JOURNALOF

Ceramic Processing Research

Sublimation and high-temperature stability of SnO₂-doped Bi₂O₃ ionic materials in controlled atmosphere

Yu-Hung Cheng, Yen-Yu Chen and Wen-Cheng J. Wei*

Department Mat. Sci. Eng., National Taiwan University

Sublimation of Bi_2O_3 -based materials is an important degradation issue for the long-term applications of many electronic devices. A series of SnO_2 -doped Bi_2O_3 materials (SBO), was synthesized, densified, and then tested in air or strong reducing atmosphere. The SnO_2 -doping effects and sublimation kinetics of the SBO materials were studied by X-ray diffraction (XRD), scanning electron microscope (SEM) and precise mass loss measurement. The results show that formation of $Bi_2Sn_2O_7$ phase greatly retards the mass loss of SBO. The SBO samples show a surface sublimation in an energy of 52.6 kJ mol⁻¹. However, the sublimation is also controlled by surface microstructure as the amount of vaporizing species (the Bi or gaseous Bi-oxides) is more than 0.1 mass%. The evaporation is retarded on the rough surface and the mechanism of surface evaporation is changed to diffusional control.

Key words: Bi₂O₃, SnO₂, Mass loss, Sublimation, Kinetics.

Introduction

 Bi_2O_3 is a low-melting temperature oxide widely used for sintering ZnO [1] and many other electronic ceramics, for instance, electrolyte materials of solid oxide fuel cells [2]. Vaporization of Bi_2O_3 species, e.g. $Bi_{(g)}$ or $BiO_{(g)}$ [3], possibly occurs above the melting point of 825 °C as sintering at liquid formation temperatures. The Bi_2O_3 -based liquid phase helps densification and may transform to glass boundary or secondary boundary crystals.

The boundary phases can also sublimate below their liquidation temperature, and different Bi-containing phases continue changing the composition of the boundary phase until it transforms to stable crystals at the boundary. The sublimated vapor condenses on the cool side of furnace or reacts with other hot parts, and finally results in contamination in the furnace. This undesirable vapor is well known, but no precise measurements and studies have been reported.

Various oxides are capable to form solid-solution with Bi_2O_3 [4-5], mostly aliovalent oxides (e.g. Nd, Y) [6,7]. Those dopants tend to form a solid solution to a level as high as 20 mol%. However, our previous study [8] found that SnO_2 shown a very limit solid solution (<1 mol%) and the intermediate phase of $Bi_2Sn_2O_7$ (abb. "227" in this study) is closest to pure Bi_2O_3 in the binary phase diagram [8] of Bi_2O_3 -SnO₂. The basic crystalline structure of various Bi_2O_3 -based materials is fluorite. One of the phases. δ - Bi_2O_3 , is unstable at the temperatures below 750 °C due to the phase transformations of δ - to α -phase and/or δ - to β phase during cooling. The δ -phase Bi_2O_3 causes a dramatic decrease in electric/ionic conductivity [4, 9].

This study uses the binary system of SnO₂-doped Bi_2O_3 to clarify the evaporation behavior of Bi_2O_3 based materials below the melting point for following reasons. First, SnO₂ is a high-melting-temperature oxide, with a temperature (1630 °C) much higher than that (825 °C) of Bi_2O_3 . The system, which is especially in Bi₂O₃-rich compositions, shows no solid solution other than the Bi2Sn2O7 phase, whereas the other systems may show only a very limited solid-solution δ phase (abbreviated as "Css"). High-SnO₂-doped Bi₂O₃ normally appears a dual-phase microstructure, and tends to change the content of 227 in the Css-matrix as the surface sublimates and loses Bi₂O₃ content. Therefore, the mass loss is so low without a precise mass measurement to report a quantitative analysis of the microstructure and kinetic issues of the asevaporated samples. Furthermore, the SnO₂-doping might affect the sublimation kinetics, so the electrical conductivity of the SBO materials are another significant topic for the properties of ceramics doped with Bi₂O₃.

Experimental

 SnO_2 -doped Bi_2O_3 samples (SBO) were prepared by a solid-state reaction method. Bi_2O_3 powder (99.99%, Alfa Aesar, USA) and SnO_2 powder (99.9%, Alfa

^{*}Corresponding author:

Tel:+886-2-233661317

Fax: +886 2-23634562

E-mail: wjwei@ntu.edu.tw

Aesar, USA) were mixed in de-ionized water with various dispersants, and then balled for 24 hr to obtain well-dispersed slurries of Bi₂O₃ and SnO₂, respectively. Two slurries were then mixed together, according to the specified molar ratio of XSBO ($X = 1 \sim 10$), and dried by a rotary vacuum evaporator to obtain a mixture of XSBO samples. The molar percentage of SnO₂ dopant in this study was selected in the range from 1 to 10 mol%, and the sample names are abbreviated as 1SBO, 2SBO, 4SBO, and 10SBO. The mixtures of the dried powders were calcined at 700 °C for 1 hr before being die-pressed to make green tablets ($\phi = 10$ mm, thickness 1.0 mm) of the XSBO samples. The green tablets were subsequently sintered at 800 °C for 2 hr in air.

Crystalline phases of xSBO samples were determined by X-ray diffractometry (XRD, Rigaku TTRAX 3, Japan) with scanning conditions from 20° to 60° in steps of 0.02° . Microstructures of the samples were observed by scanning electron microscope (SEM, JSM 6510, JEOL, Japan).

Pure Bi₂O₃, 1SBO, and 10SBO tablets were used for the sublimation test. The solid samples were heattreated at 650 °C in a box-type furnace with a volume of 4.5 L (dimensions of the hot space $15 \times 15 \times 20$ cm³) in either air or a reducing atmosphere. In addition, the mass loss of the tablets was also tested in a tubefurnace with a steady-state flow of air at the rate of $1.0 \text{ L} \times \text{min}^{-1} \times \text{cm}^{-2}$, controlled by a flow meter (Mass Flow Controller, ALICAT SCIENCE, USA). The refreshing rate of the atmosphere in the tube was 5 cycles/min (tube volume of 0.2 L). The mass of the samples was measured by an electronic analytic balance (Digital Analytical Scale Balance, Sartorius R160P, Germany) with an accuracy of 0.01 mg (6 significant figures). Before each measurement, the sample was cleaned in ethanol by an ultrasonic cleaning machine (Delta D80, Taiwan) and dried in an oven (Vacuum Oven, SHELAB, USA) at 100 °C for 4 hr. Its mass was recorded until the value on the balance was stable (normally taking 60 min to wait for first measurement). The oxygen partial pressure in the reducing atmosphere was controlled using either H₂/H₂O mixing gases and the oxygen partial pressure was 10^{-24} atm measured by an O2 analyzer (R2100, Cambridge Sensotec LTD, England).

Results and Discussion

Mass loss behavior in air in box furnace

Fig. 1 shows the XRD results of SBO samples after the mass loss test in air for the pure Bi_2O_3 , 1SBO, and 10SBO samples after heat-treatment at 650 °C for 100 hr. The major phase is α -Bi₂O₃ in the 1SBO sample, but a trace of the 227 phase is observed after the heat-treatment. Some SnO₂ dopant is possibly dissolved into α -phase Bi₂O₃, but the residue appears as the 227 phase after the treatment. No other phases (γ or β -phase) are found in the 1SBO sample. Similar to the 1SBO sample, the 10SBO sample after the heattreatment also consists of a small fraction of Bi₂Sn₂O₇ phase, but its level is significantly higher than that of 1SBO sample.

Fig. 2 shows the SEM micrographs of polished surfaces of 800 °C/2 hr sintered SBO samples in dense regions. Inhomogeneous dark regions (for instance, the regions in Figs. 2(d) and 2(f)) are 227 confirmed by a compositional analysis of energy-dispersive spectroscopy (EDS). Micrographs show the BSE contrast arising from the secondary phase (227) well dispersed in the Bi₂O₃-matrix in 2SBO and 4SBO samples, but hardly found in 1SBO. The increased amount of the Bi₂Sn₂O₇ phase as the SnO₂-dopping level is also noted in the figure. The solid solution of SnO₂ in Bi₂O₃ may be less than 1.0 mol% at room temperature in equilibrium state. Therefore, 1 mol% SnO₂-dopant can partially dissolve into α -Bi₂O₃ phase after being sintered at 800 °C for 2 hr.

Due to the low melting point of Bi_2O_3 (825 °C in air), the mass loss of solid state SBO materials is investigated. There are two possible reactions of Bi_2O_3 that induce the mass loss. One is the sublimation of Bi_2O_3 below the melting temperature in air. The other is the reduction of the valence states of Bi ion, i.e. conversion of O^{2-} to oxygen gas, as the following equation describes.

$$O^{2-} = \frac{1}{2}O_2 + 2e^{-}$$
(1)

These reactions may happen simultaneously since Bi_2O_3 is reduced to Bi metal in reducing atmosphere.

The mass loss of the SnO_2 -doped Bi_2O_3 samples (SBO) in air are shown in Fig. 3(a), and the loss of all samples are less than 0.2% after holding at 650 °C for 24 hr. The mass loss rate decreases with the content of



Fig. 1. XRD results of the sintered bulky (a) pure Bi_2O_3 , (b) 1SBO, and (c) 10SBO samples tested at 650 °C for 100 hr in air.



Fig. 2. SEM micrographs illustrating the microstructures of the polished SBO samples sintered at 800 °C for 2 hr. (a) 1SBO imaging by second electron (SE) mode, (b) 1SBO by backscattering electron (BSE) mode, (c) 2SBO by SE mode, (d) 2SBO by BSE mode, (e) 4SBO by SE mode, and (f) 4SBO by BSE mode. The darker features as pointed are 227 phase.

SnO₂, implying the structure of the 227 phase is more stable to suppress the evaporation of the SBO samples. This is one reason why the mass loss of the 10SBO is lower than that of the 1SBO samples.

The volatilization of Bi_2O_3 (s) at temperatures lower than 600 °C has been reported to be detrimental to its application as a solid electrolyte [10]. However, the phenomenon of the mass loss in air is not obvious. According to the result for mass loss rate of SBO samples in Fig. 3(a), the loss could be considered as a combination of diffusion-controlled and surface sublimation-controlled mechanisms.

According to the mass loss rates of the 1SBO samples shown in Fig. 3(b), the calculated activity energy of the mass loss of 1SBO is 52.6 kJmol⁻¹. The enthalpy of fusion of the δ -phase to the liquid state of Bi₂O₃ is 16.7 kJmol⁻¹ [11]. Fusion energy is significantly smaller than the sublimation energy of those xSBO in solid state.

The other mechanism of Bi-sublimation is speculated

because a high activity energy may be also controlled by the testing environment of this study, which was limited by the space of the box furnace. In this case, the vapor pressure in the furnace may have been saturated in a closed system after a period of time. Therefore, testing in a vented tube was conducted.

Fig. 4(a) shows the mass loss behavior of 1SBO samples testing at 600, 650, and 700 °C in air under the same conditions as in Fig. 3. The mass loss behavior of 1SBO samples is all similar from 600 °C to 700 °C, e.g. only maximal 0.08 wt% loss, and the mass loss rate increases with the testing temperature. The mass loss rate is only slightly different over this temperature range, as shown in Fig. 4(b), indicating that the sublimation is temperature dependent, and the higher the temperature, the faster the rate.

Mass loss behavior in vented tube furnace

Fig. 5 shows the mass loss behavior of bulky 1SBO samples tested in the same temperature range, but in



Fig. 3. (a) Mass loss (%), and (b) mass loss rate of the bulky Bi_2O_3 based samples plotted against treatment time, tested at 650 °C for various periods in an air box furnace.

either a tube furnace vented with a steady-state air flow or box furnace. The mass loss behavior is quite different in these two cases, implying that gaseous Bi species are continuously removed from the sample "surface" in the early stage of the test. However, the subsequent mass loss rate reduced to be nearly constant after 40 hr in the box furnace. Below, a change of sublimation mechanism will be discussed for the test conditions conducted in the tube furnace.

The mass loss tested in a tube furnace with a steadystate airflow is concerned. The mass loss rate remains constant in Fig. 5, implying that surface-controlled evaporation induced the mass loss. However, since the mass loss was more than a fraction of one percentage, (see data in Fig. 4(a)), the loss rate was reduced, implying a possible change of this mechanism to diffusion control.

Surface roughness of the tested sample observed by SEM reveals details (Fig. 6) of a sublimated case (100 hr). The porous microstructure shows uniform porosity distribution, implying substantial sublimation of the gaseous species (e.g. $Bi_{(g)}$, $BiO_{(g)}$, etc.) [3] at the



Fig. 4. (a) Mass loss of the bulky 1SBO samples as a function of the testing time at 600, 650, and 700 °C in an air box furnace, and (b) mass loss rate of the samples in (a).

grain boundaries. With a thicker inter-diffusing gas layer, there is a slower rate.

Morphological evolution in reducing atmosphere

The morphologies of one typical Bi₂O₃-based sample (1SBO) over various testing periods in the reducing atmosphere ($P_{O2} \sim 10^{-24}$ atm) are shown in Fig. 7. The behavior of microstructure evolution in the reducing atmosphere ($P_{O2} = 10^{-24}$ atm) at 650 °C can be separated into three stages. In the first 1 min, parts of the surface Bi₂O₃ grains were reacted to small Bi metal agglomerates, as shown in Fig. 7(b), and confirmed by EDS analysis. The reduction of α -phase Bi₂O₃ to Bi metal occurred less than 1 min after heat-treatment at 650 °C.

As soon as the isolated Bi metal particles connect with each other (Fig. 7(c)) and form a network, surface property can be dominated by the Bi metallic phase. After 5 min, a continuous Bi metal network covers the surface of the 1SBO sample (Fig 7(d)). A metallic surface is resulted.

More intensive reduction testing was conducted by leaving the disk-shape sample in Al_2O_3 crucible.



Fig. 5. Mass change of bulky pure Bi_2O_3 and various SBO samples tested at 650 °C in a tube furnace vented with a constant air flow. One testing data in an air box furnace is also shown for comparison.



Fig. 6. SEM micrograph of as-annealed surface of the 1SBO sample after annealing at $650 \,^{\circ}$ C for 100 hr in air box furnace.

Apparent reduction of the SBO mass can be visually observed when testing for 2 hr at 650-700 °C in a reducing atmosphere ($P_{O2} \sim 10^{-24}$ atm). As we judged from the appearance of the sample surface turning from white to metallic color, only the pure Bi₂O₃ sample exhibits a significant degradation at 650 °C. The mass loss of 1SBO and 10SBO is generally less than that of pure Bi₂O₃ at 650 °C due to the stabilization effects of the SnO₂-dopant.

Fig. 8 shows the XRD results of Bi₂O₃-based samples reduced in $P_{O2} \sim 10^{-24}$ atm at 650 °C for 2 hr. The 1SBO and 10SBO samples show Bi peaks at 650 °C, but slightly reduced to Bi and Sn metals at 600 °C. If the atmosphere is changed to oxygen partial pressure of $10^{-16} \sim 10^{-6}$ atm, no metallic phases are observed on 1SBO as long as 84 hr at 650 °C.

Conclusions

Dense SnO₂-doped Bi₂O₃ (SBO) materials have been synthesized and characterized to understand sublimation



Fig. 7. SEM micrographs of polished surfaces of 1SBO samples sintered and thermally etched at 550 °C for 10 min, (a) the etched surface, then held for (b) 1 min, (c) 3 min, and (d) 5 min at 650 °C in reducing atmosphere ($Po_2 \sim 10^{-24}$ atm).



Fig. 8. XRD results of (a) pure Bi_2O_3 , (b) 1SBO, and (c) 10SBO bulky samples tested under reducing atmosphere ($PO_2 \sim 10^{-24}$ atm) at 650 °C for 2 hr.

behaviors below the melting temperature as exposed in air and different reducing atmospheres. The sample containing 1-10 mol% SnO₂ shows a homogeneous α -Bi₂O₃ and 227 dual-phase microstructure, which has very little SnO₂ (<1 mol%) solid solution into α -Bi₂O₃ after 800 °C/1 hr sintering.

The mass losses of pure Bi_2O_3 and SBO samples are all less than 0.08% after treatment at 650 °C in air for a maximum of 100 hr. No metallic Bi and Sn phases are observed by the oxygen atmosphere $>10^{-16}$ atm and ≤ 600 °C. However, both Bi_2O_3 and SBO samples may transform to metallic Bi and Sn after being treated at 650 °C for 2 hr in a strong reducing atmosphere, i.e. oxygen partial pressure of 10^{-24} atm.

The sublimation of solid SBO at high temperature is a combination of surface evaporation and diffusion control, depending on the amount of vaporizing species (the Bi or gaseous Bi-oxides). When the mass loss is high (e.g. >0.1 mass%), the surface roughness increases, of which the rough surface retards the evaporation. This changes the sublimation mechanism to diffusional control as the sublimation proceeds to further extent. The sublimation energy was determined to be 52.6 kJ.mol⁻¹.

Acknowledgements

The authors thank the funding given by MOST at Taiwan by the contract MOST105-2221-E-002-055.

References

- 1. W.D. Kingery, J. B. Vander Sande, T. Mitamura, J. Am. Ceram. Soc. 62 (1979) 221-222.
- 2. B.C.H. Steele, in High Conductivity Solid Ionic Conductors:

Recent Trends and Applications, editted by T. Takahashi (World Scientific, Singapore, 1989), p. 402-446.

- 3. N.A. Asryan, T.N. Kol'tsova, A.S. Alikhanyan, G.D. Nipan, Neorg. Mater. 38 (2002) 1351-1358.
- 4. N.M. Sammes, G.A. Tompsett, H. Näfe, F. Aldinger, J. Europ. Ceram. Soc. 19 (1999) 1801-1826.
- 5. S.C. Singhal, Solid State Ionics 135 (2000) 305-313.
- 6. C.-H. Weng, W.C.J. Wei, J. Am. Ceram. Soc. 93 (2010) 3124-3129.
- M. Drache, P. Roussel, J. Wignacourt, Chem. Rev. 107 (2007) 80-96.
- T.C. Kuo, Y.L. Kuo, W.C.J. Wei, J. Europ. Ceram. Soc. 31 (2011) 3153-3158.
- 9. H.A. Harwig, A.G. Gerards, Thermochimica Acta 28 (1979) 121-131.
- G. Müller, A. Heinzel, G. Schumacher, A. Weisenburger, J. Nucl. Mater. 321 (2003) 256-262.
- 11. D. Cubicciotti, H. Eding, xide. J. Chem. Eng. Data 12 (1967) 548-551.