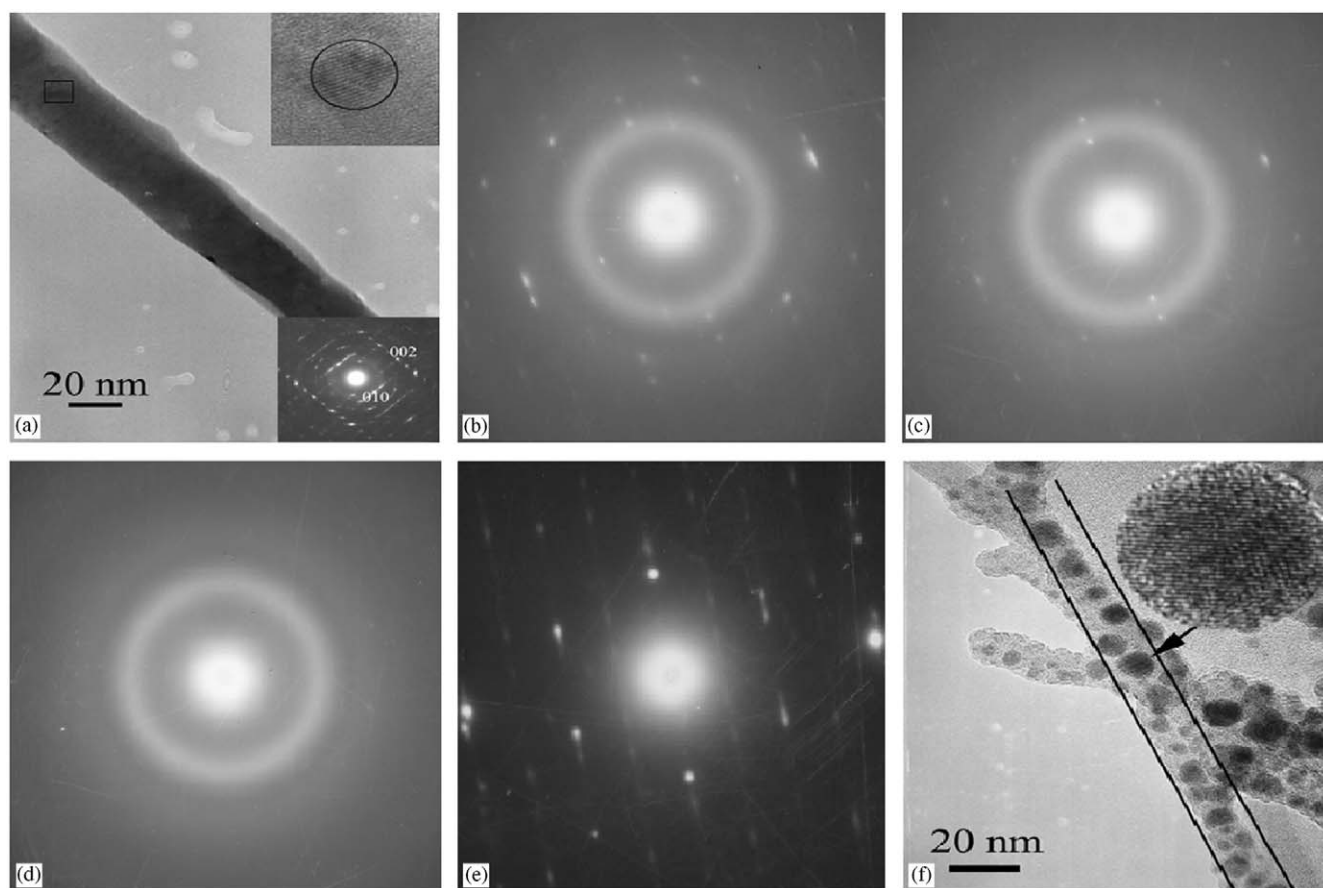

Fig. 6.

The difference in stabilities of silicates nanowires under electron beams may be attributed to the difference in thermal stabilities or the effects of electron beams (for example, the movement of the transitional metal ions may be accelerated by the electrons). Nevertheless, the gradual changes in stabilities of these nanowires show one of the properties that may undergo a gradual change with the different metal ions; further studies may be carried out to find some underlying principles in these nanowires materials.

4. Conclusions

In this manuscript, a series of silicates nanowires have been successfully prepared from a water–ethanol mixed-solution system through a hydrothermal synthetic way. The formation process of these silicates nanowires has been studied in detail. Due to their rich sources and possible novel properties from reduced dimensionalities, we believe that the synthesis of these silicates nanowires may bring some new opportunity in the solid state chemistry and nanoscience and technology fields, etc.

Acknowledgments

References

[1] J.T. Hu, T.W. Odom, C.M. Lieber, Acc. Chem. Res. 32 (1999) 435.

[2] R. Tenne, Chem. Eur. J. 8 (2002) 5297.

[3] G.R. Patzke, F. Krumeich, R. Nesper, Angew. Chem. Int. Ed. 41 (2002) 2446.

[4] Y.N. Xia, P.D. Yang, Y.G. Sun, Y.Y. Wu, B. Mayers, B. Gates, Y.D. Yin, F. Kim, Y.Q. Yan, Adv. Mater. 15 (2003) 353.

[5] Y.D. Li, J.W. Wang, Z.X. Deng, Y.Y. Wu, X.M. Sun, D.P. Yu, P.D. Yang, J. Am. Chem. Soc. 123 (2001) 9904.

[6] Y.G. Sun, Y.N. Xia, Adv. Mater. 14 (2002) 833.

[7] B. Gates, Y.D. Yin, Y.N. Xia, J. Am. Chem. Soc. 122 (2000) 12582.

[8] Y.D. Li, H.W. Liao, Y. Ding, Y.T. Qian, L. Yang, G.E. Zhou, Chem. Mater. 10 (1998) 2301.

[9] Y.D. Li, H.W. Liao, Y. Ding, Y. Fan, Y. Zhang, Y.T. Qian, Inorg. Chem. 38 (1999) 1382.

[10] X.F. Duan, C.M. Lieber, Adv. Mater. 12 (2000) 298.

[11] Z.A. Peng, X.G. Peng, J. Am. Chem. Soc. 123 (2001) 1389.

[12] W.W. Yu, X.G. Peng, Angew. Chem. Int. Ed. 41 (2002) 2368.

[13] M.H. Huang, S. Mao, H. Feick, H.Q. Yan, Y.Y. Wu, H. Kind, E. Weber, R. Russo, P.D. Yang, Science 292 (2001) 1897.

[14] J. Goldberger, R.R. He, Y.F. Zhang, S.W. Lee, H.Q. Yan, H.J. Choi, P.D. Yang, Nature 422 (2003) 599.

[15] X.F. Duan, Y. Huang, Y. Cui, J.F. Wang, C.M. Lieber, Nature 409 (2001) 66.

[16] Z.W. Pan, Z.R. Dai, Z.L. Wang, Science 291 (2001) 1947.

[17] X.M. Sun, X. Chen, Y.D. Li, Inorg. Chem. 41 (2002) 4996.

[18] M. Nath, C.N.R. Rao, Angew. Chem. Int. Ed. 41 (2002) 3451.

[19] Y.D. Li, X.L. Li, R.R. He, J. Zhu, Z.X. Deng, J. Am. Chem. Soc. 124 (2002) 1411.

[20] Y. Feldman, E. Wasserman, D.J. Srolovitz, R. Tenne, Science 267 (1995) 222.

[21] R. Tenne, L. Margulis, M. Genut, G. Hodes, Nature 360 (1992) 444.

[22] R.R. Hao, X.Y. Fang, S.C. Niu, Series of Inorganic Chemistry, vol. 3, Science Press, Beijing, 1998 (p. 212).

[23] Y. Tian, G.D. Li, J.S. Chen, J. Am. Chem. Soc. 125 (2003) 6622.

[24] D.Y. Zhao, J.L. Feng, Q.S. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548.

[25] S.A. Solin, Annu. Rev. Mater. Sci. 27 (1997) 89.

[26] X. Wang, J. Zhuang, J. Chen, K.B. Zou, Y.D. Li, Angew. Chem. Int. Ed. 43 (2004) 2017.

[27] X. Wang, Y.D. Li, J. Am. Chem. Soc. 124 (2002) 2880;
X. Wang, Y.D. Li, Chem. Eur. J. 9 (2003) 300;
X. Wang, Y.D. Li, Chem. Commun. (2002) 764.

[28] X. Wang, Y.D. Li, Angew. Chem. Int. Ed. 41 (2002) 4190;
X. Wang, Y.D. Li, Angew. Chem. Int. Ed. 42 (2002) 3497;
X. Wang, Y.D. Li, et al., Adv. Mater. 15 (2003) 1442;
X. Wang, Y.D. Li, Eur. Chem. J. 9 (2003) 5627.