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Facile synthesis and purplish blue luminescence of the binary mixed valence compound Bi_4O_7 microcrystals

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ABSTRACT

We presented a facile chemical strategy to synthesize the pure mixed valence compound $Bi(III,V)_4O_7$ microcrystals. Our results indicated that Bi_4O_7 microcrystals could transformed from Bi_2O_4 with the increase of temperature in the hydrothermal synthesis. The reaction temperature and the pH value of solution play the vital role in the phase transformation. The luminescent behavior of the product was investigated and there exists a broad band emission from 400 to 475 nm in the visible region, which corresponds to the purplish blue light. Therefore, the Bi_4O_7 can be used as a potential candidate for the purplish blue light emitters.

1. Introduction

Bismuth oxide is an interesting dielectric material with potential applications such as microwave integrated circuits, optical coatings and metal/insulator/semiconductor (MIS) capacitors [1–3]. The binary Bi–O system contains several intermediate phases, such as Bi_2O_3 (with four polymorphs α-, β-, γ- and δ-Bi_2O_3), Bi_2O_4, Bi_2O_{2-x}, Bi_8O_{11}, Bi_6O_7, Bi_4O_7, and BiO [4–7]. Recently, Bismuth oxides with mixed valence Bi have attracted more and more attention [5,8–13]. For example, $Bi(II, III)_6O_7$ thin films, nanosheets, and microspheres were synthesized by chemical vapor deposition, electrolytic corrosion and chemistry precipitation methods [11,13,14]. Bi_6O_7 was detected with one strong UV emission at room temperature and had excellent electrochemical performance as the electrode materials for supercapacitors.

Bi_4O_7, another bismuth oxide with Bi (III, V) mixed valence, seems to be the key for understanding the superconductivity in $BaPb_{1-x}Bi_xO_3$ and $Ba_{1-x}Bi_xO_3$, which are the typical copper-free oxide high-temperature-superconductors (HTSC) [9,10]. Bi_4O_7 is the most closely related to the reported fully charge ordered system, like $Ag_{25}Bi_2(III)Bi(V)O_{18}$ and $Bi(III)Bi(V)O_4$ which have clearly distinct sites for the two valences of bismuth [9,15]. However up to now, the reported method to synthesize the pure Bi_4O_7 is only the thermal decomposition of both the amorphous and the crystalline bismuth(III, V) oxide hydrating at high temperature [9,10]. In other cases, Bi_4O_7 generally appears as impurities and twinned crystals in the bismuth oxides and bismuth oxide-based materials by the chemical methods [15]. Therefore, the large-scale preparation of pure Bi_4O_7 material via chemical methods is still a challenge.

Here, we presented a facile and chemical strategy to synthesize the pure Bi_4O_7 by a simple hydrothermal method. The purplish blue luminescent behavior of products was also firstly investigated, which usually means a broad-band emission with main peaking located at 400–450 nm [16,17].

2. Experimental section

All analytical grade chemicals were purchased from Beijing Chemical Corporation and used as received without further purification.

In a typical synthesis, 0.158 g $NaBiO_3$ was ultrasonically dispersed in 22 mL distilled water. After strong stirred, the above solution was sealed in a 35 mL autoclave and heated at the temperature of 220 °C for 6 h. The system was then allowed to cool to room temperature. The final sample was collected by centrifugation, washed with deionized water to remove any possible ionic remnants, and then dried in a vacuum at 60 °C.

The sample was characterized using XRD with a Philips X'Pert Pro Super diffractometer with Cu *K*α radiation ($\lambda = 1.54178$ Å). XPS measurements were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an excitation source of Mg *K*α = 1253.6 eV. The field emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JSM-6700F SEM. All the luminescence spectra were recorded using Perkin Elmer instrument LS55 photoluminescence spectrophotometer equipped with a 450 mW xenon lamp as the excitation source at room temperature.

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3. Results and discussion

3.1. Phase identification of Bi_4O_7 microcrystals

Fig. 1a shows the XRD pattern of Bi_4O_7 microcrystals prepared by the hydrothermal method. All of the diffraction peaks can be indexed to the triclinic structure with space group of P-1 (PDF No. 72-4663 and ICSD Code: 51778). The red line in Fig. 1a is a simulative XRD pattern according to the data by Dinnebier et al [9]. The results show that our experiment data are consistent very well with those by Dinnebier et al. and proves the product is the pure Bi_4O_7 phase.

In order to further verify the phase of the products, the thermogravimetry (TG) of product was carried out. As shown in Fig. 1b, the TG curve indicates the one step weight loss. The observed weight loss (1.52%) agrees with the calculated value (1.51%) very well on the assumption that Bi_4O_7 changes to Bi_2O_3 by release of oxygen. As shown in Fig. 1c, the X-ray powder pattern of the sample heated up to the weight loss can be indexed as Bi_2O_3, which means the weight loss is certainly caused by the complete reduction of Bi^{5+} to Bi^{3+}. Obviously, the TG result is an evidence of the obtained pure Bi_4O_7 phase.

3.2. Morphology of microcrystals

The morphologies and EDS spectrum of Bi_4O_7 microcrystals as prepared are shown in Fig. 2a and b, respectively. As SEM image (Fig. 2a) shows, the morphologies of Bi_4O_7 as prepared have the rod microcrystal shape and smooth surface. The width of Bi_4O_7 rods varies from 0.1 to 1 μm. The thickness is in the range of 0.1–0.3 μm and the length reaches several micrometers range. The EDS spectrum (Fig. 2b) of the Bi_4O_7 indicates the presence of Bi, O and Cu and no any other impurities. The Cu peak should be attributed to the substrate copper sheet where the sample was dropped.

Hence, it is confirmed by the XRD, EDS and TG studies that our product is Bi_4O_7 and there isn't any other impurity or secondary phases in the sample.

3.3. Effects on phase formation

3.3.1. pH effect

We employed nitric acid or sodium hydroxide to adjust pH values of the reaction solutions. The amount of $NaBiO_3$ precursor in each reaction was fixed at 0.0158 g. Reaction conditions were fixed at 220 °C for 6 h.

Fig. 3a shows the XRD patterns of the obtained samples after hydrothermal treatments at different pH values. It can be seen that in an acidic medium (pH < 6), a mixture of Bi_4O_7 (●) and Bi_2O_3 (■) was formed, and pure phase Bi_4O_7 was not obtained. As the pH values further increased to 7–9, the pure Bi_4O_7 was generated. if we continuously increased the pH value to 10, a mixture including Bi_4O_7 and Bi_2O_4 (▼) occurred again. These results indicated that the pH value of the solution plays a vital role in the chemical synthesis of the pure Bi_4O_7 microcrystals.

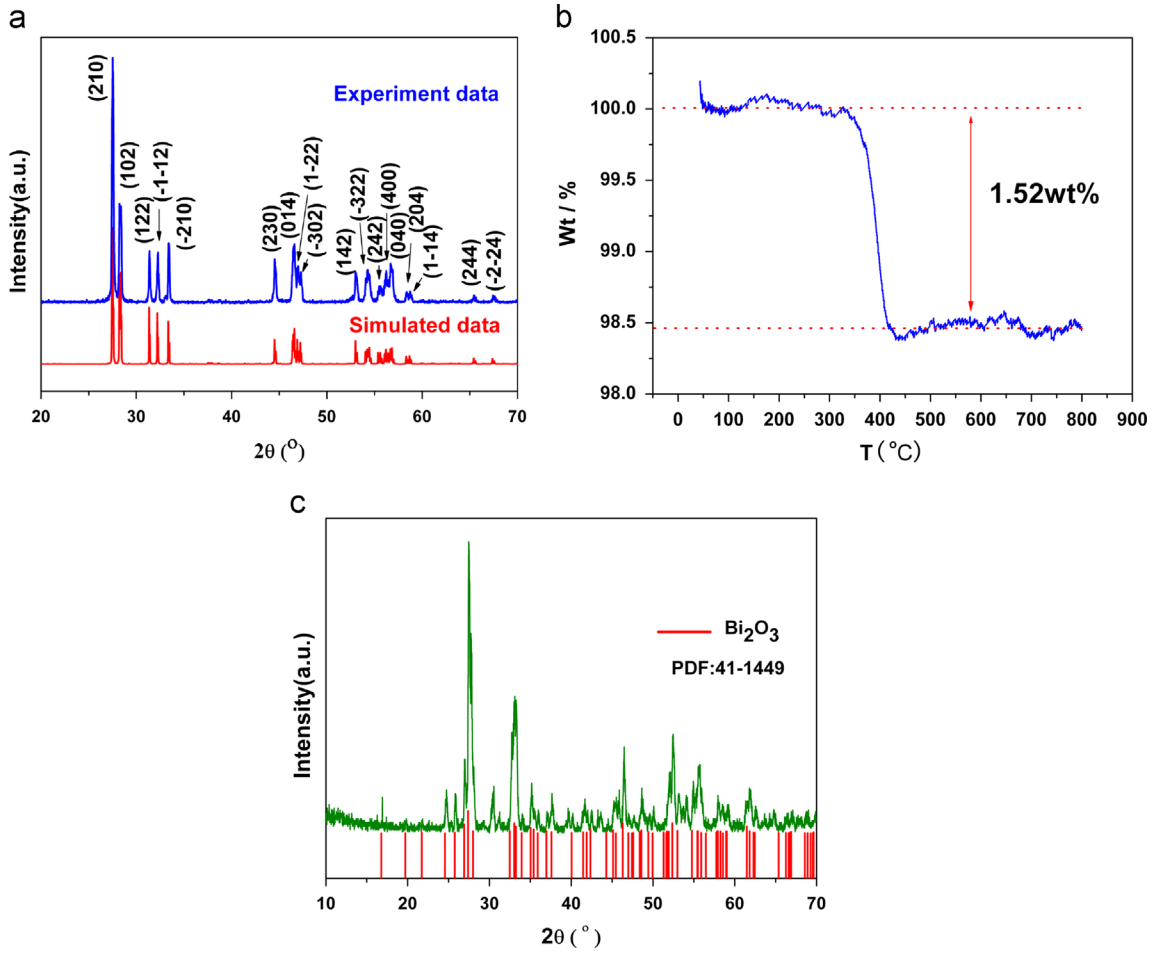

Fig. 1. (a) XRD pattern (the PDF number for simulated peaks: No. 72-4663); (b) TG curve of Bi_4O_7 microcrystals; and (c) XRD pattern of the sample heated up to the weight loss (450 °C). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)