Measurement and properties of the oxide ionic conductivity of β-phase in the binary system of $(Bi_2O_3)_{1-x}(Sm_2O_3)_x$

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ABSTRACT

The tetragonal β-phase in the binary system of $(Bi_2O_3)_{1-x}(Sm_2O_3)_x$ was synthesized by solid-state reactions with doping Sm_2O_3 into the monoclinic Bi_2O_3, in the stoichiometric ratio of range $0.01 < x < 0.10$. X-ray powder diffraction (XRD) data showed that the unit cell parameters of produced tetragonal-type materials increased with the increasing doping of Sm_2O_3. We have measured the total electrical conductivity (σ_T) depending on the temperature and doping concentration. Bi_2O_3-based ceramic system doped with Sm_2O_3 showed an oxide anionic-type electrical conductivity which is increased with the increase of the dopant concentration and temperature. In the investigated system, the highest value of conductivity was observed $\sigma_T = 0.029\,\Omega^{-1}\,cm^{-1}$ at 670 °C, for the composition of 7 mole% Sm_2O_3 addition. The phase transition which manifests itself by the jump in the conductivity curves was also verified by DTA measurements which are in good agreement with the observed results of electrical conduction. The electrical conductivity curves of studied materials revealed regular increase with the temperature in the form of the Arrhenius-type conductivity behavior and the activation energies (E_a) were calculated by using these graphs.

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1. Introduction

Because of the Bi_2O_3 polymorphs having excited electrical conductivity properties, they are used as the basic precursors of some solid electrolytes in the industry [1,2]. They can be used in SOFC applications since their ionic conductivity is higher than zirconia (ZrO_2)-based electrolytes at the same temperature [3]. The conductivity mechanism is based on oxygen ionic conductivity; therefore, they can be used for the manufacturing of the oxygen detectors [1,2,4–6]. In recent years, many experimental researches have mostly focused on improving of the Bi-based electrolytes which have high oxide ionic conductivity at low temperatures and better performance in SOFC.

Bi_2O_3 shows an extraordinarily rich-phase polymorphism, they are denoted by α-Bi_2O_3 (monoclinic), β-Bi_2O_3 (tetragonal), γ-Bi_2O_3 (cubic, bcc), δ-Bi_2O_3 (cubic, fcc), ε-Bi_2O_3 (orthorhombic) and ω-Bi_2O_3 (triclinic). α, β, γ and δ forms are intensely studied and well-known phases of Bi_2O_3 out of its six crystal modifications

[1,2,7,8]. Through the cooling of δ-Bi_2O_3 from high temperature to room temperature, a large thermal hysteresis effect is formed with the possible occurrence of two intermediate metastable phases, viz.: β-phase or the γ-phase. On the slow cooling, β-Bi_2O_3 occurs at around 650 °C, whereas the γ-form appears at ∼630 °C. Usually these metastable phases transform to the α-phase below 500 °C. The tetragonal β-Bi_2O_3 shows oxygen ionic conductivity property and can be stabilized by the doping of small amounts of other dopant M_2O_x-type oxides, such as: M = Y, Eu, Mo, Sb, Dy, Pr, Er [3,9–11]. In the synthesis of Bi_2O_3 phases, the parameters like the dopant type, stoichiometric ratio of the dopant, heat treatment time, annealing temperature, cooling rate (furnace cooling or quenching), grinding time and number of grindings, grain size, etc. are the important variables which affect the structural characteristics and electrical properties of the polymorphs [3,9–11]. Generally, their unit cell parameters change with the type and amount of doping material [1,2,9–11].

Doped β-Bi_2O_3 phase has the some defects in the crystal structure and these are described as the O^{2-} vacancy type lattice imperfections which can increase with the increase of the dopant rate [1,2,7,9–11]. If the dopant is one of the oxide compounds of Ln^{3+} group elements, the common composition formula of the

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stable single tetragonal phase of $(Bi_2O_3)_{1-x}$–$(Ln_2O_3)_x$ binary system can demonstrate as follows [9–11]:

$$Bi(III)_{2-2x}Ln(II)_{2x}O_{3-x}\square_x$$
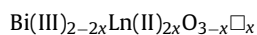
where $\square$ denotes the oxygen ion vacancy which occurs during the solid-state reactions of Bi_2O_3 and Ln_2O_3 compound. Although valence number of Ln cation is 3+ in Ln_2O_3, these incorporated Ln ions are reduced to bivalent state while the replacements of Ln cations with the host Bi cations in the tetragonal structure. When the charge balance is considered, O^{2-} ions should be oxidized spontaneously to O_2 molecules with the increase of Ln_2O_3 addition. This total oxidation–reduction is seen by the following chemical reaction [1,9–11]:

$$2O^{2-} + 4Ln^{3+} \rightarrow O_2\,(gas) + 4Ln^{2+} + 2\square\,(lattice)$$
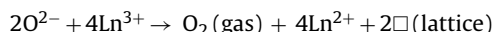
Thus, O^{2-} vacancies occur in the crystal structure during the stabilization of the single tetragonal phase and these vacancies have a random arrangement in the O^{2-} sublattice. The number of vacancies and the difference in ionic radii affect the electrical conductivity of the single phase of $(Bi_2O_3)_{1-x}(Ln_2O_3)_x$ binary systems [2,12].

2. Experimental details

The solid materials were synthesized by solid-state reaction method. The ceramic oxide mixtures of $(Bi_2O_3)_{1-x}(Sm_2O_3)_x$ binary system in the range $0.01 \leq x \leq 0.1$ (10 different compositions) have been prepared by mixing and homogenizing with the stoichiometric amounts of the monoclinic Bi_2O_3 and Sm_2O_3 in an agate mortar. The starting compounds were high-purity ($\geq$99.99% Merck) powders. The powder mixtures are firstly calcined at 650 °C during 15 h. After grinding and homogenization of pre-annealed mixtures were heat treated at 700, 750 and 800 °C, respectively. All these heat treatments were made in air atmosphere for 48 h, in alumina crucibles 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). Around a half amount of each powder sample, which was annealed at 800 °C, was transferred into gold crucible and heated to 830 °C in a vertical tube furnace, kept at that temperature 15 min in air then quenched by dropping the specimen into ice–water mixture.

The X-ray powder diffraction (XRD) data of the samples were recorded on a computer-interfaced Bruker AXS D8 advanced diffractometer operating in the Bragg–Brentano geometry (Cu Kα radiation, graphite monochromator, 40 kV and 40 mA) over a $10° \leq 2\theta \leq 90°$ angular range. The divergence and receiving slits of 1 and 0.1 mm, respectively, were located on the diffractometer. The diffraction patterns were scanned by 0.002° (2θ) steps and the diffracted beams were counted with a NaI(Tl) scintillation detector. The thermal measurements were made by using a simultaneous PerkinElmer Diamond DTA system. The specimens, usually 11.5 mg in mass, were heated at a rate of 10 °C min^{-1} from room temperature to ~700 °C. Measurements were made in dynamic atmosphere using a platinum sample holder and α-Al_2O_3 inert reference substance.

The total electrical conductivity (σ_T) measurements were made using standard four-probe dc method. The circular samples with tetragonal structure were pressed into pellets with 0.1 cm thickness (t) and 1.3 cm diameter (d) under 980 MPa pressure. The pellets were calcined at 600 °C for 10 h in air. After this heat treatment some XRD measurements showed that any phase change in the tetragonal samples was not observed. For reducing contact resistance, fine platinum wires directly attached to the surface of the samples. The ohmic character of the wire contacts was checked prior to the each measurement. The contacts were positioned symmetrically with respect to the center of the circular pellet and the contact separations (s) were 0.2 cm. The conductivity measurements were made at temperatures between 200 and 800 °C. The increase in temperature in the furnace was 20 °C steps in air atmosphere initially and near the phase transition the increase in temperature was 5 °C steps. During the measurements the sample temperature was determined by a thermocouple, 5 mm away from the sample. This thermocouple had a cold (0 °C) junction. All experimental data were made by Keithley 2400 sourcemeter and Keithley 2700 electrometer which are controlled by computer.

3. Result and discussion

During the synthesis of the binary systems, color change, mass loss and hardness were investigated in all samples. This indicates a change in crystal structure and the atomic arrangement. All the
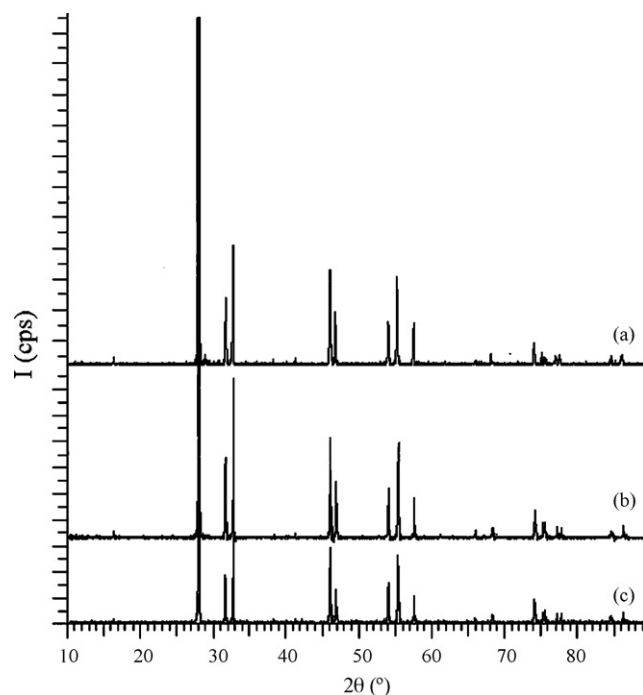

Fig. 1. XRD patterns of β-Bi_2O_3 doped with Sm_2O_3: (a) 7 mole% doped after heating at 800 °C; (b) 4 mole% doped after heating at 800 °C; (c) 4 mole% doped after heating at 750 °C.

changes during the experimental processes are the results of the solid-state synthesis reaction.

3.1. Structural analysis

XRD patterns of 4 and 7 mole% Sm_2O_3 are given in Fig. 1. XRD patterns of other single β-phase samples were quite similar to the patterns of single-phase samples given in these figures. 750 °C was the minimum solid-state reaction temperature at which the β-phase was obtained from the furnace cooled samples in the range of $0.03 \leq x \leq 0.05$. Single β-phase samples were also produced for the doping ranges of $0.03 \leq x \leq 0.07$ at 800 °C heat treatment conditions. For these Sm_2O_3 doping ranges, all of the observed XRD pattern peaks were indexed in the tetragonal crystal system. This result showed that the doping of Sm_2O_3 into Bi_2O_3 can make easy stabilization of the β-phase, when the doping concentration of Sm_2O_3, heating temperature and heating time are correct for the formation of phase. The diffusion speed of the dopant cations into the lattice is rather slow and requiring long heat treatment durations for the completion of the synthesis [1,9–11]. If the temperature of solid-state reaction is 750 or 800 °C, the Sm cations diffuse into monoclinic Bi_2O_3, then the solid solutions of Bi_2O_3–Sm_2O_3 binary system can form as the stable single β-phase at room temperature, during the upon cooling of the solid oxide mixtures. These observed XRD results were also agreement with the previous investigation

Table 1
The change in the unit cell parameters of Sm_2O_3-doped β-phase solid mixture

x (mole%)	Synthesis temperature (°C), 800 °C	
	a (Å)	c (Å)
3	7.7409	5.6494
4	7.7483	5.6530
5	7.7540	5.6555
6	7.7652	5.6553
7	7.7687	5.6573