Preparation and Vibrational Properties of BiI_3 Nanocrystals

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Nanocrystalline BiI_3 with average size of 10–20 nm is prepared by a hydrothermal method at 180–200 °C for the first time. The vibrational properties of as-prepared BiI_3 were investigated by the Raman spectra at room temperature.

The family of quasi-molecular solids of XI_3 (where X=As, Sb, Bi) belongs to highly anisotropic materials, which has long been recognized as probe of structure and bonding in these important systems.[1–4] All three members of the tri-iodide family have crystallographically equivalent structures[4–6] though it has been found that the molecular character of the XI_3 units differs as a result of internal degrees of freedom. The molecular character is lost in BiI_3, which exhibits near-perfect sixfold coordination of the metal. Each Bi atom is octahedrally coordinated with adjacent six iodine atoms, and each structural layer consists of three close-packed atomic layers in the sequence of I–Bi–I.[7] The thickness of the unit layer is 6.98 Å.[8]

BiI_3 is promising for non-silver based and thermally controlled photographic applications and a candidate material for development as a room temperature and γ-ray detector.[9,10] The band gap of bulk BiI_3 has been reported as ~2 eV.[11] In addition, due to its strong intrinsic optical anisotropy, considerable prior interest has been exhibited in the optical properties of this material. The optical characterization of BiI_3 has been carried out by means of optical transmission, optical reflection, and photoluminescence measurements.[12–17] There has been several reports on confinement effect[18] or nonlinear optical effects[19] in clusters of BiI_3, and in excitons associated two-dimensional defects of BiI_3 bulk crystals.[20,21] The optical properties of nanostructures in layered metal tri-iodide crystals have been reviewed by T. Komatsu and coworkers.[22] Recently, the optical function of BiI_3 has been measured using two-modular generalized ellipsonmetry.[23]

BiI_3 powders were synthesized by reaction between element bismuth and iodine[24] or the reaction between HI and $BiCl_3$,[25] and post treatment requiring a high temperature (above 450 °C).

To our knowledge, the preparation of BiI_3 nanocrystallines by a hydrothermal method has not been reported previously. In this letter we report the synthesis of nanocrystal BiI_3 through a hydrothermal route and the vibrational properties.

For BiI_3 preparation, Bi_2S_3 nanocrystals[26] and analytically pure iodine (molar ratio 1:3) were added to a autoclave of 50 mL capacity, which was filled with distilled water up to 80% of the total volume. The autoclave was maintained at 180–200 °C for 8–10 h and then cooled to room temperature naturally. The precipitate was filtered and washed with distilled water several times. A black powder was obtained after dried in vacuum at 70 °C for 2 h.

X-ray powder diffraction (XRD) pattern was obtained on a Rigaku Damax γA X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). The XRD pattern for the BiI_3 sample is shown in Figure 1. All reflections can be indexed as the hexagonal BiI_3 phase with cell constants a = 7.525 Å, c = 20.710 Å, which are consistent with the value reported in the literature (JCPDS, 7-269). The diffraction peaks ranging from 12.2° to 13.0° for the (003) plane indicate that the powders display preferential 001 orientation. No impurities such as BiOI were detected.

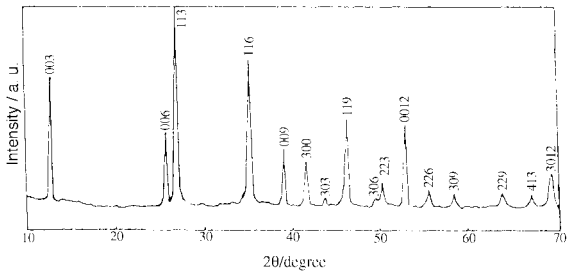

Figure 1. XRD pattern of as-prepared BiI_3.

Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscopy, using an accelerating voltage of 200 kV. Figure 2 shows the TEM image of the as-prepared BiI_3 sample, which consisted of slice with an average size of 10–20 nm. Some of them coalesce each other to form big sheets.

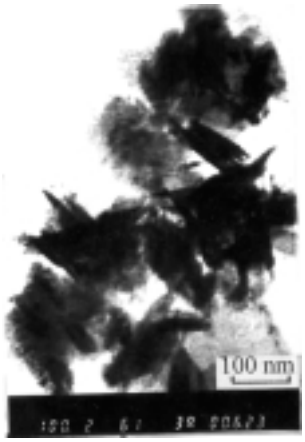

Figure 2. TEM images of as-prepared BiI_3.

The synthesis was based on the disproportionation reaction of I_2:

$$6I_2 + 6H_2O \longrightarrow 6HI + 6HIO \quad (1)$$

$$6HOI \longrightarrow 3I_2 + 3H_2O + 3/2O_2 \quad (2)$$

$$Bi_2S_3 + 6HI \longrightarrow 2BiI_3 + 3H_2S \quad (3)$$

BiI_3 dissolves in the hot water.[27] However, the initial pH value of the starting materials is about 7. In the hydrothermal process,

the pH value of the reaction system decreased, which is smaller than 1. So it is believed that BiI_3 nanocrystallines is indissoluble in hot water under strong HI acidic condition. In addition, due to the unsteadiness of HOI (see eq (2)), the reaction did not produce BiOI, which is consistent with the result of XRD.

The effect of different bisumth salt on the formation nanocrystalline BiI_3 was studied. $Bi(NO_3)_3$ and Bi_2O_3 were used to replaced Bi_2S_3 keeping the other reaction identical. T he reaction did not occur.

The influence of reaction time and temperature in the preparation of BiI_3 nanocrystallines was also investigated. It was found that the optimum condition for the formation of nanocrystal BiI_3 was 180–200 °C for 8–10 h. If the temperature was lower 170 °C or the time shorter than 6 h, the yield of BiI_3 was lower and the as-synthesized BiI_3 was poorly crystalline.

Raman spectra were recorded on SPEX-1403 spectrometer with 514.5 nm radiation from a 200-MW argon ion laser. The sample was investigated at room temperature. The observed Raman mode frequencies of as-synthesized BiI_3 are shown in Table 1 at room temperature along with its symmetry labels and mode type. The Raman spectra (RS) from which this result is obtained is shown in Figure 3. The RS of as-prepared BiI_3 is broadened and appears a new vibrational mode in comparison with that of bulk materials.[3,28] The line at 143 cm^{-1} in Figure 3 is not observed in the RS of the bulk BiI_3[3,28]. We cannot assign it, which may be a new vibrational mode in the BiI_3 nanocrystallines or a vibrational mode of the other impurities. We tend to think that this mode (at 143 cm^{-1}) may be a new mode. Because no other impurities was detected by XRD.

Table 1. Observed Raman frequencies of as-synthesized BiI_3 at room temperature

Symmetry	300 K	300 K[a]	2 K[b]
A_g	108	115.5	113.3
E_g		87.4	95
A_g	48	56.3	
A_g		52.8	58.3
A_g		34.6	53.5
E_g			36.7
E_g			33.5
A_g(RL)		22.4	22.8
E_g(RL)			12.9

The frequencies are units of cm^{-1}. RL stands for rigid layer.

[a]Ref. 3; [b]Ref. 28.

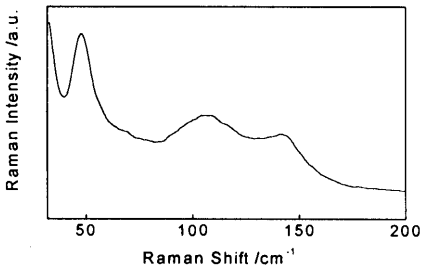

Figure 3. Raman spectra at room temperature for as-synthesized BiI_3.

In a summary, we have succeeded in the synthesis of nanocrystal BiI_3 by hrdrothermal reaction between Bi_2S_3 and I_2. This method can be readily employed to prepare other nanocrystalline metal mono-, and di-iodide materials such as CuI, AgI and PbI_2. A detailed study on this synthesis method is in progress. The vibrational properties of BiI_3 nanocrystallines were studied by the Raman spectra.

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