

Research Letter

Synthesis of β -Phase $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Dy}_2\text{O}_3)_x$ ($0.01 < x < 0.10$) System and Measurement of Oxygen Ionic Conductivity

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Received 6 September 2007; Accepted 9 December 2007

Recommended by Robert S. Averback

β -phase $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Dy}_2\text{O}_3)_x$ system with tetragonal structure is synthesized for $0.01 < x < 0.10$ molar doping. Unit cell parameters increased with increasing the doping. We have studied the dependence of total electrical conductivity on temperature, doping concentration of β -phase systems. The phase transition which manifests itself by the jump in the conductivity curve was also verified by DTA and both measurements are rather compatible. The electrical conductivity curves of β -phase structure revealed regular increase in the form of an Arrhenius curve. The activation energies are calculated from these graphs. Bi_2O_3 -based Dy_2O_3 doped ceramics show ionic oxygen conductivity. The conductivity increased as the doping concentration increased. The highest value of conductivity is $0.006 \text{ ohm}^{-1} \text{ cm}^{-1}$ (600°C) for the β -phase $(\text{Bi}_2\text{O}_3)_{0.91}(\text{Dy}_2\text{O}_3)_{0.09}$ (800°C). The sample with the highest conductivity is $(\text{Bi}_2\text{O}_3)_{0.91}(\text{Dy}_2\text{O}_3)_{0.09}$ (800°C) binary system where $1.450 \text{ ohm}^{-1} \text{ cm}^{-1}$ (745°C).

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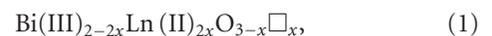
1. INTRODUCTION

Bi_2O_3 polymorphs can be used in SOFC applications and oxygen detectors since their oxygen ionic conductivity is higher than that of Zirconia (ZrO_2)-based electrolytes at the same temperature [1–3]. Moreover, it can be used as an insulating layer in Bi-based bulk and cable superconductors [4].

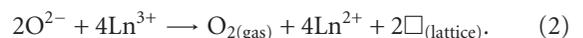
Monoclinic phase (α - Bi_2O_3), bcc phase (γ - Bi_2O_3), fcc phase (δ - Bi_2O_3), and tetragonal (β - Bi_2O_3) phase are intensely studied four phases of Bi_2O_3 out of its six crystal modifications [1, 2, 5, 6]. For pure Bi_2O_3 , the stable allotroph in room temperature is the monoclinic α - Bi_2O_3 phase. The other three forms are unstable at room temperature and they show ionic oxygen conductivity. These metastable phases could be stabilized at room temperature by doping [3, 7–9]. In the synthesis of Bi_2O_3 phases, the parameters like the dopant, stoichiometric rate of the dopant, heat treatment time, heat treatment temperature, cooling rate, grinding time and number of grindings, the grain size, and so on are important [7–9]. These variables affect the structural characteristics such as unit cell constants [3, 7–9]. Doped δ - Bi_2O_3 , γ - Bi_2O_3 , and β - Bi_2O_3 phases have crystal defects which in-

crease with increasing doping rate and these defects are reported to result in O^{2-} ion deficiency [1, 2, 5, 7–9].

If the dopant is one of the oxide compounds of Ln^{2+} group elements, the structure of the stable monophase of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Ln}_2\text{O}_3)_x$ compound is [7–9]



where Ln(II) is the Ln^{2+} cation, Bi(III) is the Bi^{3+} cation, \square is the oxygen ion vacancy due to the oxygen gas leaving the structure; x is the molar dopant amount in the bi-compound where monophase is observed. The doped Ln_2O_3 oxide compounds are reduced according to the reaction below and oxygen vacancy is produced after the reaction



During the reaction, Ln^{3+} cations are reduced to Ln^{2+} cations and are located at the Bi^{3+} cations lattice points [1, 7–9]. The amount of doping increases the lattice parameter of the unit cell changes [1, 2, 7–9]. The reasons of this change are different in the effective ion radii of the cations [1, 7–9]. The difference in ionic radii also affects electrical conductivity [2, 10].

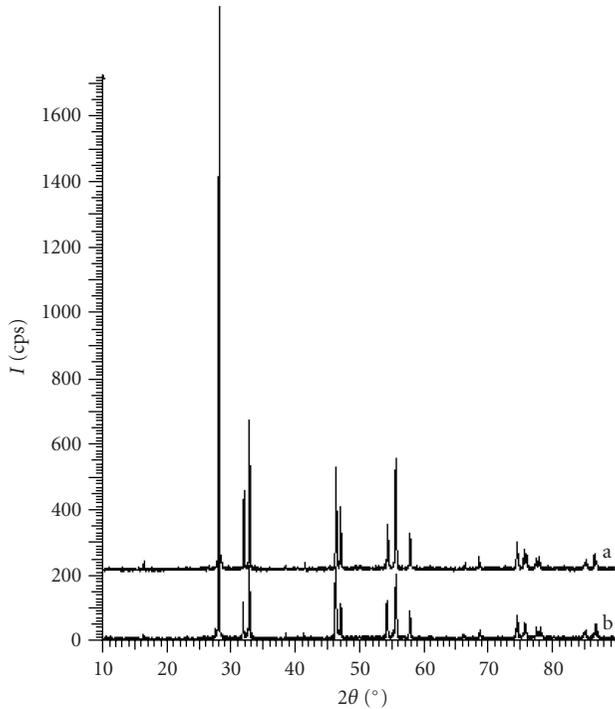


FIGURE 1: XRD patterns of β - Bi_2O_3 doped with 7 mole % Dy_2O_3 (a) after heating at 800°C , (b) after heating at 750°C .

The total electrical conductivity (σ_T) for an ionic solid that can be determined experimentally is [1, 3, 11–13]

$$\sigma_T = \sigma_0 \cdot e^{-E_a/kT}, \quad (3)$$

where E_a , T , k , σ_0 are the activation energy, temperature, Boltzmann constant, and pre-exponential factor, respectively. The activation energy can be calculated from the $(\ln(\sigma_T) - 10^3/T)$ Arrhenius curves [3, 5, 11, 13]. In the studies, it is extensively reported that the Arrhenius curves have two regimes in oxygen ionic materials [2, 3, 14]. This indicates a change or a phase transition in the conductivity mechanism.

2. EXPERIMENTAL DETAILS

The solid mixtures were synthesized via solid-state reactions. Bi_2O_3 , Dy_2O_3 (Merck % 99.99) are used as predecessors. After grinding and homogenizing solid mixtures in agat mortar, they were heat treated for 48 hours. All these heat treatments were performed as loose powders, in alumina crucibles, in air and without any compaction. After the final annealing at 830°C , powder samples were quenched into a mixture of distilled water and ice.

The total electrical conductivity 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 contacts were made using a kit that made from alumina. The contacts were positioned symmet-

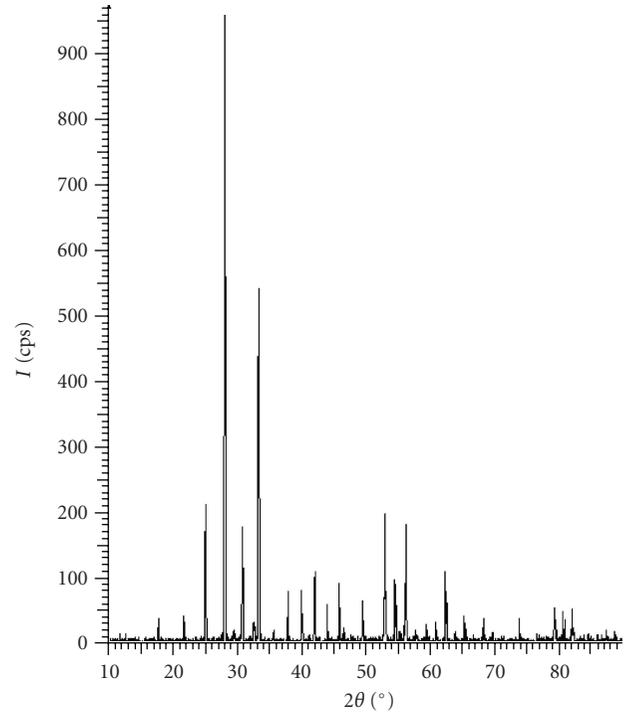


FIGURE 2: XRD pattern of γ - Bi_2O_3 doped with 4 mole % Dy_2O_3 after heating 830°C .

rically with respect to the center of the circular pellet and enabled contact on the top of the sample. The contact separations (s) were 0.2 cm. The conductivity measurements were made at temperatures between 200°C and 800°C . During the measurements, the sample temperature was determined by a thermocouple 5 mm away from the sample.

3. RESULT AND DISCUSSION

3.1. Structural analysis

XRD results revealed that tetragonal β - Bi_2O_3 solid mixture is a dominant single phase (Table 1). One of the basic factors dictating which unstable phase of Bi_2O_3 will become stable at room temperature is the type of Dy_2O_3 compound and the others are reaction temperature and the conditions of the reaction.

Measured sample XRD patterns of 7, 4, 9 mole % Dy_2O_3 addition are given in Figures 1, 2, and 3. The XRD patterns of the other single β -phase samples were quite similar to the patterns of the single phase sample given in Figure 1. XRD patterns of some of the multiphase samples are given in Figure 4 and assignments of individual peaks to α , β , γ , or δ phases were indicated on the patterns.

The unit cell parameters calculated for the monophasic increase as the doping concentration increases (Figure 5). The reason for this increase is the change in ionic radii and charge balance since the reduced Dy^{2+} cations replace Bi^{3+} ions. The reported ionic radii of Bi^{3+} , Dy^{3+} , and Dy^{2+} cations are 1.02 Å [15], 0.91 Å [15], and 1.07 Å [16], respectively.

TABLE 1: Phases in the system of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Dy}_2\text{O}_3)_x$.

Synthesis temperature (°C)	Dy ₂ O ₃ doping (mole %)									
	1	2	3	4	5	6	7	8	9	10
700	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$
750	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	β	β	β	$\alpha + \beta$	$\alpha + \beta$
800	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	β	β	β	β	β	$\alpha + \beta$
825	$\alpha + \gamma$	$\alpha + \gamma$	γ	γ	$\gamma + \beta$	$\gamma + \beta$	$\gamma + \beta$	$\gamma + \beta$	$\gamma + \beta$	$\gamma + \beta$
825 (w.q.)	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \delta$	$\alpha + \delta$	$\alpha + \delta$	δ	δ

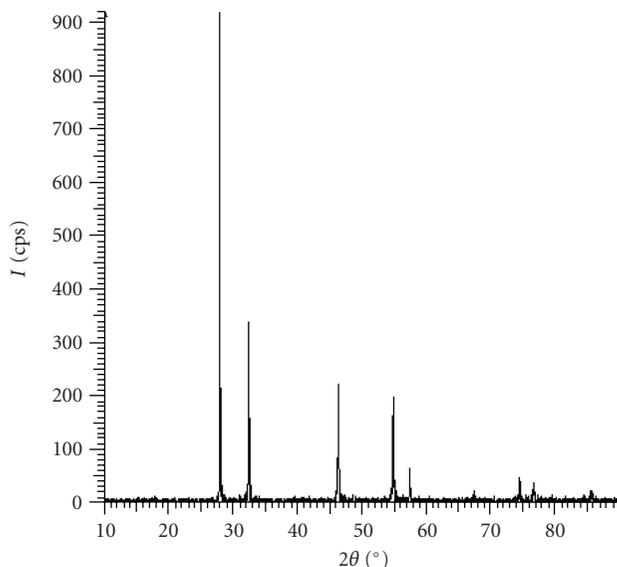


FIGURE 3: XRD pattern of δ -Bi₂O₃ doped with 9 mole % Dy₂O₃ after quenched 830°C.

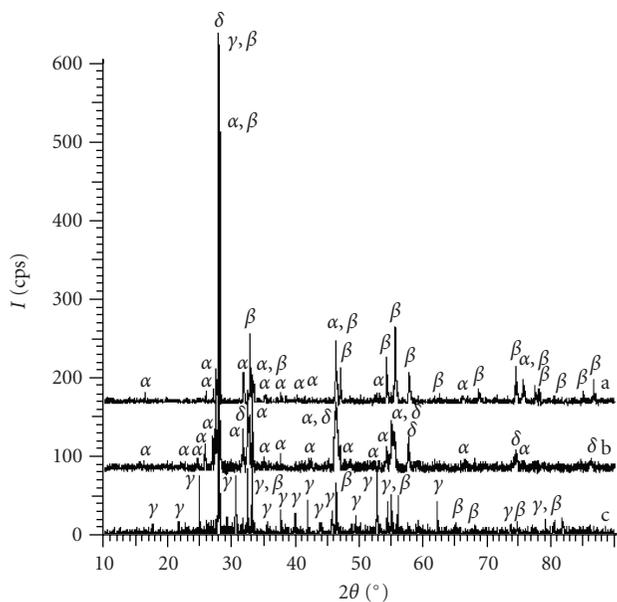
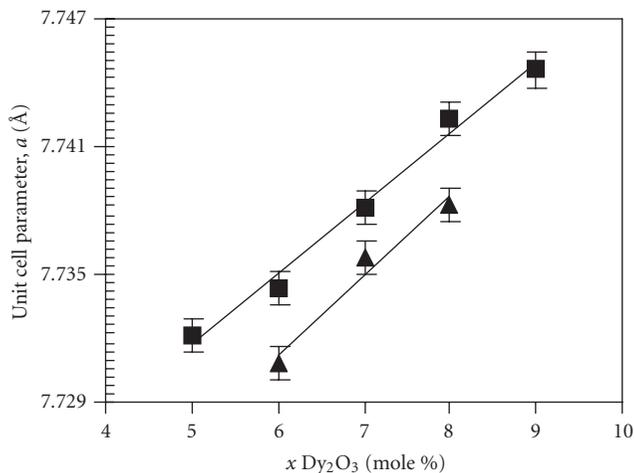
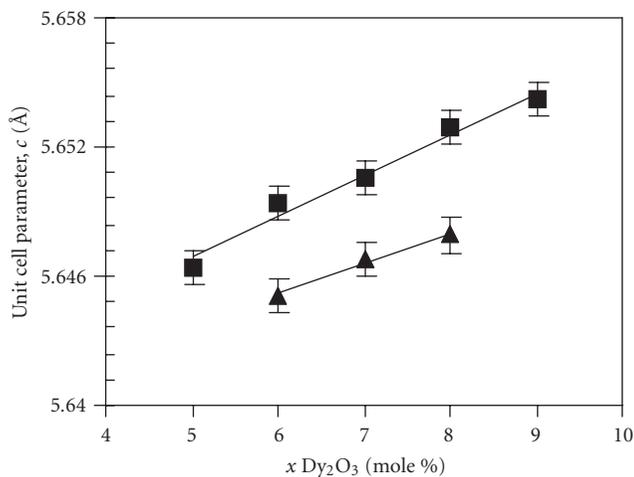


FIGURE 4: XRD patterns of some of the multiphase samples. (a) 4 mole % Dy₂O₃ addition (after heating at 750°C), (b) 7 mole % Dy₂O₃ addition (after quenching at 825°C), (c) 5 mole % Dy₂O₃ addition (after heating at 825°C).



(a)



(b)

FIGURE 5: (a) The change in the unit cell parameters of Dy₂O₃-doped β -phase (tetragonal) solid mixture as a function of doping concentration. (b) Unit cell constant *a*. Unit cell constant *c* (■: after heat treatment at 800°C, ▲: after heat treatment at 750°C).

3.2. Electrical conductivity

As the Dy₂O₃ doping quantity increases, the concentration of oxygen ion vacancy at the lattice and thus the nonstoichiometric character increase. The increase of vacancies in the lattice increases the chance of oxygen ions to become mobile

TABLE 2: The highest values of conductivities in $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Dy}_2\text{O}_3)_x$ binary system.

$(\text{Bi}_2\text{O}_3)_{1-x}(\text{Dy}_2\text{O}_3)_x$				
Synthesis temperature (°C)	x (mole)	Phase	Ambient temperature (°C)	σ_T ($\text{ohm}^{-1}\text{cm}^{-1}$)
750	8	β	600	0.002
800	9	β	600	0.006
800	9	—	745	1.450

particles and thus electrical conductivity increases. The total electrical conductivity is calculated using

$$\sigma_T = \frac{I}{V} \cdot G^{-1}, \quad (4)$$

where G is the geometric resistivity correction factor. According to the sample dimensions when d/s and t/s ratios are considered, in the light of previous studies, G is obtained [17–21],

$$G = 2 \cdot \pi \cdot s \cdot F' \left(\frac{d}{s}, \frac{t}{s} \right),$$

$$F' \left(\frac{d}{s}, \frac{t}{s} \right) = \frac{t/s}{2 \cdot \ln \left(\sinh(t/s) / \sinh(t/2s) \right)} \quad (5)$$

$$\times \frac{\ln 2}{\ln 2 + \ln \left[\left((d/s)^2 + 3 \right) / \left((d/s)^2 - 3 \right) \right]}.$$

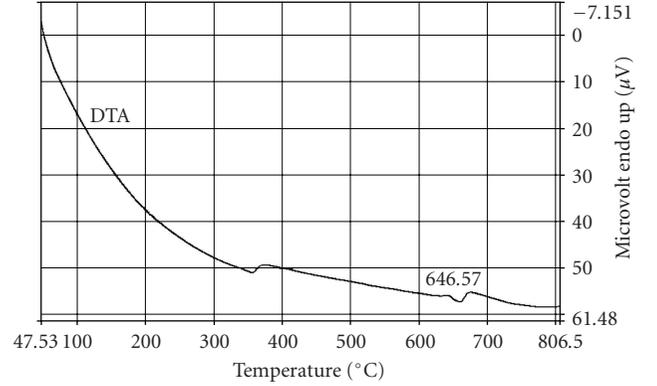
To compare the conductivities of all samples a table including the highest conductivities of the binary systems is given in Table 2. According to the table, conductivities are higher than the previous studies [2, 10, 22, 23]. When the graphs of conductivity versus temperature are analyzed, peaks are seen at the phase transition temperatures. It is considered that phase transition starts at the peak temperatures. These peak temperatures are consistent with the real phase transition temperatures detected by DTA (Figure 6).

As can be seen on Figure 6, the transition temperature is 646.57°C as determined by DTA while the transition temperature in the conductivity versus temperature graph is in the range of $610\text{--}665^\circ\text{C}$. At high temperatures, along with the phase transition, the resistivity of the sample drops abruptly. The reasons of the abrupt increase in conductivity are the phase change and the change in the crystal structure possibly causing a change in the conductivity mechanism. The structural disorder during transformation may also contribute to the improvement of ionic conductivity. The β - δ phase change for pure β - Bi_2O_3 at about $660\text{--}670^\circ\text{C}$ temperatures is reported using DTA thermal analysis, high temperature XRD analysis, and conductivity change graphs [5, 6].

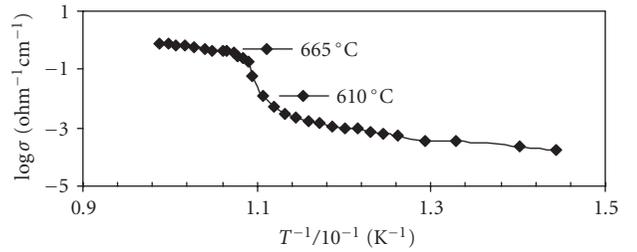
The amount of doping has pronounced effects on conductivity. In Figure 7, mole % doping versus the maximum value of conductivity of β -phase is plotted. Increasing doping concentration increases conductivity.

3.3. Activation energy

From the Arrhenius curves drawn for all samples the activation energy E_a is calculated (Table 3). When Table 3 is ex-



(a)



(b)

FIGURE 6: (a) The DTA and (b) conductivity graph of $x = 0.08$ molar doped $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Dy}_2\text{O}_3)_x$ binary system synthesized at 800°C .

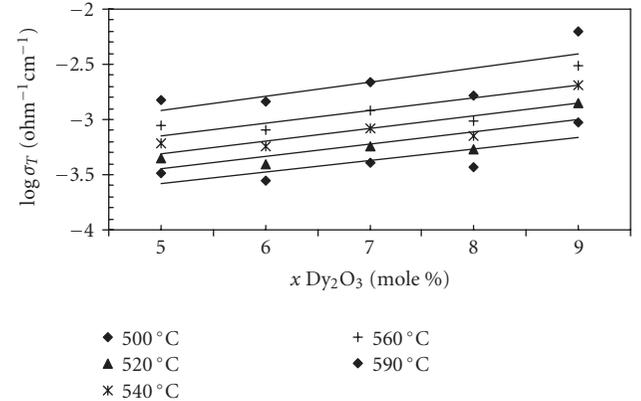


FIGURE 7: The effect of doping concentration on conductivity for Dy_2O_3 -doped β -phase samples synthesized at 800°C .

amined, activation energies are roughly about 0.9 eV . Moreover, the two regimes of Arrhenius conductivity curves prove that the activation energies are different for high temperatures and low temperatures and so the conductivity mechanisms are different for the two regimes. This is typical behavior of Bi_2O_3 -based solid electrolytes as we mentioned earlier.

4. CONCLUSIONS

Tetragonal β -phase $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Dy}_2\text{O}_3)_x$ ($0.01 < x < 0.10$) binary oxide compounds that have oxygen ionic conductivity are synthesized. To obtain the tetragonal structure, high

TABLE 3: The comparison of activation energies for $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Dy}_2\text{O}_3)_x$ binary system.

Synthesis temperature ($^{\circ}\text{C}$)	x (mole %)	E_a (eV)
750	6	1,09
	7	0,87
	8	0,92
800	5	0,88
	6	0,89
	7	0,88
	8	0,92
	9	0,96

temperature and long heat treatment duration are needed. The unit cell parameters are observed to increase as the doping concentration increases. The reason is the settlements of dopant cations with interchange reactions and the reduction reactions of the dopant cations occurring in the meantime. Jumps in the conductivity curves indicating phase transitions are observed. The conductivity of these ceramic materials increased as the dopant concentration increased. The reason is the introduction of more lattice defects due to the increase in vacant lattice points. Enlargement of unit cell dimensions and modification of charge balance may also be responsible. The sample with the highest conductivity of $1.450 \text{ ohm}^{-1}\text{cm}^{-1}$ (745°C) is the $(\text{Bi}_2\text{O}_3)_{0.91}(\text{Dy}_2\text{O}_3)_{0.09}$ (800°C) and $0.006 \text{ ohm}^{-1}\text{cm}^{-1}$ (600°C) for the β -phase $(\text{Bi}_2\text{O}_3)_{0.91}(\text{Dy}_2\text{O}_3)_{0.09}$ (800°C) binary systems. The activation energies of the tetragonal compounds for which the conductivity increases following Arrhenius curve are lower than 1 eV for almost all samples.

5. DISCUSSION

Beside the factors examined in this study, also the other factors that affect the synthesis of tetragonal phase should be examined. In this study, the structure of lattice has not been examined, in the further studies this could also be examined. The structure that has been appeared at high temperature should be examined by high-temperature XRD analysis.

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