

Stabilization of Bi₂O₃ Polymorphs with Sm₂O₃ Doping

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The synthesis of bismuth trioxide polymorphs in the binary system (Bi₂O₃)_{1-x}(Sm₂O₃)_x in the range $0.01 \leq x \leq 0.1$ has been investigated by adding small amounts of Sm₂O₃ into pure α -Bi₂O₃. The polymorphic changes, crystallographic properties, and Sm₂O₃ content dependence of the lattice parameters of the observed β - and δ -phases are reported. All the obtained solid solutions had nonstoichiometric compositions and nonstoichiometry increases with the increasing amount of mole % Sm₂O₃ addition. Because of nonstoichiometry, the produced phases have lattice defects. These defects are mainly oxygen ion vacancies.

Polymorphs of the Bi₂O₃ system are being intensely investigated owing to their technological potential as catalysts in promoting heterogeneous catalytic reactions and as solid electrolytes in electrochemical cells. Solid electrolytes such as polymorphs of Bi₂O₃ are essential components in the production of solid-state electrochemical devices. They also have high ionic conductivity, which constitutes a potential to be used in oxygen sensor production. Samarium is used in the nuclear industry as an absorber and to dope CaF₂ crystals for use in optical masers or lasers. Samarium trioxide is catalytic for the dehydration and dehydrogenation of ethanol. Its compounds act as sensitizers for phosphorus excited in the infrared region. Samarium is easily magnetized and very difficult to demagnetize. This suggests an important future for solid-state and superconductivity applications [1–7].

Bismuth trioxide compound has four polymorphs: The body-centred cubic (*bcc*) γ -form, face-centred cubic (*fcc*) δ -form, tetragonal β -form, and monoclinic α -form. Monoclinic form of pure Bi₂O₃ is stable at room temperature. When this α -Bi₂O₃ phase is heated to about 730 °C, structural transformation to the δ -Bi₂O₃ occurs. The δ -phase is stable between 730 °C and 825 °C, which is the melting point of this oxide. δ -Form transforms to β -form (at 650 °C) and to γ -form (at 639 °C) upon cooling, showing large thermal hysteresis effects. The metastable tetragonal β -phase is also formed at 650 °C upon cooling of molten oxide. The γ -phase can be obtained by slow cooling of β -Bi₂O₃ [5, 8–10]. Usually these metastable phases transform to the α -phase in the temperature range of 500–650 °C [6–14]. δ -, β -, and γ -phases of bis-

muth trioxide, as stable phases at room temperature, can be obtained only by addition of small amounts of dopant oxides such as V₂O₅, Gd₂O₃, Y₂O₃, MoO₃, CoO, Sb₂O₃, WO₃, SrO, CaO, La₂O₃, and Eu₂O₃ [4–16].

In the present work, Sm₂O₃-doped Bi₂O₃ polymorphs were studied. After accomplishing the stability of Bi₂O₃ polymorphs by the solid-state reactions, the lattice parameters have been determined at room temperature for each doping ratio. The solubility limits, colour changes, and nonstoichiometry of the obtained phases were investigated. Moreover, the effects of heat-treatment temperature and Sm₂O₃ doping ratio in the Bi₂O₃–Sm₂O₃ binary system were studied.

EXPERIMENTAL

The powder samples were prepared by mixing the appropriate amount of monoclinic Bi₂O₃ (99.99 %, Merck) with Sm₂O₃ (99.99 %, Merck) without further purification. The solid oxide mixtures which contained increasing amount of Sm₂O₃ from 1 to 10 mole % were prepared by mixing and homogenizing in an agate mortar. These oxide mixtures were preannealed at 650 °C for 48 h. The preannealed powders were ground and heat-treated at 700 °C for 48 h. These oxide powders were heat-treated further at 750 °C and 800 °C for 48 h each, with intermediate grindings. All the heat treatments of powders were performed in gold crucibles in air and without any compaction. At the end of each heat treatment procedure, annealed powders were slowly cooled in the furnace by switching it off (uncontrolled). Each of these prepared powder sam-

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Table 1. The Observed Phases in the System of (Bi₂O₃)_{1-x}(Sm₂O₃)_x; 0.01 ≤ x ≤ 0.1

Temperature/°C	x(Sm ₂ O ₃ addition)/mole %									
	1	2	3	4	5	6	7	8	9	10
700	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β	α + β
750	α + β	α + β	β	β	β	α + β	α + β	α + β	α + β	α + β
800	α + β	α + β	β	β	β	β	β	β + δ	β + δ	α + β
830 wq*	α + β	α + β	β	β	β	β	β	α + β	δ	δ

*Water quench.

ples was further heat-treated separately at 830 °C in a vertical tube furnace in air, and quenched by dropping the sample into ice—water mixture. Quenching experiments were performed to observe high-temperature phase transitions in the synthesized samples of all addition ratios.

Powder diffraction data of the samples were recorded with Bruker AXS D8 advanced diffractometer using a Bragg—Brentano geometry with graphite monochromator CuKα radiation, operated at 40 kV and 40 mA. The divergence and receiving slits of 1 mm and 0.1 mm, respectively, were located on the diffractometer. Diffraction patterns were scanned by 0.002° (2θ) steps over the angle range 10°—90° (2θ). Diffracted beams were counted with a NaI(Tl) scintillation detector and the obtained XRD patterns were compared with the reference data [20].

Microprobe analyses of the samples were made with LEO 440 scanning electron microscope (SEM). These analyses data were taken from flat surface of the pressed samples. At least five different analyses were made from different regions of each sample at high magnification and mean values from these measurements were used for calculations.

RESULTS AND DISCUSSION

In the (Bi₂O₃)_{1-x}(Sm₂O₃)_x system observed single phases and heterogeneous solid mixtures, depending on the reaction temperature, are presented in Table 1. Heat treatment temperatures below 750 °C produced the mixture of α- and β-phases for all of Sm₂O₃ additions. As seen in Table 1, dominant single-phase regions have tetragonal β-Bi₂O₃ type crystal structure which is a two-dimensional superstructure of the δ-Bi₂O₃ structure [9, 17—19]. 750 °C was the minimum temperature at which β-phase was synthesized from furnace-cooled specimens in the range 0.03 ≤ x ≤ 0.05. β-Phase was synthesized at 800 °C over the range 0.03 ≤ x ≤ 0.07 for furnace-cooled samples and for quenched samples, x was also between 0.03 and 0.07 for synthesizing of this phase. In these doping ranges, all of the XRD pattern peaks were indexed in the tetragonal crystal symmetry.

XRD patterns of 4 mole % and 7 mole % Sm₂O₃ (for 750 °C and 800 °C followed by furnace cooling and quenching heat treatments at 830 °C) are given

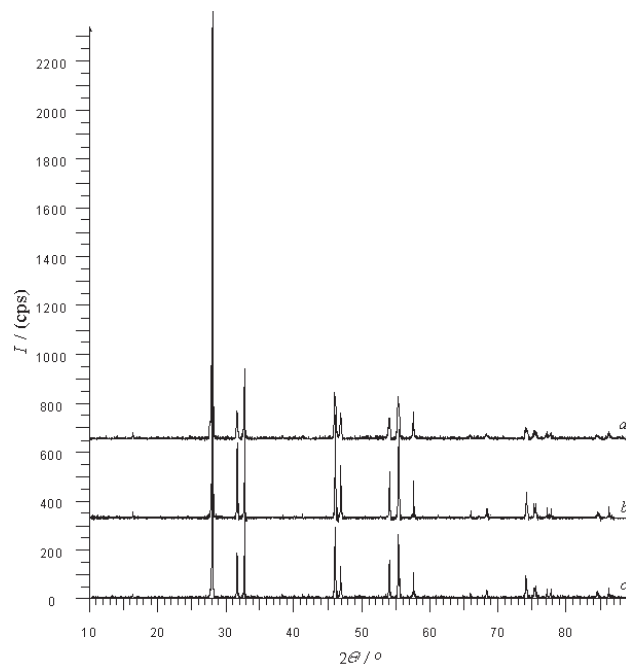


Fig. 1. XRD patterns of β-Bi₂O₃ doped with 4 mole % Sm₂O₃ (a) after quenching at 830 °C, (b) after heating at 800 °C, (c) after heating at 750 °C.

in Figs. 1 and 2, respectively. XRD patterns of other single β-phase samples were quite similar to the patterns of single-phase samples given in these figures. At 750 °C heat treatment conditions, XRD measurements revealed that doping with more than 5 mole % and less than 3 mole % Sm₂O₃ had caused the coexistence of β- and α-forms. XRD patterns of some of the multi-phase samples are given in Fig. 3 and assignments of individual peaks to α-, β- or δ-phases are indicated on the patterns.

The relationship between the calculated unit cell parameters (*a* and *c*) of β-Bi₂O₃ and x(Sm₂O₃)/mole % addition is illustrated in Fig. 4. As seen in this figure, both lattice parameters slightly increase with substitution of Bi ion with Sm ion. The slight increase of lattice parameters with increasing Sm₂O₃ content was in good agreement with effective ionic radii considerations. Reported ionic radii are 1.02 Å for Bi³⁺, 1.41 Å for Sm²⁺, and 0.96 Å for Sm³⁺, based on 1.40 Å for O²⁻ ion [21]. When Sm²⁺ ions replace Bi³⁺, lat-

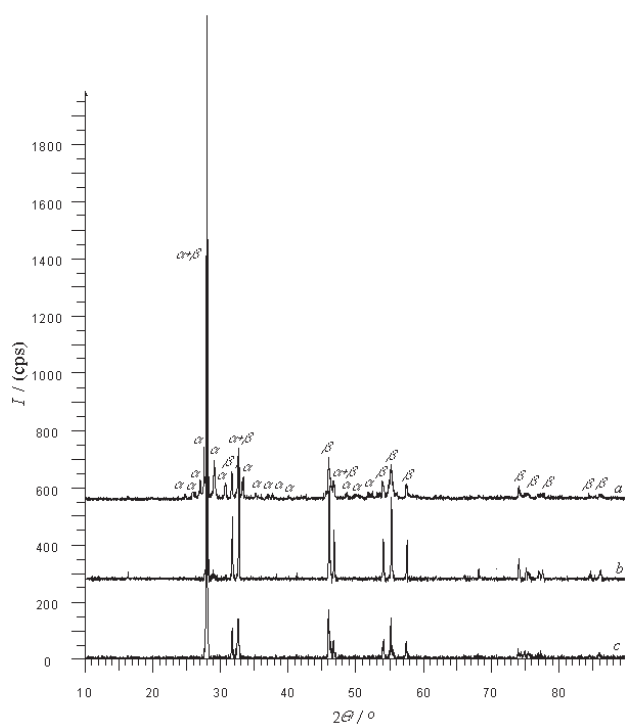


Fig. 2. XRD patterns of 7 mole % Sm_2O_3 doped samples: *a*) after heating at 750 °C (mixture of α - and β -phases), *b*) after heating at 800 °C (single β -phase), *c*) after quenching at 830 °C (single β -phase).

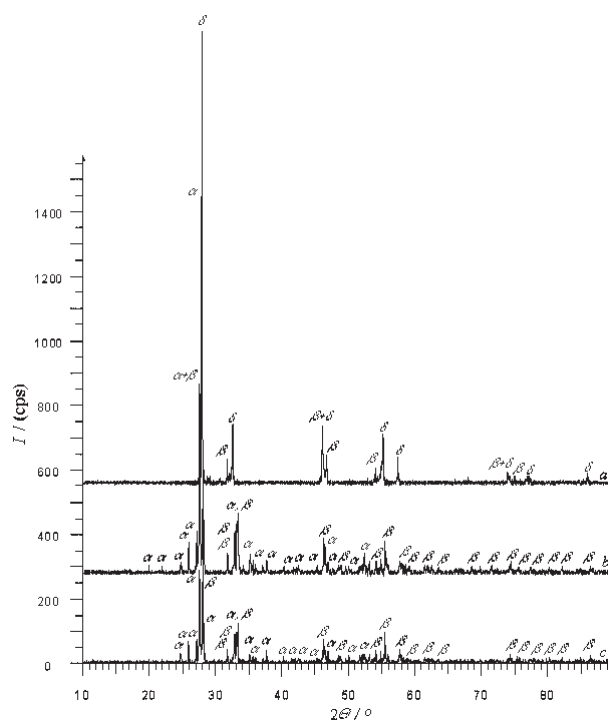
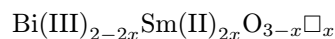


Fig. 3. XRD patterns of some of the multiphase specimens. *a*) 8 mole % Sm_2O_3 addition (after heating at 800 °C), *b*) 2 mole % Sm_2O_3 addition (after heating at 800 °C), *c*) 2 mole % Sm_2O_3 addition (after quenching at 830 °C).

tice parameters enlarge (Bi^{3+} ion has smaller ionic radius than Sm^{2+}) and these enlargements are consistent with our observations on lattice parameter changes. It was also observed that lattice parameters of the same composition differ for different heat treatment temperatures, being slightly larger for 830 °C (water quench) compared to 800 °C. Solid solutions of Bi_2O_3 and Sm_2O_3 were obtained as single β -phases in the $x(\text{Sm}_2\text{O}_3)$ range of 3–5 mole % addition, when the oxide mixture is heat-treated at 750 °C. When the heat treatment temperature is increased to 800 °C or the samples are quenched at 830 °C, solubility range widens to $x(\text{Sm}_2\text{O}_3)$ 3–7 mole %. This experimental observation is explained with insufficient solid-state reaction at 750 °C, rather than solubility limitation. This is conclusive with larger unit cell parameters at higher annealing temperatures for the same compositions as outlined above.

On the other hand, formation of tetragonal type $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Sm}_2\text{O}_3)_x$ solid solution was a very slow process requiring a long heat treatment duration. It was concluded from this fact that the diffusion rate for samarium ions into bismuth trioxide was quite low. Through this slow diffusion mechanism, Sm cations substitute Bi cations in the crystal structure. Although valence number of Sm cation is +3 in Sm_2O_3 , these incorporated Sm ions would probably be reduced to bivalent in the obtained tetragonal type solution.

When the charge balance is considered, as the addition of Sm_2O_3 increases, O^{2-} ions should spontaneously be oxidized to O_2 molecules. Then, some oxygen ion vacancies should occur in the O^{2-} sublattices of the tetragonal $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Sm}_2\text{O}_3)_x$ solution. As a result, the obtained solid solution acquires nonstoichiometric character. For the substances of this type, oxygen deficiency nonstoichiometry has been reported [9, 16–19]. Therefore, the composition of the β -type solid solution can be expressed as

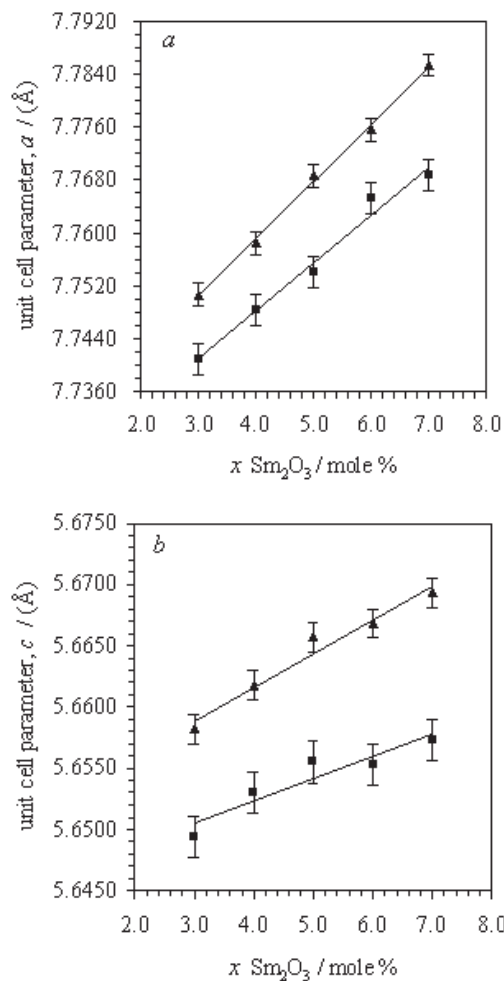


where \square denotes oxygen ion vacancy. x Values are in the $0.03 \leq x \leq 0.05$ range for heat treatment at 750 °C, and they are in the range of $0.03 \leq x \leq 0.07$ for heat treatment at 800 °C and water quench (830 °C).

The calculated mass ratio values of elements, obtained using the approximations outlined above, are given in Table 2. The values of mass% Bi and Sm were calculated according to the nonstoichiometric formula. Mass ratio values measured using SEM microprobe analysis are also given in Table 2. These measured values are in good agreement with the calculated ones. Cation concentrations are higher than the expected stoichiometric values indicating oxygen deficiency in the crystal structure. Although this is not a solid proof for oxygen deficiency, it nevertheless is in agreement

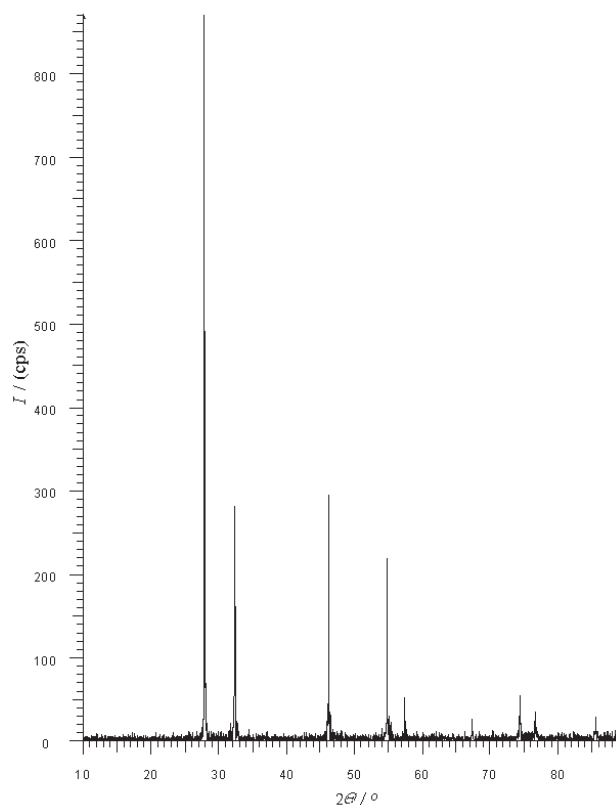
Table 2. The Microprobe Analysis for the Tetragonal (β) Type Solution of the (Bi₂O₃)_{1-x}(Sm₂O₃)_x System

$x(\text{Sm}_2\text{O}_3)$ mole %	After heating at 800 °C		After quenching at 830 °C		Calculated	
	mass % Bi	mass % Sm	mass % Bi	mass % Sm	mass % Bi	mass % Sm
0.03	87.66 ± 0.22	1.93 ± 0.06	87.91 ± 0.19	1.88 ± 0.15	87.77	1.95
0.04	87.37 ± 0.15	2.49 ± 0.11	87.46 ± 0.22	2.54 ± 0.11	87.11	2.61
0.05	86.64 ± 0.13	3.08 ± 0.06	86.61 ± 0.16	3.13 ± 0.14	86.46	3.28
0.06	86.02 ± 0.21	3.85 ± 0.18	85.73 ± 0.23	3.90 ± 0.16	85.79	3.94
0.07	85.25 ± 0.13	4.56 ± 0.17	85.23 ± 0.10	4.44 ± 0.22	85.13	4.61

**Fig. 4.** The relationship between the amount of Sm₂O₃ doping and the lattice parameter of β -Bi₂O₃ phase; a) unit cell parameter a , b) unit cell parameter c (■ after heating at 800 °C, ▲ after quenching at 830 °C).

with the cited literature. This oxygen deficiency may lead to variations in the electrical conductivity of these doped samples.

The colour of our annealed samples had a systematic change depending on the amount of samarium trioxide addition. The colour of the sintered specimens was observed to change from light yellow to red brown as the content of the oxide mixture increased. For chemical composition of 3 mole % Sm₂O₃ the colour

**Fig. 5.** XRD pattern of δ -Bi₂O₃ doped with 10 mole % Sm₂O₃ (after quenching at 830 °C).

of the specimen was light yellow and with increasing x values the colour lost its brightness gradually and became darker for 7 mole % Sm₂O₃. The observed colour change phenomenon provides further support for nonstoichiometry in our samples since nonstoichiometry causes darkening.

Previously reported studies of Bi₂O₃ polymorphs resulted in the proposed nonstoichiometric phase β -Bi₂O_{2.5} with unit cell parameters $a = 7.50 \text{ \AA}$ and $c = 5.63 \text{ \AA}$ in the space group $P42_1c$. The locations of the bismuth ions in the crystal structures of stoichiometric and nonstoichiometric bismuth three oxides are almost identical while locations of oxygen ions exhibit differences. For stoichiometric compounds of this type, all particular cationic and anionic sites in the tetragonal crystal system are fully occupied. The nonsto-

ichiometric β -phase has oxygen ion vacancies in the crystal structure [9, 17, 18]. The calculated lattice parameter values of the observed β -type solid solutions (Fig. 4) are in agreement with the unit cell parameters of β - Bi_2O_3 phase [18], indicating oxygen nonstoichiometry in the synthesized tetragonal solid solutions. Higher doping rates introduce more defects into the structures, hence tetragonality is enhanced.

The δ -phase was obtained from the samples of $x(\text{Sm}_2\text{O}_3)$ 9–10 mole % addition by melting at 830 °C, then quenching to 0 °C in the water–ice system. For 8 mole % doping, quenching causes coexistence of a solid mixture of α - and β -phases. XRD pattern of $x(\text{Sm}_2\text{O}_3)$ 10 mole % specimen is seen in Fig. 5. The unit cell parameters were calculated as $a = 5.5479 \text{ \AA}$ and $a = 5.5511 \text{ \AA}$ for $x = 9$ and 10 mole % additions of Sm_2O_3 , respectively. The change in the lattice parameters with increasing addition shows that Sm_2O_3 dissolves in the δ -phase. The *fcc* δ -form has an oxygen-deficient fluorite structure with two formula units, and two O^{2-} vacant sites per unit cell [9, 17–19].

In conclusion, metastable δ - and β -phases of Bi_2O_3 polymorphs and related solid solutions have been obtained as room temperature stable phases by doping pure monoclinic α - Bi_2O_3 material with Sm_2O_3 , and employing solid-state reaction techniques. Heat treatment temperature, cooling rate, and amount of Sm_2O_3 are effective factors in the synthesis of these polymorphs. We have found that β -phase can be obtained as room temperature stable phase by doping with Sm_2O_3 from 3 up to 5 mole % at 750 °C and from 3 up to 7 mole % at 800 °C when furnace cooled. Solubility of Sm_2O_3 in β -phase when quenched at 830 °C ranges between 3 and 7 mole %. We determined that all of the observed phases were nonstoichiometric. Higher doping rates introduce more defects into the structures, the predominant defects being oxygen vacancies which increase with increasing the amount of Sm_2O_3 . Because of the oxygen vacancies, these materials can have oxygen ionic conductivity and can be used as the solid electrolytes in industrial applications.

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