A Mild Solution Route to Bismuth Selenoiodide Rod-like Crystals

Liying Zhu, Xiuwen Zheng, Xing Yin, Xiang Liu, Yunbo Jia, and Yi Xie*
Structure Research Laboratory and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

(Received November 29, 2002; CL-021017)

Bismuth selenoiodide (BiSeI) millimeter-scale rod-like crystals were synthesized for the first time via a mild solution route based on the reactions of $BiCl_3$, Se with NaI or Bi_2Se_3 with BiI_3 in ethanol solvent at 200 °C. A possible growth mechanism of the rod-like BiSeI was proposed.

Bismuth selenoidide (BiSeI) being one of the V-VI-VII group compounds, which belongs to the orthorhombic system with the space group Pbnm, exhibits interesting properties, such as photoelectric,[1] ferroelectric[2] and piezoelectric,[3] and shows both n-type and p-type conductivity depending on the method of growth.

In the past, various methods have been developed to synthesize BiSeI. Traditionally, the melt growth by the Bridgeman-Stockbarger technique[4] and the growth from the vapor[5] have been applied to prepare the crystal BiSeI. However, all of these methods generally require special, complicated devices, or sophisticated techniques. Moreover, the growth temperature is high (>600 °C) and the temperature gradient has to be carefully controlled.

Recently, development of the solution routes in the mild temperature range 100 °C–200 °C has been motivated by current interest in the design of solid-state chalcogenides with low–dimensional structure due to the simple operation. For example, the crystal BiSeI has been synthesized via chemical transport reactions[1] and the hydrothermal method,[6] however, in the processes, the toxic gas H_2Se was used. In this work, we report for the first time the growth of rod-like crystal BiSeI via an ethanothermal process. The synthesis is based on the following two reactions:

$$Bi_2Se_3 + BiI_3 \rightarrow BiSeI \quad (1)$$

$$BiCl_3 + Se + NaI \rightarrow BiSeI + NaCl \quad (2)$$

The analytical grade reactants Bi_2Se_3 (1 mmol) with BiI_3 (1 mmol) or $BiCl_3$ (1 mmol), Se (1 mmol) with NaI (1 mmol) were added into a Teflon-lined autoclave of 50 mL capacity with ethanol solution up to 85% of the total volume, respectively. The autoclaves were heated at 200 °C for 12 h, and then gradually cooled to the room temperature. The black powders obtained were washed with distilled HCl, distilled water and ethanol sequentially for several times, respectively. Finally, the products were dried in vacuum at 60 °C for 4 h.

The X-ray diffraction (XRD)[7] pattern of the rod-like crystal BiSeI is shown in Figure 1. All the reflections can be indexed those of the corresponding pure orthorhombic phase BiSeI.[8] The calculated cell parameter of BiSeI is $a = 8.6899$ Å, $b = 10.5937$ Å, $c = 4.221$ Å, which is consistent with the literature ($a = 8.7053$ Å, $b = 10.5827$ Å, $c = 4.2199$ Å) within the experimental errors.

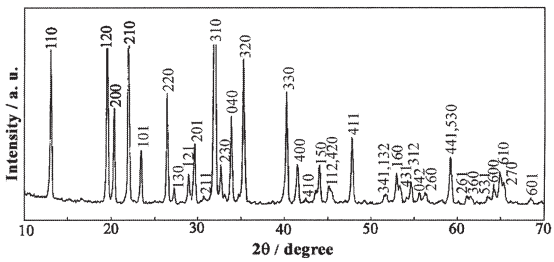

Figure 1. The XRD pattern of the product BiSeI.

The morphology and size of as-prepared products were observed by scanning electronic microscopy (SEM)[9] and the typical SEM image is shown in Figure 2. Figure 2a displays rod-like crystals BiSeI obtained from the reaction of Bi_2Se_3 and BiI_3 with the dimensions of ca. (1–5) μm × (10–30) μm. Moreover, the BiSeI crystals prepared based on the reaction $BiCl_3$, Se and NaI also showed rod-like morphology with diameters of ca. 2–4 μm and lengths of ca. 20–50 μm (Figure 2b) and the corresponding electron diffraction (ED) patterns[9] (Figure 2c) obtained from a

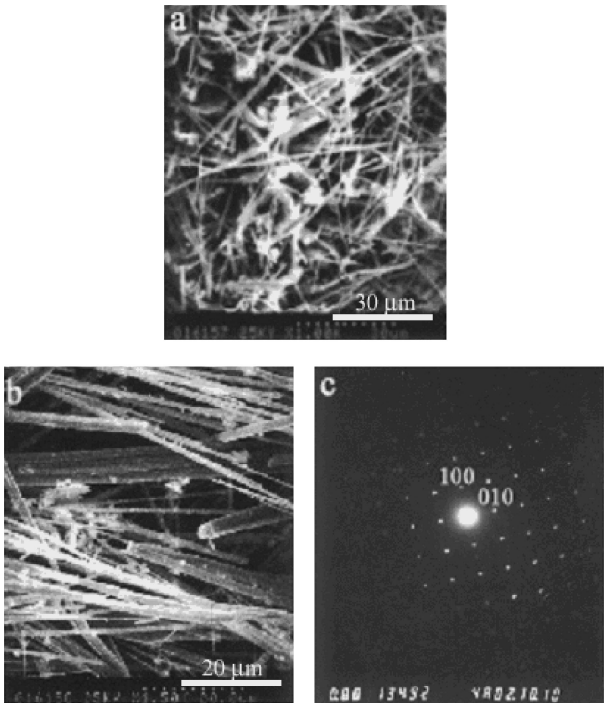

Figure 2. a) TEM images of the rod-like crystal BiSeI obtained using Bi_2Se_3 and BiI_3 as the reactants b) TEM images of the rod-like crystal BiSeI prepared based on the reaction of $BiCl_3$, Se and NaI c) the corresponding electron diffraction (ED) patterns of rod-like crystal BiSeI in Figure 2b.

selected area of rod crystals BiSeI displays the diffraction spots, indicating the monocrystal feature of the rod-like crystals.

The chemical composition of the product was determined using X-ray photoelectron spectra (XPS).[10] No obvious impurities could be detected in the sample. The binding energy values are 159.00 eV for Bi 4f, 54.90 eV for Se 3d and 619.95 eV for I 3d, respectively, which coincide with the reported values.[11] The result of XPS also reveals that the rod-like crystals are composed of Bi, Se, I and the quantitative analysis indicates that the atomic ratio of Bi:Se:I is approximate 1:1:1.

In the prepared experiment No. 2, the possible process of the formation of BiSeI is similar to that of BiSCl[12] and can be described as bellows:

$$BiCl_3 + H_2O \rightarrow BiOCl + HCl \quad (3)$$

$$BiOCl + CH_3CH_2OH \rightarrow Bi + CH_3CHO + HCl + H_2O \quad (4)$$

$$Bi + Se \rightarrow Bi_2Se_3 \quad (5)$$

$$BiCl_3 + NaI \rightarrow BiI_3 \quad (6)$$

$$Bi_2Se_3 + BiI_3 \rightarrow BiSeI \quad (7)$$

Firstly the reactant $BiCl_3$ hydrolyzes to BiOCl due to the trace of water in absolute ethanol (Eq 3). Then BiOCl can be reduced to active Bi by ethanol at 200 °C, thus the newly activated Bi atom can easily combine Se atom to Bi_2Se_3 (Eq 4 and 5). In the meantime, after NaI is added, the color of the solution changing to brick red proves the formation of BiI_3[13] (Eq 6). Then the crystal BiSeI can be obtained from the reaction of BiI_3 with Bi_2Se_3 (Eq 7).

As for the morphology of BiSeI, whatever the selenium source was Se or Bi_2Se_3, all the products display rod-like morphology, which is probably associated with its inherent structure characteristic of the bond anisotropy. The BiSeI structure consists of a double chains of $(Bi_2Se_2I_2)_n$ parallel to the *c*-axis (Figure 3).[14] The forces between the chains are much less than the exchange forces within the chains and are bonded via van der Waals forces and exchange interaction. The crystals possessing bond anisotropy will lead to the growth rate anisotropy. Molnar et al. ever estimated the growth rate to be more than 50 times parallel to the *c*–direction than that perpendicular to it.[15] It is the structure characteristic that results in the formation of rod-like morphology.

In the reaction process, the heating temperature had another important influence on the formation of BiSeI rod-like crystals. If the temperature is below 200 °C, there are no products obtained because Bi_2Se_3 cannot be produced at lower temperature.

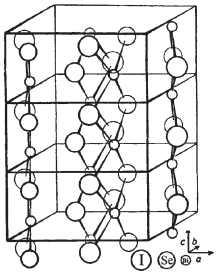

Figure 3. The structure of three unit cells of BiSeI.

In conclusion, two kinds of reaction routes via a mild ethanothermal process were applied to prepare BiSeI rod-like crystals. In the process, the possible reaction mechanisms for BiSI using $BiCl_3$, Se and NaI as raw materials is that ethanol reduce BiO^+ to active atom Bi, which can combine atomic Se to Bi_2Se_3, and then Bi_2Se_3 reacts with BiI_3 producing from the reaction of $BiCl_3$ and NaI to BiSeI. The morphologies of the products are firstly associated with their inherent structures of the bond anisotropy, which consists of a double chains of $(Bi_2Se_2I_2)_n$ parallel to the *c*-axis.

Financial support from the Chinese National Foundation of Nature Science Research and Chinese Ministry of Education is gratefully acknowledged.

References and Notes

1 J. Horak, I. D. Turjanica, and K. Nejezchleb, *Krist. Tech.*, **231**, 3 (1986).
2 T. A. Pikka and V. M. Fridkin, *Fiz. Tverd. Tela*, **3378**, 10 (1968).
3 D. M. Bercha and M. P. Zayachkovskii, *Ukr. Fiz. Zh.*, **1432**, 19 (1971).
4 R. Nitsche and W. I. Merz, *J. Phys. Chem. Solids*, **154**, 13 (1960).
5 a) T. A. Pikka, *Kristallografiya*, **1075**, 12 (1967). b) T. A. Pikka and V. M. Fridkin, *Sov. Phys. Solid State*, **378**, 10 (1968).
6 V. I. Popolitov, O. N. Zver'kova, and A. N. Lobachev, *Zh. Prikl. Khim.*, **1490**, 47 (1974).
7 The XRD analysis was carried out with a Japan Rigaku D/max-γ rotation anode X-ray diffractometer, using Ni-filtered Cu Kα radiation at 25 °C. A scanning rate of 0.05 °·s^{-1} was applied to record the patterns in the 2θ range of 30–80 °C. The reflection data was collected at 25 °C.
8 JCPDS Card: File No 44–462 for orthorhombic BiSeI.
9 The images of scanning electronic microscopy (SEM) were performed on an X-650 scanning electron micro-analyzer and electron diffraction (ED) patterns were taken with Hitachi H-800 transmission electron microscope at the acceleration voltage 200 kV.
10 The X-ray photoelectron spectra (XPS) were recorded on an ESCALab MKII X-ray photoelectron spectrometer with Mg Kα X-ray as the excitation source.
11 C. D. Wagner, W. W. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg, in "Handbook of X-ray photoelectron Spectroscopy," Perkin-Elmer Corporation, Physics Electronics Division, U.S.A. (1979).
12 L. Y. Zhu, Y. Xie, X. W. Zheng, X. Yin, and X. B. Tian, *Inorg. Chem.*, **4560**, 41 (2002).
13 "CRC Handbook of Chemistry and Physics," Various ed., ed. by D. R. Lide, CRC Press Inc., Boca Raton, FL.
14 E. Donges, *Z. Anorg. Allg. Chem.*, **263**, 112 (1950).
15 B. Molnar, R. Johannes, and W. Haas, *Bull. Am. Phys. Soc.*, **109**, 10 (1965).