

Synthesis of the β and δ Phases of Bi_2O_3 Stabilized by Gd_2O_3

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We report here the synthesis of bismuth trioxide polymorphs in the binary system $(\text{BiO}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ ($0.01 \leq x \leq 0.1$) by adding small amounts of Gd_2O_3 into pure monoclinic $\alpha\text{-Bi}_2\text{O}_3$. We also studied on the polymorphic changes, crystallographic properties and Gd_2O_3 content dependence of the lattice parameters of the phases investigated. We found that minimum and maximum solubility for Gd_2O_3 in $\beta\text{-Bi}_2\text{O}_3$ are 2 and 7 mole % respectively depending on heat treatment procedure. The $\delta\text{-Bi}_2\text{O}_3$ phase could only be obtained with 9-10 mole % Gd_2O_3 addition.

Key Words: Bismuth trioxide, Gadolinium trioxide, Bismuth trioxide polymorphs

INTRODUCTION

The solid electrolytes are important components of solid state electrochemical devices, which are becoming increasingly important for applications in energy conversion, chemical processing, sensing and combustion control. Bi_2O_3 polymorphs based solid materials have been intensely investigated as catalysts, structural and electronic promoters of heterogeneous catalytic reactions and oxide ion conducting solid electrolytes in electrochemical cells. The polymorphs of Bi_2O_3 are also used in oxygen sensor production and for this application, a relatively high ionic conductivity of the solid electrolyte is required for the device performance. ZrO_2 based high oxide ion conducting solid electrolytes have been worked and reviewed¹⁻⁶.

Bismuth trioxide shows a polymorphism which is determined by the stability relationship of the four polymorphs using DTA and high temperature X-ray diffraction⁵⁻¹⁰. The body centered cubic (*bcc*) γ -form, face centered cubic (*fcc*) δ -form, tetragonal β -form, and monoclinic α -form are the four polymorphs of the Bi_2O_3 . One of the stable phases of pure Bi_2O_3 at low temperature is $\alpha\text{-Bi}_2\text{O}_3$ which is reported as monoclinic or pseudo-orthorhombic⁷⁻¹². When $\alpha\text{-Bi}_2\text{O}_3$ is heated to about 730°C, transition to the $\delta\text{-Bi}_2\text{O}_3$ occurs. This high temperature $\delta\text{-Bi}_2\text{O}_3$ phase is stable between 730°C and melting point 825°C. On the cooling of the δ -form, large thermal hysteresis effects are present and the δ -phase transforms to one of the two intermediate phases which are β -form (formed at 650°C) and γ -form (formed at 639°C). The metastable tetragonal β -phase is

formed at 650°C on cooling from the melt or from the high temperature phase. The γ -phase which is known as sillenite group of compounds can be obtained by controlled cooling of $\beta\text{-Bi}_2\text{O}_3$. Usually these metastable phases transform to the α -phase in the temperature range of $500\text{--}600^\circ\text{C}$.⁶⁻¹³ The polymorphs of bismuth trioxide can only be obtained as room temperature stable phases by addition of small amounts of other dopant oxides, *i.e.*, Y_2O_3 , MoO_3 , CoO , Sb_2O_3 , WO_3 , SrO , CaO and La_2O_3 ⁶⁻¹².

The *bcc* γ -phase is characterised in the *I23* space group. This phase is isomorphous with the *bcc* compound $\text{Bi}_{24}\text{Si}_2\text{O}_{40}$, where bismuth atoms occupy the silicon sites in the crystallographic structure. Other investigations indicate that the pure $\gamma\text{-Bi}_2\text{O}_3$ contains $\text{Bi}_{26}\text{O}_{39}$ in the cell with a lattice parameter in the range of $10.10\text{--}10.27 \text{ \AA}$. This indicates that $\gamma\text{-Bi}_2\text{O}_3$ has the largest unit cell parameter of the series of the reported sillenite group compounds. The $\gamma\text{-Bi}_2\text{O}_3$ phase is also reported to be isomorphous with several other metal oxides giving the general formula $\text{Bi}_{24}\text{M}_2\text{O}_{39}$. It has not a perfect crystal system. On the other hand, the crystal lattice has a perfect structure where the M cation is tetravalent giving the general formula $\text{Bi}_{24}\text{M}_2\text{O}_{40}$ in the unit cell⁶⁻¹⁰. It has been proposed that the β -form crystallizes in the *P4b2* or *C42b* space group, and has a two-dimensional superstructure of the cubic δ -phase with slight deviations in oxygen atomic positions. The lattice parameters and atomic positions were reported in terms of the base-centered unit cell *C42b*, where $a = 10.93$ and $c = 5.63 \text{ \AA}$. Another investigator reported that β -phase crystallizes in the *P42₁c* symmetry group with lattice constants of $a = 7.7425$, and $c = 5.6313 \text{ \AA}$. A study of Bi_2O_3 thin films resulted in the proposed new phase $\beta\text{-Bi}_2\text{O}_{2.5}$ with lattice constants of $a = 7.50$ and $c = 5.63 \text{ \AA}$. The locations of the bismuth ions in both the crystal structures are nearly identical, with larger differences for the oxygen ions. For stoichiometric compounds of this type, all particular cationic and anionic sites in the tetragonal unit cell are fully occupied. The non-stoichiometric phase has two fewer oxygen ions per unit cell^{7, 11, 13}. The *fcc* cubic δ form has an oxygen deficient fluorite structure with two formula units, and two oxygen vacant sites per unit cell. According to the literature survives, its unit cell parameter is $a = 5.66 \text{ \AA}$, with a *Pn3m* space group or $a = 5.66 \text{ \AA}$, with a *Fm3m* space group. The bismuth ions in both structures are located on *fcc* sites, and differ only in the location of the oxygen ions, and the choice of space groups⁷⁻¹⁴.

We have carried out this work in order to investigate the effect of Gd_2O_3 doping in Bi_2O_3 . After accomplishing the stability of δ and β phases by the solid state reactions, we have determined lattice parameters at room temperature for each doping ratio, the solubility limits of the observed phases, color changes of the samples, and nonstoichiometry of the obtained phases. Moreover, the effects of temperature and doping ratio of Gd_2O_3 in the $\text{Bi}_2\text{O}_3\text{-Gd}_2\text{O}_3$ binary system were investigated.

EXPERIMENTAL

The powder samples in our study were prepared by mixing the appropriate amount of monoclinic Bi_2O_3 (99.99% Merck), and Gd_2O_3 (99.99% Merck)

without further purification. The solid mixtures that contained different amounts of Gd_2O_3 doping (1 to 10 mol % Gd_2O_3) were prepared. Mixing and homogenizing were performed in an agate mortar. These oxide mixtures were calcined in a furnace, in gold crucibles, in air, at 650°C for 24 h. The calcined powders were ground and heat-treated at 700°C for 48 h. Calcined powders were re-ground and annealed at 750 and 800°C for 48 h respectively. All these heat treatments were done as loose powders, in gold crucibles and in air. After the treatment procedure, loose powder samples were slowly cooled in the furnace by switching it off (uncontrolled). Each sample was separately ground into fine powder after the heat treatment. The colour of the sintered specimens was observed to change from light yellow to dark yellow as the Gd_2O_3 content of the oxide mixture is increased. Each of these prepared powder samples was further heat treated separately at 750 , 800 and 830°C in a vertical tube furnace in air, and quenched in ice-water system. As the quenching experiments were performed, phase transitions occurred in the synthesized samples.

Powder diffraction data of the samples were recorded with Bruker AXS D8 advanced diffractometer using a Bragg-Brentano geometry with graphite monochromator $\text{CuK}\alpha$ radiation operated at 40 kV and 40 mA. The divergence and receiving slits of 1 and 0.1 mm respectively were located on the diffractometer. Diffraction patterns were scanned by steps 0.002° (2θ) over the angle range 10 – 90° (2θ). Diffracted beams were counted with a NaI(Tl) scintillation detector and the obtained XRD data were compared with the reference data.

RESULTS AND DISCUSSION

The obtained phases in the system of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$, x being $0.01 \leq x \leq 0.1$, are given in Table-1 depending on the reaction temperatures. Samples of tetragonal β - Bi_2O_3 were obtained by doping with Gd_2O_3 according to the formula of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$, x being $0.02 \leq x \leq 0.07$. Mixed raw oxide mixtures were furnace cooled to room temperature after being annealed at 750° or 800°C . Heat treatment temperatures below 750°C did not produce any single phase. In this doping range 2–7 mol %, all of the XRD patterns of the solid specimens were identified as having the tetragonal crystal symmetry. XRD patterns of 4 mole % Gd_2O_3 are given in Fig. 1. XRD patterns of other samples were quite similar to the pattern given in this figure. Under the same heat treatment conditions, XRD measurements revealed that doping with more than 7 mole % Gd_2O_3 had caused the coexistence of β and δ forms on the XRD patterns. On the other hand, Gd_2O_3 addition smaller than 2 mole % leads to the coexistence of a heterogen solid mixture of α and β phases.

The relationship between the calculated unit cell parameters (a and c) of β - Bi_2O_3 and mole % Gd_2O_3 addition was illustrated in Fig. 2. As seen in this figure, lattice parameters increase moderately with increasing Gd_2O_3 substitution. It showed that we obtained solid solution of two oxides, and Gd_2O_3 was completely soluble in β - Bi_2O_3 , in the range of $0.02 \leq x \leq 0.07$, since there is a continuous increase in the lattice parameter with increasing Gd_2O_3 content. Therefore we concluded that the maximum solubility limit for Gd_2O_3 was 7 mole

per cent ($x = 0.07$), and minimum solubility was 2 mole per cent ($x = 0.02$) in tetragonal type $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ solid solution.

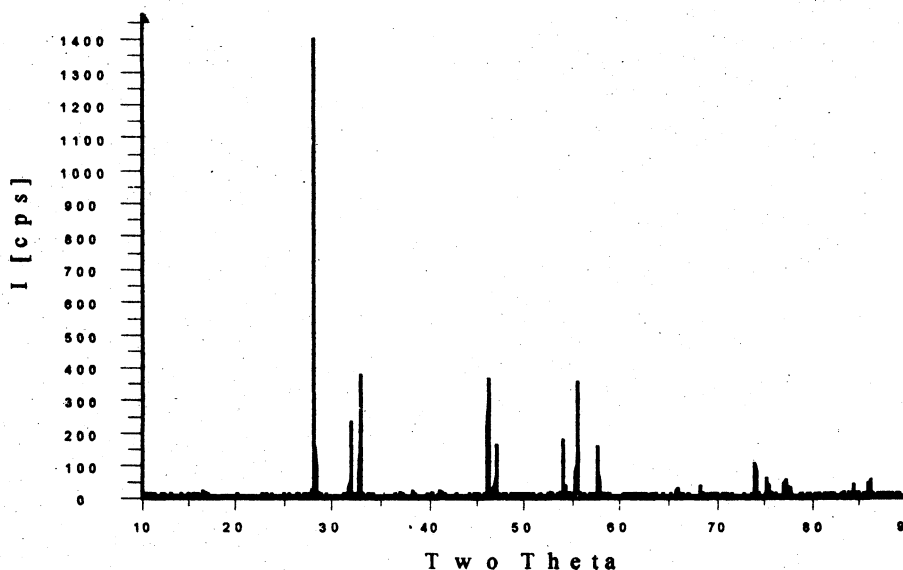


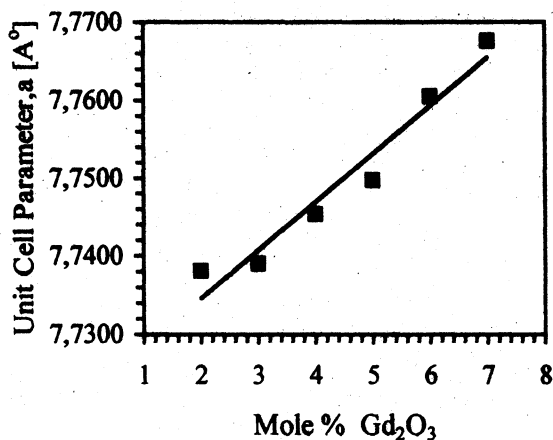
Fig. 1. XRD pattern of β - Bi_2O_3 doped with 4 mole % Gd_2O_3

TABLE-1
THE OBSERVED PHASES IN THE BINARY SYSTEM Bi_2O_3 - Gd_2O_3

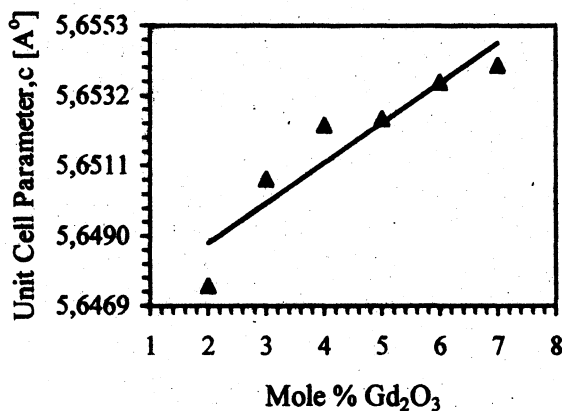
Temperature ($^{\circ}\text{C}$)	Mole % Doped Gd_2O_3									
	1	2	3	4	5	6	7	8	9	10
750	$\alpha + \beta$	β	β	β	β	β	β	$\beta + \delta$	$\beta + \delta$	$\beta + \delta$
800	$\alpha + \beta$	β	β	β	β	β	β	$\beta + \delta$	$\beta + \delta$	$\beta + \delta$
750 (w.q.)*	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	β	β	β	β	$\beta + \delta$	$\beta + \delta$	$\beta + \delta$
800 (w.q.)*	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\beta + \delta$	$\beta + \delta$	$\beta + \delta$
830 (w.q.)*	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \delta$	δ	δ

*Water quench

A modest increase of lattice parameter with increasing Gd_2O_3 content is in good agreement with effective ionic radii considerations (reported ionic radii are 0.102 nm for Bi^{3+} , and 0.104 nm for Gd^{3+} respectively¹⁵). Bi^{3+} ions have smaller ionic radii than Gd^{3+} ions (but there is a little difference between ionic radius). This mechanism is considered to be responsible for a modest increase in lattice parameter with increasing doping ratio. Thus by increasing the amount of Gd_2O_3 , the crystal structure of the solid solution was modified toward higher unit cell dimensions. On the other hand, formation of β - Bi_2O_3 phase was very slow requiring long heat treatment duration (at least 48 h). It was concluded from this fact that diffusion rate for gadolinium ions into bismuth trioxide was quite low. Through this slow diffusion mechanism, gadolinium cations substituted bismuth



(a)



(b)

Fig. 2. The relationship between the amount of Gd₂O₃ additions, and the lattice parameters of β -Bi₂O₃: (a) Unit cell parameter a, and (b) Unit cell parameter c.

cations in the crystal structure, and the oxygen anions are probably located randomly at the interstitial sites. The observed color change in our annealed samples had a systematic change depending on the amount of gadolinium trioxide addition. For chemical composition of $x = 0.02$ the colour of the specimen was light yellow and with increasing x values the colour lost its brightness gradually and became dark yellow for $x = 0.07$. The colour change phenomenon may be considered to be related to degree of non-stoichiometry of the samples. Increasing coloration in $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ series indicated an increasing non-stoichiometry with addition ratio and as a result samples should contain more defects (mainly O^{2-} vacancies) in the crystal structure at higher levels. The existence of oxygen vacancies in the crystal structure can also contribute to the colour, because vacancy points (the so called "color points") may be occupied by electrons through a light absorption mechanism.

The $\delta\text{-Bi}_2\text{O}_3$ phase was prepared from the samples of 9–10 mole % Gd_2O_3 additions by melting at 830°C , then quenching to 0°C . This phase could not be obtained with lower Gd_2O_3 additions, and the other water quench heat treatments. The XRD patterns of the 9 mole % samples were indexed in the face-centered cubic crystal symmetry. Fig. 3 shows the XRD patterns of these phases. The calculated lattice parameters a of 9, and 10 mole % Gd_2O_3 were found 5.4557, and 5.4593 Å respectively. This was again an indication that Gd_2O_3 dissolves in $\delta\text{-Bi}_2\text{O}_3$ matrix.

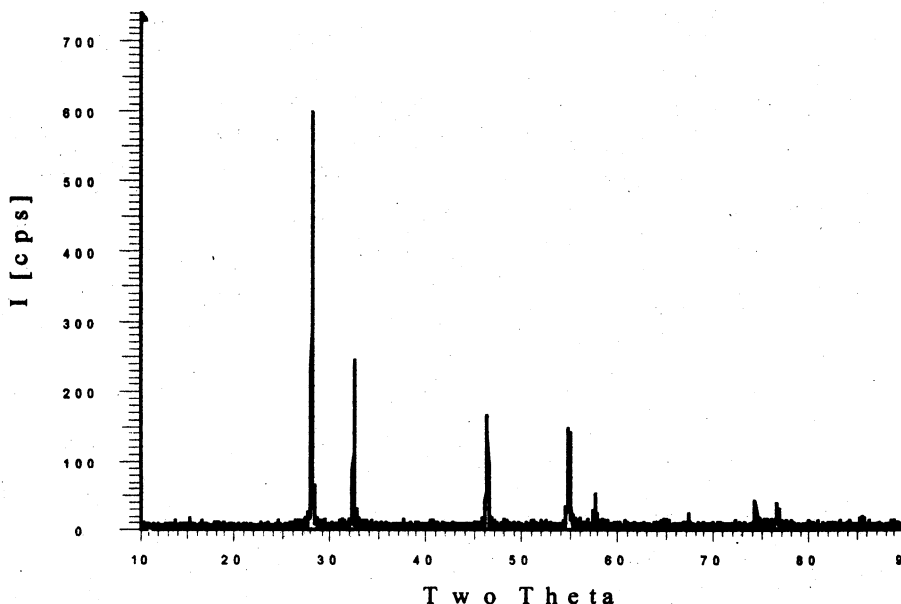


Fig. 3. XRD pattern of $\delta\text{-Bi}_2\text{O}_3$ doped with 9 mole % Gd_2O_3

Metastable δ and β phases of Bi_2O_3 polymorphs have been obtained as room temperature stable phases by doping pure monoclinic $\alpha\text{-Bi}_2\text{O}_3$ material with Gd_2O_3 , and employing solid state reaction techniques. Heat treatment temperature, cooling rates, and amount of Gd_2O_3 are effective factors in the synthesis of these polymorphs. We have found that $\beta\text{-Bi}_2\text{O}_3$ can be obtained as room temperature stable phase by doping with Gd_2O_3 which is soluble from 2 up to 7 mole %. This tetragonal type $\text{Bi}_2\text{O}_3\text{-Gd}_2\text{O}_3$ solid solution is stable up to 800°C but transforms to $\alpha + \beta$ heterogen solid mixture at higher temperatures. $\delta\text{-Bi}_2\text{O}_3$ phase could only be prepared with 9–10 mole % Gd_2O_3 addition, from *ca.* 830°C to 0°C . Moreover, both of these phases are nonstoichiometric compounds, and they have distorted defect crystal structure. We have concluded that higher doping rate introduces more defects into the structure, and the most predominant defect in these materials are oxygen vacancies.

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