Combustion synthesis of porous bismuth oxide

Yajun Wang1,*, Shihui Li1 and Zisheng Jiang2,*
1State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China
2Jiangnan Industry Group Co. Ltd., Xiangtan 411100, Hunan, China
*Corresponding author e-mail: yajunwang@bit.edu.cn

Abstract. Bismuth oxides with a micro porous structure were prepared by a simple combustion reaction between oxidizer (bismuth nitrate) and fuel (citric acid). These porous bismuth oxides were prepared at different values of the stoichiometric coefficient. The as-prepared products were characterized by X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results show that many pores distributed in tetragonal bismuth oxides (β-Bi₂O₃) granules which have varied crystallinity and particle sizes at different oxidizer/fuel ratio. Increasing the fuel concentration improved the crystallinity and purity of β-Bi₂O₃. A further calcination could also increase the particle size, crystallinity and transform the phase structure from β-Bi₂O₃ to pure α-Bi₂O₃.

1. Introduction

Bismuth oxide (Bi₂O₃) has a lot of excellent physical and chemical properties determined by its numerous polymorphs, such as wide band gap (2−3.96 eV) [1], high oxygen-ion conductivity (1.0 S/cm) [2], high refractive index (n_β-Bi₂O₃=2.9) [3], high dielectric permittivity (ε_r=190), and prominent photoconductivity and photoluminescence [4]. Due to its excellent properties, over the past decades, bismuth oxide is one of the most important functional materials which have been used in a variety of areas, such as solid oxide fuel cells [2], gas sensors [5], catalysts [6], energetic materials [7] and so on. Additionally, it is well known that bismuth oxide has six main crystalline phases, denoted by α-Bi₂O₃, β-Bi₂O₃, γ-Bi₂O₃, δ-Bi₂O₃, ε-Bi₂O₃, and ω-Bi₂O₃ [8-10], respectively. Therefore, bismuth oxides have attracted much attention and have been studied widely.

Recently, different methods have been developed for preparing bismuth oxide, such as (co)-precipitation [11], sol–gel method [12], solvothermal method [13], microwave-assisted method [14], sonochemical [15], laser irradiation [16], and others. Different structures of bismuth oxide have been prepared, for examples, nanoparticles [17], thin film [12], nanowires [18], nanoflakes [19], and so on. However, operating complexity, high costs, and disposal expense of the by-products often limit the large-scale application of these techniques. Combustion synthesis can produce large-scale metal oxide particles in a short time at low costs using simple equipment [20]. By far, there are not so many reports on the preparation of micro porous bismuth oxide through combustion synthesis.

In this study, micro porous bismuth trioxide (β-Bi₂O₃) particles was prepared via a simple combustion reaction between bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) and citric acid monohydrate (C₆H₈O₇·H₂O) and high crystalline bismuth trioxide (α-Bi₂O₃) obtained by a further thermal treatment. Product properties such as the microstructure, morphology and phase transformations, as well as the behavior of combustion were analyzed.
2. Materials and methods

2.1. Materials

All reagents used were of analytical grade and were purchased without further purification. Bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O) was received from Beijing Sinopharm Chemical Reagent Co., Ltd, China. Citric acid monohydrate (C$_6$H$_8$O$_7$·H$_2$O) was purchased from Guangdong Xilong Chemical Co., Ltd, China. Nitric acid (HNO$_3$) (67% in purity) was purchased from Beijing Chemical Factory, China. Deionized water was self-made in the laboratory.

2.2. Synthesis of porous bismuth oxides

Synthesis process was adapted from the method reported by Martirosyan et al [20-22]. Combustion synthesis of bismuth oxides produced micro porous powders, and highly crystallized and highly purified bismuth oxides were obtained by further calcination. Bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O) was used as the oxidizer and organic compound citric acid monohydrate (C$_6$H$_8$O$_7$·H$_2$O) the fuel. Several types of bismuth oxides were produced by combustion synthesis by the reaction [20]:

$$\text{Bi(NO}_3\text{)}_3 \cdot 5\text{H}_2\text{O} + \frac{5}{6} f (\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}) \rightarrow \frac{1}{2} \text{Bi}_2\text{O}_3(\text{s}) + 5f\text{CO}_2(\text{g}) + \left(\frac{25}{6} f + 5\right)\text{H}_2\text{O}(\text{g}) + \frac{3-y}{2} \text{N}_2(\text{g}) + y\text{NO}_x(\text{g}) + \frac{15}{4} \left(1 - \frac{2xy}{15} - f\right)\text{O}_2(\text{g})$$

where, $f$ is the stoichiometric coefficient of the fuel that shows if the combustion is oxygen enriched ($f<1-2xy/15$) or poor ($f>1-2xy/15$), $\omega$ is the bismuth nitrate pentahydrate weight percent in the original mixture, $M_b$ and $M_c$ are the molecular weight of bismuth nitrate and citric acid monohydrate, respectively. The terms (g) and (s) stand for gas and solid phase, respectively.

To avoid the hydrolysis of bismuth nitrate in water, we dissolved bismuth nitrate pentahydrate into a 24 mL nitric acid solution ($V(\text{HNO}_3):V(\text{H}_2\text{O})=1:8$) under magnetic stirring. And then the citric acid at a certain values of $f$ (0.2, 0.225, 0.25, 0.275, 0.3) were added in the above solution. Then the obtained solution were heated to 80 °C and maintained at 80 °C for 3 h to remove water and nitric acid under constant stirred condition. And a clear homogeneous solution formed and was transferred into a porcelain evaporating dish. The clear homogeneous solution was then introduced into electric heater preheated up to about 200 °C. The mixture boiled, followed by frothing. It then ignited with releasing a lot of gases, and producing fluffy powders. The products were collected and placed into muffle furnace to anneal at 500 °C for 2 h with a heating rate of 10 °C/min.

2.3. Characterization

The crystal phase of the as-synthesized products was obtained by X-ray diffraction (XRD) analysis using a Bruker D8 advance diffractometer, with the X-ray diffractometer using Cu Kα ($\lambda=1.54056$ Å) over a wide range of $2\theta$=(20°–70°) at 0.05° $2\theta$ s$^{-1}$. The morphologies of the as-made products were observed on a scanning electron microscope (SEM, Hitachi S4800).

3. Results and discussion

3.1. Combustion behavior

The ratio between the oxidizer (bismuth nitrate pentahydrate) and the fuel (citric acid monohydrate) had a great influence on the mixture combustion behavior, such as the combustion temperature, velocity. The combustion could not be maintained when the fuel stoichiometric coefficient $f$ was below 0.2. At $f=0.2$ the combustion was self-sustained and propagated at a low velocity without flame. A lot of gas mainly composed of CO$_2$, N$_2$, H$_2$O vapor and a small amount of nitrogen oxides (NO$_x$) that generated from the combustion reaction between bismuth nitrate and citric acid increased the product volume, and then faint yellow fluffy powders formed.
Increasing the value of $f$ within limits increased the combustion temperature and velocity. The effect of the stoichiometric coefficient $f$ on the combustion mode of the reaction and products color is shown in Table 1. As we observed in the experiment, when $0.2<f<0.3$ the combustion propagated at a low velocity without flame, and producing bismuth oxide precursor powders of different colors from white-yellow to orange-red formed with the $f$ increase. At $0.3<f<0.4$ the combustion proceeded very fast in a deflagration way with a few sparkles and generated a large amount gas, and it was difficult to collect the synthesized product as it spattered violently. At $0.4<f<0.7$ it was very dangerous that the mixture exploded instantaneously with increase in temperature. While, the velocity of reaction descended and it burned with a lot of flame when the value of $f$ increased to 0.7. Therefore, the value of $f$ at $0.2<f<0.3$ is suitable for the combustion synthesis and operating safely.

| $f$ range | Combustion mode       | Products color                  |
|-----------|-----------------------|---------------------------------|
| $0.2<f<0.3$ | Combustion without flame | White yellow to orange red       |
| $0.3<f<0.4$ | Conflagration with spark | Orange red                      |
| $0.4<f<0.7$ | Explosion             | NF                              |
| $0.7<f$    | Combustion with flame | Grey black                      |

Note: NF-not find.

### 3.2. Phase structure

The powder X-ray diffraction (XRD) patterns of products and calcinated bismuth oxides prepared by combustion synthesis at different values of $f$ are shown in Figure 1. As shown in Figure 1, the pattern features of the original precursors obtained at the combustion step correspond to the pure tetragonal phase of bismuth oxide ($\beta$-Bi$_2$O$_3$) (JCPDS No. 78-1793) with the feature peaks $2\theta = 27.9^\circ$, $32.7^\circ$, $46.2^\circ$. The crystallinity of the products powders was calculated by the equation $C=(P/T)\times100\%$. $C$ is the degree of crystallinity; $P$ the diffraction peak intensity and $T$ the total intensity. The calculated crystallinity of the precursors powders prepared at $f=0.2$, 0.225, 0.25, 0.275 and 0.3 were 88%, 87%, 89%, 93% and 98%, respectively. It could be concluded that the content of $\beta$-Bi$_2$O$_3$ was higher at elevated $f$. Hence, the precursors required further calcination to decompose the impurity and complete the phase conversion. Their morphologies and surface structures were then studied by SEM.

**Figure 1.** XRD patterns of as prepared bismuth oxides at $f=0.2$, 0.225, 0.25, 0.275 and 0.3.
3.3. Morphology

The morphology and microstructure of the prepared β-Bi₂O₃ powders were observed on scanning electron microscope (SEM) as shown in Figure 2 (a)-(b). It can be noticed that the morphology of the bismuth oxides particles are spongy porous that many irregular pores are distributed in a particle and not very homogeneous, especially in Figure 1 (a). It can be attributed to the generation of gas from the combustion reaction which increased the product volume. The diameter of bismuth oxide particle is about micrometer. It also can be found that the agglomerations of particles are increased with the increase of \( f \). Some spherical particles were formed and the structures are more closely packed at high value of \( f \). It should be noted that the porous structure of β-Bi₂O₃ is well formed at low value of \( f \).

![Figure 2. SEM images of precursors prepared by combustion synthesis at \( f = 0.2 \) (a), 0.25 (b).](image)

3.4. Effect of calcination

It can be observed from Figure 3 that, after calcination at 500 °C, all diffraction peaks of the samples can be unambiguously assigned to the most stable monoclinic phase of bismuth oxide (α-Bi₂O₃) with narrow and strong intensity peak at \( 2\theta = 27.5^\circ \) with lattice parameters \( a = 5.831 \text{ Å}, b = 8.148 \text{ Å}, c = 7.487 \text{ Å} \). No impurity peaks are observed, indicating a high purity of the products. The XRD pattern was unchanged a lot with the increase of \( f \). This suggested that the value of \( f \) has little effect on the phase of the sample after calcination. The calculated crystallinity of the products powders prepared at different values of \( f \) were >99\%, which indicate that the prepared particles have been well crystallized. Compared to the β-Bi₂O₃, annealing the precursors leads to the increase of crystallization and peak intensity, which indicate that the phase structure of the samples transformed from the tetragonal and amorphous phase into the pure monoclinic phase after calcination.

![Figure 3. XRD patterns of as annealed bismuth oxides at \( f = 0.2, 0.225, 0.25, 0.275 \) and 0.3.](image)
The morphology and microstructure of the as annealed pure α-Bi$_2$O$_3$ powders were observed on scanning electron microscope (SEM) as shown in Figure 4(a)-(b). It can be seen that the diameter of bismuth oxide particle is about micrometer. Compared to β-Bi$_2$O$_3$, the morphology and microstructure of α-Bi$_2$O$_3$ powders changed a lot. The microstructure of α-Bi$_2$O$_3$ is dendritic particles which exhibit many irregular pores, as shown in Figure 3(a), whereas the obtained α-Bi$_2$O$_3$ at high value of $f$ consists of randomly structures, as shown in Figure 3(b).

**Figure 4.** SEM images of as annealed porous bismuth oxides at $f=0.2$(a); 0.25 (b).

### 4. Conclusion

In this paper, we prepared micro porous β-Bi$_2$O$_3$ by a simple combustion reaction between bismuth nitrate and citric acid, and high crystalline α-Bi$_2$O$_3$ was obtained after a further thermal treatment. The oxidizer (bismuth nitrate) / fuel (citric acid) ratio and calcination have strong impacts on the bismuth trioxide phase structure and crystallinity. By changing the ratio between the oxidizer and fuel the purity could be improved. Compared to the β-Bi$_2$O$_3$, annealing the products not only leads to the increase of crystallite sizes and crystallinity, but also transforms the phase structure from the tetragonal and amorphous phase into the pure monoclinic phase.

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