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Hydrothermal Synthesis of $BaSiF_6$ Hexagonal Needles

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Hexagonal needles of $BaSiF_6$ microcrystals have been prepared by using a hydrothermal method with $Ba(NO_3)_2$, SiO_2, and HF in the presence of NH_4Cl or ethylenediamine dihydrochloride as the metal chelating agent. The metal chelating agent plays an important role in controlling the aspect ratios of the $BaSiF_6$ microcrystals. X-ray diffraction was used to confirm that the axes of the hexagonal needles of $BaSiF_6$ are aligned along the *c* axis.

Anisotropy is an elementary property of single crystals. One-dimensional structures usually have strong anisotropy. One-dimensional wires, rods, and tubes have attracted significant interest because of their novel properties and potential applications.[1–3] A variety of methods have been used for preparing these one-dimensional inorganic materials, most of which are synthesized in the presence of either hard templates or soft directing agents.[3–6] One of the main challenges in the preparation of one-dimensional inorganic materials is the control of their sizes and aspect ratios.

Barium hexafluorosilicate ($BaSiF_6$) is used as an insecticide and as a host material for vacuum ultraviolet (VUV) phosphors.[7] $BaSiF_6$ is a trigonal crystal with $R\bar{3}m$ space group.[8] However, there has been only one study of the morphology of $BaSiF_6$ to the best of our knowledge. One-dimensional rod-like $BaSiF_6$ with an average length of 5 µm was prepared by carrying out a hydrothermal reaction between $Ba(NO_3)_2$ and K_2SiF_6.[9] In this paper, we report a simple hydrothermal method for the preparation of hexagonal $BaSiF_6$ microneedles from $Ba(NO_3)_2$, SiO_2, and HF in the presence of NH_4Cl or ethylenediamine dihydrochloride as the metal chelating agent. The aspect ratios of the resulting hexagonal microneedles can be controlled through the choice of the metal chelating agent.

$Ba(NO_3)_2 \cdot 2H_2O$ (99%, Aldrich), SiO_2 (99.6%, Aldrich), NH_4Cl (99%, Aldrich), ethylenediamine dihydrochloride (99%, Aldrich), and HF (35 wt % solution in water, Aldrich) were used as received. In a typical hydrothermal experiment, 1 mL of HF was added to 0.6 g of SiO_2 in 50 mL of water. The mixture was stirred for 30 min and then centrifuged. A 50-mL portion of top clear solution was added to a mixed solution of 40 mL of 0.125 M $Ba(NO_3)_2$ and 10 mL of 0.5 M NH_4Cl stirred for 1 min in a polypropylene beaker. A 70-mL aliquot of this solution was then transferred to a 100-mL Teflon-lined autoclave and heated at 60 °C for 12 h. In order to investigate the effects of the choice of the metal chelating agent, ethylenediamine dihydrochloride was also used instead of NH_4Cl. The products were filtered, washed several times with water and ethanol, and then dried at 60 °C for 24 h in an oven. The structures of the resulting $BaSiF_6$ materials were analyzed by using powder X-ray diffraction (XRD, PANalytical X'pert PRP MPD) with Cu Kα radiation, and their morphologies were determined with scanning electron microscopy (SEM, Hitachi S-4300) and high-resolution transmission electron microscopy (HRTEM, Jeol JEM-3010).

Figure 1a shows a SEM image of $BaSiF_6$ prepared without using a metal chelating agent. The product is composed of spindle-like microcrystals with an average length of 7 µm (the aspect ratio is 14). When NH_4Cl was used as the metal chelating agent, hexagonal needle-like $BaSiF_6$ crystals with an average width of 3 µm and a length of 120 µm were formed, as shown in Figure 1b. The aspect ratio of these hexagonal needles is approximately 20. Figure 1c shows the tip area of a hexagonal needle, in which three end-capped faces are present. When ethylenediamine dihydrochloride was used, ultralong hexagonal needles were obtained, as shown in Figure 1d. The average length of the ultralong hexagonal needles is approximately 300 µm, with an aspect ratio of 150.

Figure 2 shows the XRD patterns of three typical $BaSiF_6$ products prepared by using different metal chelating agents. All products consist of a single trigonal crystal system of $BaSiF_6$ (JCPDS 15-0736, $a = 7.185$ Å, $c = 7.010$ Å). Since no other peaks were detected, we conclude that this method yields $BaSiF_6$ free from impurities. The comparison of the relative intensities shown in Figure 2 shows that the three products are different. The relative intensities of the Miller indices (110), (220), and (330) in Figures 2b and 2c are higher than those in Figure 2a. However, the relative intensities of the Miller indices (012), (211), and (113) in Figures 2b and 2c are lower than those in Figure 2a. The intensity ratios of (110) to (211) increases with increase in the aspect ratio of the $BaSiF_6$ crystals. For the ultralong hexagonal needles obtained by using ethylenediamine dihydrochloride, the intensities of the (110), (220), and (330) peaks are strong but those of the other peaks are diminished, which indicates that the axes of the hexagonal needles of $BaSiF_6$

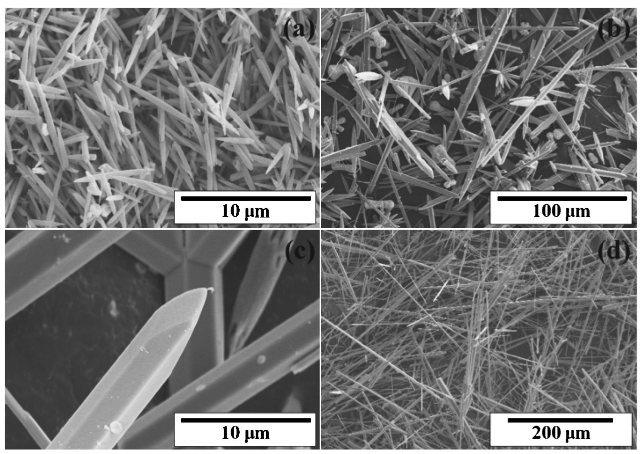

Figure 1. SEM images of $BaSiF_6$ synthesized (a) without a metal chelating agent, (b), (c) with NH_4Cl, and (d) with ethylenediamine dihydrochloride.

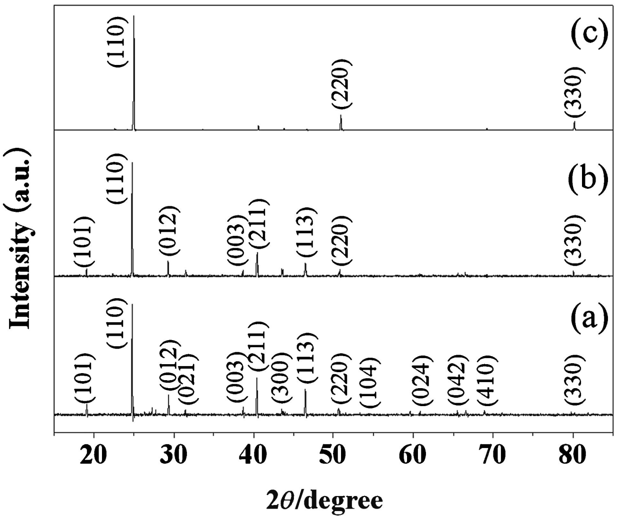

Figure 2. XRD diffraction patterns of $BaSiF_6$ synthesized (a) without a metal chelating agent, (b) with NH_4Cl, and (c) with ethylenediamine dihydrochloride.

produced with the metal chelating agents are aligned along the crystallographic *c* axis. Accordingly, ethylenediamine dihydrochloride and NH_4Cl were found to act as morphology-modifying agents.

The metal chelating agent assisted reactions involved in the formation of $BaSiF_6$ are as follows:

$$Ba^{2+}(aq) + 8NH_4Cl \rightarrow [Ba(NH_3)_8]^{2+}(aq) + 8HCl \quad (1)$$

$$[Ba(NH_3)_8]^{2+}(aq) + SiO_2 + 6HF(aq) \rightarrow BaSiF_6 + 2NH_4{}^{+}(aq) + 6NH_3 + 2H_2O \quad (2)$$

When no metal chelating agent is used, Ba^{2+} reacts directly with $SiF_6{}^{2-}$ to form spindle-like microcrystals with an average length of 7 µm, as shown in Figure 1a. There is insufficient time for the formation of hexagonal needles of $BaSiF_6$ in the absence of a metal chelating agent. In contrast, hexagonal needles of $BaSiF_6$ with lengths of approximately 120 and 300 µm were obtained in the presence of NH_4Cl and ethylenediamine dihydrochloride, respectively, as shown in Figures 1b and 1d. The metal chelating agent affects the crystal growth of $BaSiF_6$. The lack of d-orbital electrons in alkali earth metals could result in coordination number greater than six. Particularly for the large ion, Ba^{2+}, the coordination number is generally expected up to eight. Therefore, we assumed that NH_4Cl reacts with Ba^{2+} ions to form the stable $[Ba(NH_3)_8]^{2+}$ complex. Only small amounts of Ba^{2+} ions are slowly released, and thus there is sufficient time for crystal growth with an anisotropic crystal habit. As a result, under these conditions long hexagonal needles with large aspect ratios are formed. Since ethylenediamine (en) is a bidentate amine, ethylenediamine is a stronger ligand than ammonia. Ethylenediamine can combine strongly with Ba^{2+} ions to form a very stable $[Ba(en)_4]^{2+}$ complex. This chelating effect of ethylenediamine is evidently sufficiently strong under these experimental conditions to substantially reduce the availability of Ba^{2+} ions, resulting in sufficient time for the formation of hexagonal needles and hexagonal prisms of $BaSiF_6$ with lengths of approximately 300 µm. Thus, as the chelating effect is increased, the shape of the $BaSiF_6$ microcrystals changes from spindle-like to hexagonal needles with higher aspect ratios.

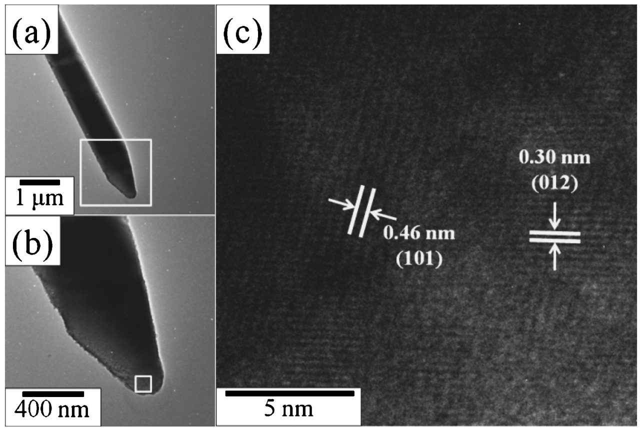

Figure 3. (a, b) TEM and (c) HRTEM images of hexagonal $BaSiF_6$ needles prepared using ethylenediamine dihydrochloride.

Figure 3 shows a TEM image of $BaSiF_6$ hexagonal needles prepared by using ethylenediamine dihydrochloride. The fringe patterns of the end-capped faces indicate spacings of 0.30 and 0.46 nm, which correspond to the (012) and (101) planes of $BaSiF_6$ hexagonal needles, respectively.

In summary, the hydrothermal method has been successfully used in the fabrication of $BaSiF_6$ microcrystals. $BaSiF_6$ hexagonal needles with average lengths of 120 and 300 µm were synthesized by using NH_4Cl and ethylenediamine dihydrochloride respectively as metal chelating agents. The metal chelating agent plays an important role in controlling the aspect ratios of the $BaSiF_6$ microcrystals.

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References

1 J. Hu, T. W. Odom, C. M. Lieber, *Acc. Chem. Res.* **1999**, *32*, 435.
2 C. N. R. Rao, F. L. Deepak, G. Gundiah, A. Govindaraj, *Prog. Solid State Chem.* **2003**, *31*, 5.
3 Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* **2003**, *15*, 353.
4 S. J. Hurst, E. K. Payne, L. Qin, C. A. Mirkin, *Angew. Chem., Int. Ed.* **2006**, *45*, 2672.
5 J. Zhang, S.-Y. Zhang, H.-Y. Chen, *Chem. Lett.* **2004**, *33*, 1054.
6 Y. Song, R. M. Garcia, R. M. Dorin, H. Wang, Y. Qiu, E. N. Coker, W. A. Steen, J. E. Miller, J. A. Shelnutt, *Nano Lett.* **2007**, *7*, 3650.
7 E. van der Kolk, P. Dorenbos, C. W. E. van Eijk, A. P. Vink, C. Fouassier, F. Guillen, *J. Lumin.* **2002**, *97*, 212.
8 B. F. Hoskins, A. Linden, P. C. Mulvaney, T. A. O'Donnell, *Inorg. Chim. Acta* **1984**, *88*, 217.
9 H.-X. Zhong, Q.-L. Huang, Y.-L. Ma, J.-M. Hong, X.-T. Chen, Z.-L. Xue, *J. Solid State Chem.* **2009**, *182*, 1679.

