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Growth of Compound Bi^{III}- VI^{A}-VII^{A} Crystals with Special Morphologies under Mild Conditions

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A series of crystals Bi^{III}-VI^{A}-VII^{A}, including the platelike crystals BiOCl, polygonal tubular crystals BiSCl, bundle-rodlike crystals $Bi_{19}S_{27}Br_3$, and BiSI, have been grown with use of mild solution routes in an ethanol system. The products are characterized by means of X-ray powder diffraction (XRD), electron diffraction (ED), scanning electronic microscopy (SEM), and Raman spectrum techniques. A possible mechanism of the reaction and of the growth of the crystals is proposed.

Introduction

The crystals with interesting morphologies, such as whiskerlike, rodlike, and platelike, have been the current focus of much attention due to special properties which have their potential applications in molecular based electronic devices, such as optical memory and switch, display, and data records. Especially, tubular structure materials[1] may be used in the synthesis of designed catalysts, as phonic band gap materials, as chemical separation media, and as selective sorbents because of their unusual electronic transport properties, their special well-defined structure, and their inherent mechanical strength.

Bi^{III}-VI^{A}-VII^{A} compounds BiSCl, $Bi_{19}S_{27}Br_3$, and BiSI evoked great interest owing to the coexistence of several physical properties,[2] such as high photoconductivity, ferroelectricity, electrooptical effect, electromechanical effect, piezoelectricity, and a large temperature dependence of the band gap. The compound BiOCl shows the properties of photoluminescence, thermally stimulated conductivity, and good catalytic activities and selectivities in the oxidative coupling of the methane (OCM) reaction.[3,4]

Some efforts have been made to prepare such multielemental inorganic materials. Traditionally, vapor phase growth has been used to produce crystals of BiOCl[5] and BiSCl and BiSI.[6] Crystals of BiSCl[7] and BiSI[8] have been obtained via melt growth by the Bridgeman−Stockbarger technique. Besides the above-mentioned two methods, crystals BiSI can also be grown by the flux technique.[9] Additionally, crystals of $Bi_{19}S_{27}Br_3$ ($9Bi_2S_3{\cdot}BiBr_3$) were synthesized by high-temperature methods and single crystals were grown from the vapor.[10] 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. Many solution routes have also been applied to synthesize these compounds. BiOCl powders have often been acquired via the hydrolysis method at room temperature.[11] However, the resulting products were poorly crystallized. The growth of BiSCl and BiSI under hydrothermal conditions was performed in a Teflon-lined apparatus.[12] The gel process has also been applied to grow BiSCl and BiSI.[13] The crystals of $Bi_{19}S_{27}Br_3$ were synthesized by chemical transport.[14] In the above-mentioned method, the toxic H_2S and HBr were used.

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Table 1. Typical Preparation Conditions of the Crystals of BiOCl, BiSCl, $Bi_{19}S_{27}Br_3$, and BiSI

crystals	reactants (mol ratio)	temp (°C)	time (days)
BiOCl	$BiCl_3$ (1)	150	1
BiSCl	$BiCl_3$ + S (2:3)	180	5
$Bi_{19}S_{27}Br_3$	$BiCl_3$ +Tu + NaBr (2:2:4)	180	1
BiSI	$BiCl_3$ +Tu + NaI (2:2:4)	180	1
	BiI_3 + Bi_2S_3 (2:2)	180	1

The crystals obtained via the above methods grow as needles due to the inherent property of the structure.

Recently, development of the solvothermal method in the mild temperature range 100−200 °C has been motivated by current interest in the design of solid-state chalcogenides with low-dimensional structure. Our group has successfully synthesized rodlike crystals of SnSe,[15] tubular crystals of Sb_2S_3 and Sb_2Se_3,[16] platelike Fe_7S_8, and rodlike $FeSe_2$ and $FeTe_2$[17] in the solvothermal system. In this present work, novel platelike crystals of BiOCl, polygonal tubular crystals of BiSCl, and bundle-rodlike crystals of $Bi_{19}S_{27}Br_3$ and BiSI have been prepared in the solvothermal process with ethanol as the system media. To the best of our knowledge, hollow crystals of BiSCl and bundle-rodlike crystals of $Bi_{19}S_{27}Br$ and BiSI are first reported. Generally, the crystal growth requires two steps: the formation of seed crystals and the later crystal growth. Thus from this point, an important advantage of this approach is that a single crystal can be grown via one pot. A possible reaction mechanism is also proposed.

Experimental Section

Analytical grade solvents and reagents were purchased from Shanghai Chemistry Co. Ltd. The sulfohalides were synthesized from $BiCl_3$ plus the different sulfur sources containing metal chalcogenides, sulfur powders, or thiourea (Tu) and sodium halide NaX (X = Br, I). Ethanol was chosen as the solvent. The corresponding experimental conditions for preparing these crystals are summarized in Table 1.

The reactants were added to a Teflon-lined autoclave of 50 mL capacity with an absolute ethanol solution up to 85% of the total volume. The autoclaves were heated at different temperatures for different times, and then gradually cooled to room temperature. Then, the platelike single-crystal BiOCl with a shinny mirrorlike surface, the black red needlelike crystal BiSCl, and the black powders $Bi_{19}S_{27}Br_3$ and BiSI obtained were washed with distilled water and ethanol sequentially several times, respectively. Finally, all the products were dried in a vacuum at 60 °C for 4 h.

The phase and the crystallographic structure of the products were determined by X-ray powder diffraction (XRD) with a Japan Rigaku D/max-rA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The scan rate of 0.05 deg/s was applied to record the patterns in the 2θ range of 10−70°. The morphology and size of the products were observed by scanning electronic microscopy (SEM), performed on an X-650 scanning electron microanalyzer. To study the structure of the products, electronic diffraction (ED) patterns taken on a Hitachi Model H-800 under an accelerating voltage of 200 kV were used. IR spectra were measured on a Bruker Vector-22 FT-IR spectrometer at room temperature. The Ramam spectra of bulk single-crystal BiOCl and BiSCl were recored on a ram-HI spectrometer provided by J. Y. Company. The samples were excitated by using the 514.5 nm wavelengh with a power of 1 mW.

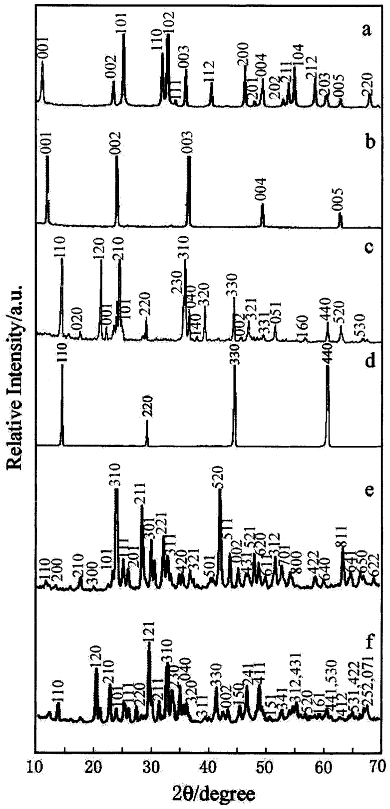

Figure 1. The XRD of the products: (a) powder BiOCl ground from single crystals; (b) single-crystal BiOCl; (c) powder BiSCl ground from single crystals; (b) single-crystal BiSCl; (e) powder $Bi_{19}Br_3S_{27}$; and (f) powder BiSI.

Results and Discussion

The XRD patterns of the as-prepared products are shown in Figure 1. In each XRD pattern, all the reflections can be indexed to those of the corresponding pure phase of BiOCl, BiSCl, $Bi_{19}S_{27}Br_3$, and BiSI, respectively.[18] The phases and lattice parameters of the samples are listed in Table 2. Figure 1a shows the XRD pattern for powder BiOCl ground from single-crystal BiOCl. And the XRD pattern of single-crystal BiOCl is displayed in Figure 1b. In contrast to that of powder BiOCl, there are only five peaks (001), (002), (003), (004), and (005) at 2θ of 11.9°, 24.1°, 36.5°, 49.3°, and 62.9°, respectively, which indicates single crystals in the form of platelets with the *c* axis perpendicular to the platelets. Figure 1c exhibits the XRD pattern of powders ground from the acicular single-crystal BiSCl, a little different from that of the common polycrystalline BiSCl powder. And the strongest peak of the former is the (110) plane rather than the (121)

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Table 2. The Cell Parameters of the Products

product	phase	lattice parameter (Å) exptl	lattice parameter (Å) lit	morphology	size
BiOCl	tetragonal	$a = 3.928$ $c = 7.538$	$a = 3.891$ $c = 7.369$	platelike	$1 \times 1\ \mu m^2$
BiSCl	orthorhombic	$a = 7.7396$ $b = 9.9824$ $c = 3.9238$	$a = 7.7486$ $b = 9.9750$ $c = 3.9938$	polygonal tubular	$(13-18) \times (17-21)\ \mu m^2$
$Bi_{19}S_{27}Br_3$	hexagonal	$a = 15.486$ $c = 4.0182$	$a = 15.432$ $c = 4.0152$	bundle-rodlike	$(2-8) \times (6-20)\ \mu m^2$
BiSI	orthorhombic	$a = 8.5138$ $b = 10.264$ $c = 4.1742$	$a = 8.5099$ $b = 10.462$ $c = 4.1909$	bundle-rodlike	$(5-10) \times (20-70)\ \mu m^2$

Table 3. Contrast Experiments at Different Temperatures for Different Times in Ethanol Solvent

reactant	no.	temp (°C)	time (day)	product
$BiCl_3$	1	120	1	powder BiOCl
	2	120	3	powder BiOCl
	3	150	1	single-crystal BiOCl
	4	150	3	single-crystal BiOCl
$BiCl_3 + S$	5	120	3	powder BiOCl
	6	150	1	single-crystal BiOCl
	7	150	3	single-crystal BiOCl
	8	180	3	powder $Bi_2S_3 + BiSCl$
	9	180	5	single-crystal BiSCl

plane in common polycrystalline BiSCl powder. In addition, the XRD pattern of the acicular single-crystal BiSCl (Figure 1d) only exhibits four peaks at 2θ of 14.5°, 29.1°, 44.4°, and 60.4°, which can be assigned to the orthorhombic (110), (220), (330), and (440) planes, respectively. The above results show that the (110) plane of the BiSCl crystals parallels the shaft of the acicular single crystals. Parts e and f in Figure 1 present the XRD of crystals of $Bi_{19}S_{27}Br_3$ and BiSI, respectively.

The SEM images of the products are shown in Figure 2. The BiOCl crystals (Figure 2a) display a layered structure, which has multiple growth spirals due to the existence of a growth defect.[6] Careful observation (Figure 2b) determined that the platelike crystals grow layer by layer. Investigations on the influence of uniaxial compression on the crystals revealed that they are isotropic along the normal to the layers.[3] The ED pattern of BiOCl is shown in Figure 2c, from which one can clearly see that layer structure morphology is perpendicular to the *c*-axis. Figure 2d illustrates the randomly distributed acicular single-crystal BiSCl with the length of ca. 0.5−1 cm under low magnification. And under high magnification, Figure 2e shows that the acicular single crystals are polygonal cross-section tubular crystals with the dimensions of ca. $(13-18) \times (17-21)\ \mu m^2$, and its ED pattern (Figure 2f) confirms the feature of single-crystal BiSCl. Parts g and i in Figure 2 display the novel buddle-rodlike crystals $Bi_{19}S_{27}Br_3$ and BiSI. From these figures, it is clear that this structure is ca. 2−8 μm in diameter and 6−20 μm in length for $Bi_{19}S_{27}Br_3$ and ca. 5−10 μm in diameter and 20−70 μm in length for BiSI. The corresponding ED patterns are exhibited in Figure 2, parts h and j, respectively.

To further characterize bulk single-crystal BiOCl and BiSCl, the Raman spectra (Figure 3) are presented to a single-crystal BiOCl obtained in the 40−450 cm^{-1} regions and BiSCl measured in the range of 30−350 cm^{-1}. The isostructural BiOCl is a tetragonal PbFCl-type structure with space group *P*4/*nnm*. For such a structure of space group D_{4h}^{7}, with two molecular formulas per unit cell, the Raman active modes are two A_{1g}, B_{1g}, and E_g. Figure 3a consists of three distinguished bands and one weak band. Because symmetric vibrations often give rise to more intense Raman bands than asymmetric vibrations, the strong bands existing at 142 cm^{-1} are assigned to the A_{1g} internal Bi−X stretching mode. The wavenumber of the other A_{1g} produced by the external Bi−X stretching mode is 59 cm^{-1}. The bands of 198 cm^{-1} can be assigned to the E_g internal Bi−X stretching mode, while E_g external Bi−X stretching is probably masked by the strong band at 142 cm^{-1}. The E_g and B_{1g} band produced by motion of the oxygen atoms at about 396 cm^{-1} is very weak, which is not easy to observed. The wavenumber here is smaller than that in the reference measure of powder BiOCl[19] (A_{1g} at 146 and 60 cm^{-1}, E_g at 202 and 400 cm^{-1}, B_{1g} at 400 cm^{-1}), which probably derives from the stronger orientation of platelike single crystals than that of powders. Figure 3b shows the Raman spctrum of single-crystal BiSCl. The structure of the crystals is the D_{2h}^{16} space group containing four molecular formulas per unit cell, which has nine Raman active modes (six A_g modes and three B_g modes). Six A_g modes contain the wavenumber of 283, 233, 103, 91, and 41 cm^{-1} and three B_g are 129 and 251 cm^{-1}. Comparing with the number in ref 20 for A_g (287, 260, 107, 95, 54, 44 cm^{-1}) and B_g (47, 138, 240 cm^{-1}), the wavenumbers of 54 (A_g) and 47 cm^{-1} (B_g) are absence here probably because of the strong band at 41 cm^{-1} masking them, or the different crystallite morphologies between them.

To understand the possible reaction process of BiOCl and BiSCl, the contrast experiments at different temperatures and times were carried out, and the results are listed in Table 3. In the process of the preparation of BiOCl, at the lower temperature (<120 °C), the products were only BiOCl powders (Nos. 1 and 2), which derived from the hydrolysis of $BiCl_3$ due to the traces of water in the absolute ethanol. When the temperature was not lower than 150 °C and the time was longer than 1 day, the single-crystal BiOCl were

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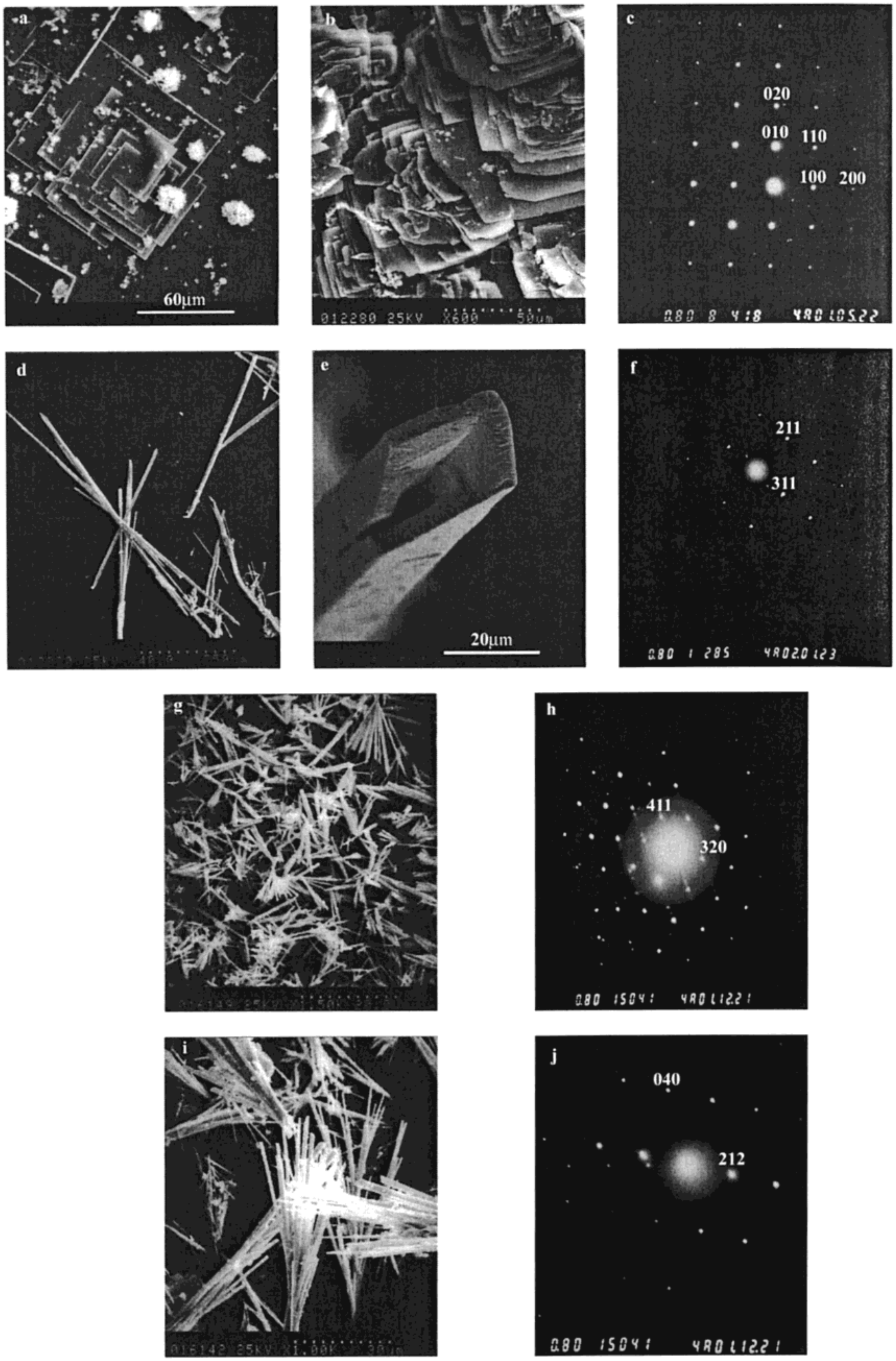

Figure 2. The SEM images of the products: (a) platelike crystal BiOCl; (b) ED patterns of single-crystal BiOCl; (c) single-crystal BiSCl distributed randomly under lower magnification; (d) polygonal-crystal BiSCl under higher magnification; (e) bundle-rodlike crystal $Bi_{19}Br_3S_{27}$; (f) ED patterns of $Bi_{19}Br_3S_{27}$; (g) bundle-rodlike crystal BiSI; and (h) ED patterns of BiSI.

always obtained (Nos. 3 and 4). The formation of platelike morphology comes from the layered structure of singlecrystal BiOCl, which is constructed by the combination of the metal oxygen $Bi_2O_2^+$ layer and double the chloride ion layers. The

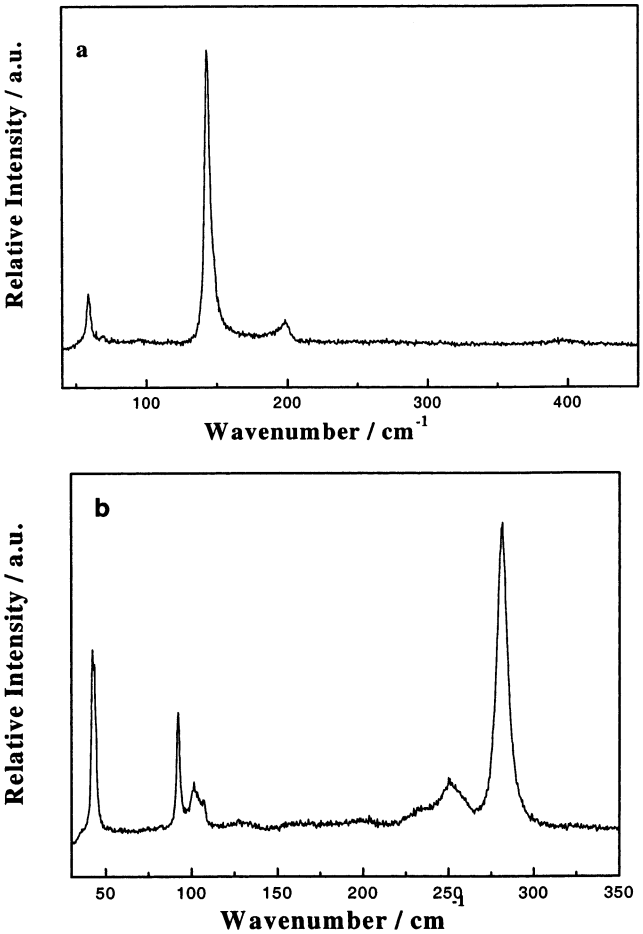

Figure 3. The Raman spectra of (a) platelike single-crystal BiOCl and (b) tubular crystal BiSCl.

bonding within the layers is strong and primarily covalent, whereas that between the layers is a van der Waals force.[21]

During the growth of BiSCl, if the temperature was below 150 °C, the products were BiOCl, indicating that elemental S did not take part in the reaction at the lower temperature (Nos. 5−7). If the temperature was as high as 180 °C, Bi_2S_3 powders easily appeared and the products turned to a mixture of Bi_2S_3 and BiSCl for 3 days, while after 5 days the acicular single-crystal BiSCl could be collected (Nos. 8 and 9). The experiments also demonstrated that the optimal reaction condition for single-crystal BiSCl was that the temperature was not lower than 180 °C and the time lasted for at least 5 days.

In addition, it has been reported that ethanol would reduce compound Sb_2O_3 to Sb.[22] Considering the cell potential ($\varphi^0 BiO^{1+}/Bi = 0.16$ V > $\varphi^0 Sb_2O_3/Sb = 0.15$ V), it can be conjectured here that, most probably, BiOCl can be reduced to Bi by ethanol under the present conditions. To further investigate the reaction mechanism, the infrared spectrum of the reaction solution for the growth of BiSCl has been taken and the result is shown in Figure 4. One can see the existence of the C=O group at about 1710 cm^{-1} is assigned to the oxidization of CH_3CH_2OH to CH_3CHO. The contrast experiment was done in the water system. The product BiSCl could not be obtained since Bi_2S_3 did not form in the process.

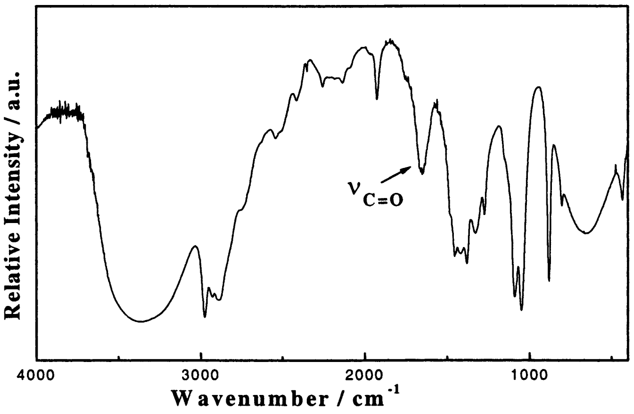

Figure 4. IR spectrum of the reaction solution for the growth of BiSCl.

On the basis of the above results, a possible mechanism for the formation of BiSCl is proposed, and the reaction process is described as follows:

$$BiCl_3 + H_2O \rightarrow BiOCl + HCl \quad (1)$$

$$BiOCl + CH_3CH_2OH \rightarrow Bi + CH_3CHO + HCl + H_2O \quad (2)$$

$$Bi + S \rightarrow Bi_2S_3 \quad (3)$$

$$Bi_2S_3 + BiCl_3 \rightarrow BiSCl \quad (4)$$

First the reactant $BiCl_3$ hydrolyzes to BiOCl due to the traces of water in absolute ethanol (eq 1). Then BiOCl can be reduced to active Bi by ethanol at 180 °C, thus the newly active Bi atom can easily combine the S atom to Bi_2S_3 (eqs 2 and 3). If the temperature is too low, the Bi atoms cannot be active enough to participate in the reaction with atom S. In the meantime, $BiCl_3$ acts with Bi_2S_3 to form BiSCl (eq 4). That single-crystal BiSCl can be easily obtained is because the BiSCl solution remains under metastable supersaturation. It is the condition that guarantees the formation of seed crystals and the perfect growth of the single crystals.

To understand the observed behavior of BiSCl, it is necessary to study its structure (Figure 5), which has been reported by Voutsas and Rentzeperis.[25] Each Bi atom is coordinated by 3 S atoms and 4 Cl atoms to form the composite coordination polyhedron (prism-pyramid). This characteristic double-polyhedron system is repeated along the *c* axis, thus forming an infinite double chain of composition $\{Bi_2S_4Cl_8\}_n$. The chain is further linked to each of four similar chains by a common $(Cl-Cl)_n$ row parallel to the *c* axis. It is understandable that the crystallite, which nucleated along the *c*-axis, grew readily due to the inherent chain type structure, and thus the needlelike morphology formed. As for the formation of hollow tubular, it is well-known that solid-state synthetic techniques have often involved solid-

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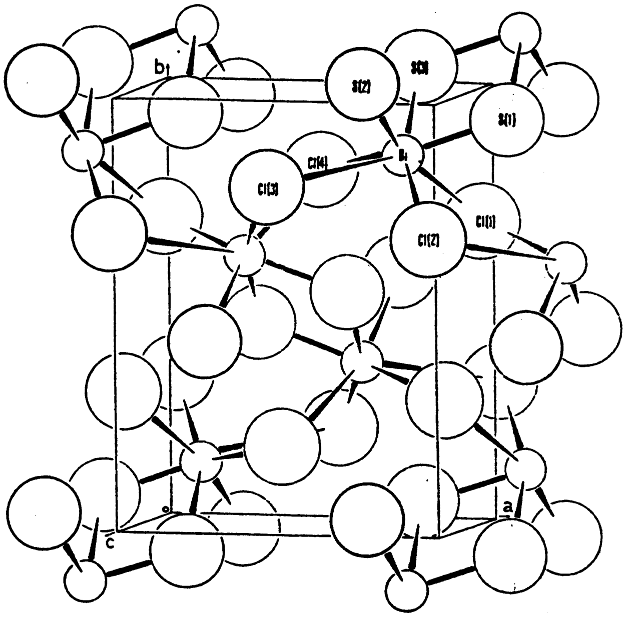

Figure 5. Clinographic projection of the unit cell of BiSCl.

state reactions at high temperature (>600 °C), which is high enough to allow adequate diffusion of atoms or ions to the site of product formation, and thus the resulting product is inclined to the structure of high density and high symmetry. Meanwhile, the effective removal of diffusion control by use of a suitable solvent tends to afford open crystal structure of relatively low density and symmetry,[26] which also have been demonstrated in the growth of the tubular crystals Sb_2S_3 and Sb_2Se_3 in the ethanol system in our previous work.[16] The hollow crystals are probably produced when new layers generated near the edge of the crystal deplete the supply of the material before the layer can reach the center of the growing surface.[27] In addition, the higher vapor pressure produced in the solvothermal condition may be propitious to the growth of hollow crystals.[28]

As to the growth of BiSI, when $BiCl_3$ and Tu were mixed, a yellow solution was obtained, which was the $BiCl_3$−thiourea complex, and the complex can decompose to Bi_2S_3 in ethanol at about 140 °C.[23] After NaI was added, the color of the solution changed to brick red because of the formation of BiI_3.[24] The crystal BiSI can be synthesized from the reaction of BiI_3 and Bi_2S_3, which has been proved and is shown in Table 1. So we speculate the process is that BiI_3 reacts with Bi_2S_3, which derives from decomposing the $BiCl_3$−thiourea complex to form BiSI. The reaction process can be expressed in detail as follows:

$$BiCl_3 + n\text{Tu} \rightarrow [\text{Bi(Tu)}_n]^{3+} + 3Cl^-$$

$$BiCl_3 + \text{NaBr/NaI} \rightarrow BiBr_3/BiI_3$$

$$[\text{Bi(Tu)}]^{3+} \xrightarrow{\text{decompose}} \text{Bi2S3}$$

$$Bi_2S_3 + BiBr_3/BiI_3 \rightarrow Bi_{19}S_{27}Br_3/\text{BiSI}$$

Table 4. Contrast Experiments of Preparing the Crystals of $Bi_{19}S_{31}Br_3$ and BiSI

no.	reactants	solvent	temp (°C)	products
10	$BiCl_3$ + Tu + NaI	ethanol	180	bundle-rodlike crystal BiSI
11	Bi_2S_3 + BiI_3	ethanol	180	
12	$BiCl_3$ + S + NaI	ethanol	200	
13	$BiCl_3$ + Tu + NaI	water	180	
14	Bi_2S_3 + BiI_3	water	180	
15	$BiCl_3$ +Tu + NaBr	water	180	bundle-rodlike crystal $Bi_{19}S_{31}Br_3$
16	$BiCl_3$ + S + NaBr	ethanol	200	

To investigate the morphology of BiSI and $Bi_{19}S_{27}Br_3$, the contrast experiments were done and the results are listed in Table 4. If the sulfur source was thiourea, Bi_2S_3, or S powders (Nos. 10−12), all the products were BiSI with bundle-rodlike crystals. When the ethanol solvent was substituted with water in the preparation of BiSI (Nos. 13 and 14), the products and corresponding morphology remain invariable. From the above experimental results, it can be seen that the morphology of BiSI cannot be affected by some external factors, such as solvents (water and ethanol), sulfur source (S, Tu, Bi_2S_3), etc. Thus most probably its bundle-rodlike morphology is associated with its inherent structure characteristic. Crystal BiSI has actually two double chains of $(Bi_2S_2I_2)_n$ in a unit cell with a strong covalent bond and each double chain is held to the next double chain only by weak Van der Wall forces.[29] The structure leads to the growth rate anisotropy, for example, Molnaretc et al. have estimated the growth rate to be more than 50 times parallel to the *c*-direction than that perpendicular to it.[30] It is this structural characteristic that results in the formation of rodlike morphology, and a modification of the growth conditions cannot be enough to change this anisotropy. Similar to the morphology of BiSI, the shape of $Bi_{19}S_{27}Br_3$ is also the bundle-rodlike structure, as confirmed in Nos. 15 and 16. The rodlike shape is also related to its structural characteristic,[31] which contains $(Bi_4S_6)_\infty$ chains in the *z*-direction linked by I atoms oriented on the trigonal axes and Bi atoms oriented on the 6_3 axes. As for the formation of the bundle-like morphology of $Bi_{19}S_{27}Br_3$ and BiSI, it is most probably because $Bi_{19}S_{27}Br_3$ or BiSI clusters are formed due to the faster velocity of nuclei than that of oriented growth at first, and many newborn clusters agglomerate together, then each of them start to grow into rod crystals along the oriented direction when the clusters are in the excess saturation state. The formation process of initial clusters and the oriented growth of clusters is similar to that of silicon nanorods in vapor−liquid−solid,[32] and the difference lies in that the clusters are easy to agglomerate in solution, which directly leads to the formation of bundle-rodlike crystals rather than detached single-rod crystals.

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Conclusion

In summary, a series of crystals Bi^{III}-VI^{A}-VII^{A} containing platelike crystal BiOCl, polygonal tubular crystal BiSCl, bundle-rodlike crystal $Bi_{19}S_{27}Br_3$, and BiSI were grown with use of different raw materials in ethanol solvent under mild conditions. The products were characterized by means of X-ray powder diffraction (XRD), electron diffraction (ED), scanning electronic microscopy (SEM), and Raman spectrum techniques. A possible reaction mechanism for BiSCl is that ethanol reduces BiO^+ to active atoms Bi, which can combine atomic S to Bi_2S_3, and then Bi_2S_3 converts to BiSCl gradually for 5 days at least. For the growth of $Bi_{19}S_{27}Br_3$ and BiSI it is probably that Bi_2S_3 driving from the decomposition of complex $(Bi-Tu)^{3+}$ connects $BiBr_3$ or BiI_3 to form $Bi_{19}S_{27}Br_3$ and BiSI. The morphologies of the products are first associated by their inherent structures. In addition, some factors, such as the preparation method, vapor pressure, etc., can also affect the shape of the as-grown crystals. These simple and novel routes are expected to grow other ternary single crystals.

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