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Metastable γ-Bi_2O_3 tetrahedra: Phase-transition dominated by polyethylene glycol, photoluminescence and implications for internal structure by etch

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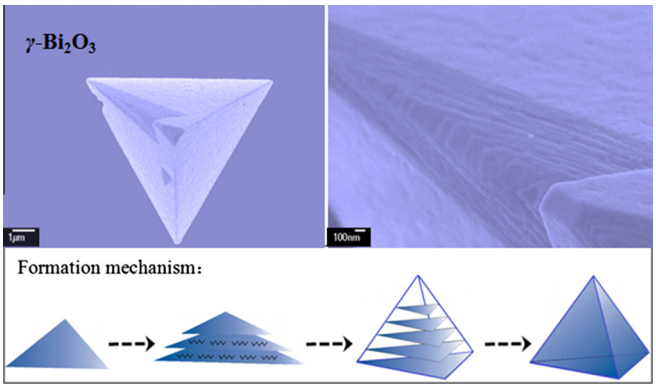
GRAPHICAL ABSTRACT



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ABSTRACT

Metastable γ-Bi_2O_3 tetrahedra have been fabricated by a facile polyethylene glycol-assistance (PEG, Mw = 400) one-step precipitation method at 70 °C. The tetrahedra of 8 μm are built up of ultrathin nanosheets via layer-by-layer self-assembly. X-ray powder diffraction, scanning electron microscopy, UV–visible spectrometer and fluorescence spectrophotometer were employed to characterize the obtained γ-Bi_2O_3. The morphology of the γ-Bi_2O_3 is significantly influenced by the feeding concentration of NaOH solution. Tetrahedra and incomplete tetrahedra whose edges are clipped in various degrees of γ-Bi_2O_3 can be obtained with different concentrations of NaOH solution. The uniform and ordered chains of PEG play a crucial role not only in the morphology, even more important in phase-transition of Bi_2O_3. The photoluminescence (PL) characteristic of the sample was investigated.

1. Introduction

Bismuth oxide (Bi_2O_3) is versatile and technologically interesting material with wide band-gap, high refractive index, dielectric permittivity, high oxygen conductivity, remarkable photoconductivity and photoluminescence [1–3]. These unique characteristics

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make Bi_2O_3 suitable for applications in solid oxide fuel cells, sensors, photoelectric materials, catalysts, glass manufacturing and functional ceramics [4–8].

Until now, at least seven polymorphs of Bi_2O_3 have been reported, including α-, β-, γ-, δ-, ε- [9], ω- [10] and high-pressure hexagonal phases [11]. Among them, α-, β-, γ- and δ-Bi_2O_3 are main polymorphic forms. The monoclinic α-Bi_2O_3 phase and face-centered cubic δ-Bi_2O_3 phase are stable at room and high temperature (730–825 °C) respectively, while the tetragonal β-Bi_2O_3 phase and the body-centered cubic γ-Bi_2O_3 phase are high temperature metastable phases and usually transform into the monoclinic phase when temperature is reduced [12,13].

Recently, there has been increasing interest in Bi_2O_3 with different polymorphic forms [14–16]. α-, β- and δ-Bi_2O_3 have been prepared in various morphologies, such as nanofibers [17], nanobelts [18], nanowires [19], nanoflakes [20], microrods [21] and thin film [22] using variety of fabrication techniques, but there are only a few reports on metastable γ-Bi_2O_3. Wang and co-workers reported the preparation of α-, γ- and α-/γ-Bi_2O_3 via a hydrothermal method [23]. Li's group successfully synthesized metastable γ-Bi_2O_3 ultrathin films via thermal annealing (above 512 °C) of α-phase Bi_2O_3 films which were prepared on silicon substrates by means of atomic layer deposition (ALD) using $Bi(thd)_3$ (thd: 2, 2,6,6-tetramethyl-3,5-heptanedionato) and H_2O as precursors [24]. Tseng et al. prepared 3D flowerlike γ-Bi_2O_3, composed of 2D building blocks via a solution precipitation method with the aid of polyethylene glycol-8000 (PEG-8000) [25]. For γ-Bi_2O_3, obtaining the "pure" phase is challenging due to this high temperature metastable phase must be stabilized by the addition of another oxide or post-transition ions [26,27].

In this work, metastable tetrahedral γ-Bi_2O_3 was synthesized through one-step precipitation method at 70 °C in presence of polyethylene glycol (PEG, Mw = 400). The effects of PEG and NaOH concentration on the sample were discussed in detail. Internal structure of tetrahedra was investigated by etch of sodium borohydride ($NaBH_4$). The probable formation mechanism was proposed based on experimental results. Crystal structure, morphology of the samples together with the optical absorption and photoluminescence (PL) characteristics were analyzed.

2. Experimental

All chemicals were of analytical grade and used as received without further purification. Distilled water was used throughout. To prepare γ-Bi_2O_3 tetrahedra, 3 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 20 mL of nitric acid aqueous solution (2 mol/L) to avoid hydrolyzation of Bi^{3+} ions, 1 mL of polyethylene glycol (PEG, Mw = 400) was added and stirred for 10 min at room temperature, the obtained solution was heated to 70 °C and then 20 mL of NaOH (2 mol/L) was quickly poured into the above solution. After 2 h's continuous stirring, the resulting yellow precipitates was isolated by centrifugation, and washed several times with pure water and absolute ethanol. Finally, the product was dried at 60 °C in air for 12 h.

The crystallite structure of the resulting samples was determined using a XRD-6000 X-ray diffractometer (XRD, SHIMADZU) with a Cu Kα radiation source (λ = 1.5405 Å). The morphology and size were observed by scanning electron microscopy (SEM, FEI XL30 ESEM-FEG). EDX analysis was performed by XL30 ESEM-FEG working at 20 kV accelerating voltage. UV–visible characterization was recorded with a UV–visible spectrometer (HITACHI U-3400) equipped with an integrating sphere attachment. The PL spectra were performed at room temperature by a RF-5301PC (SHIMADZU) fluorescence spectrophotometer.

3. Results and discussion

3.1. Structure and morphology

XRD pattern is used to determine the crystal structure of the resulting sample. A typical XRD pattern of the sample is shown in Fig. 1a. All recorded peaks are indexed to body-centered cubic Bi_2O_3 (γ-Bi_2O_3) with the calculated lattice constants $a = b = c = 10.2437$ Å, which are in accordance with the standard values ($a = b = c = 10.2501$ Å) (JCPDS 81-0563). Note that no characteristic peaks corresponding to crystalline impurities are observed in the XRD pattern of the sample, which indicates the phase purity of tetrahedra.

The morphology of sample was characterized by scanning electron microscopy (SEM). Fig. 2 demonstrates the SEM images of the as-synthesized sample. An overall view in Fig. 2a indicates tetrahedral microstructures and many of them are accumulated to form siamesed-tetrahedra (Fig. 2a and b). The high magnification image in Fig. 2c shows a single tetrahedral microstructure which is about 8 μm in size. It is worth noting that the tetrahedral microstructures are assembled by ultrathin nanosheets via layer-by-layer stacking, as shown in Fig. 2d. The chemical composition of the sample is determined using EDX attached on the SEM. As shown in Fig. 1b, only peaks of Bi and O are found in EDX spectrum, indicating that the sample is Bi_2O_3 with high purity. The Au peak in the spectrum is introduced through treatment of sample before detection.

Internal structure of tetrahedra was investigated by etch of sodium borohydride ($NaBH_4$). The detailed procedure of etch is given in Fig. 3. In etch process (see Fig. 4), the outermost faces of tetrahedra are firstly removed, internal structures of layer by layer stacking are discovered. The result also demonstrates that tetrahedra are built up of nanosheets via layer by layer self-assembly.

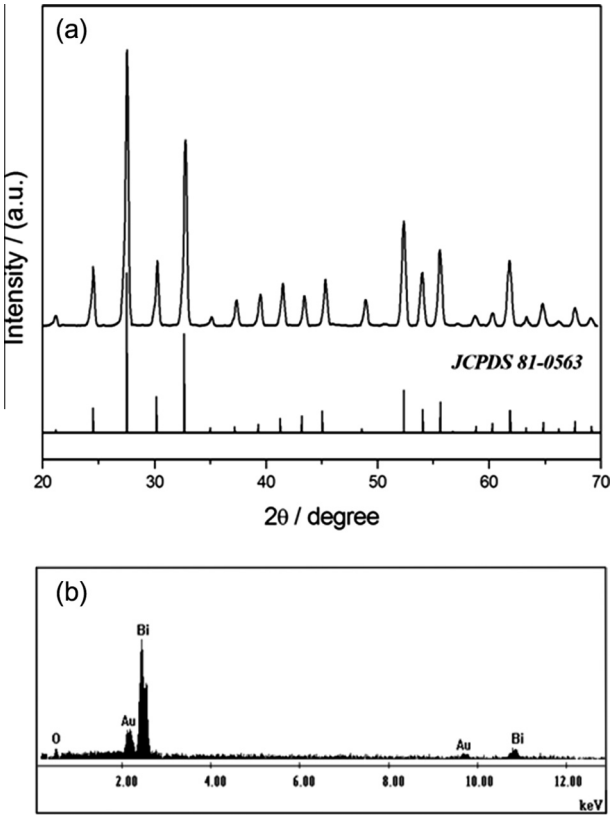

Fig. 1. (a) XRD patterns of standard γ-Bi_2O_3 and metastable γ-Bi_2O_3 tetrahedra. (b) EDX spectrum of metastable γ-Bi_2O_3 tetrahedra.