

Synthesis and structural characterization of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$ and $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ solid solutions

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Abstract. Solid solution series, $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$ and $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$, for $x = 0.10, 0.20, 0.30$ and 0.40 were synthesized by standard ceramic technique. The structural phase characterization was carried out using X-ray powder diffraction technique. It was found that the solid solution containing 20–40 mole% of Y_2O_3 had face-centred cubic structure. All samples of the solid solution series, $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$, had rhombohedral single phase in the concentration range $0.10 \leq x \leq 0.40$. Lattice parameters of *fcc* phase of Y_2O_3 doped samples were calculated from the X-ray diffraction data. The lattice constant '*a*' gradually decreases with increasing content of dopant concentration (*x*) for the Y_2O_3 doped system and obeys Vegard's rule. The unit cell parameters for the $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ doped samples showing rhombohedral phase were obtained on hexagonal setting.

Keywords. Fast ion conductors; fluorite structure; fuel cell materials.

1. Introduction

Fast ion conductors have been a subject of extensive research because of their interesting physical properties as well as their potential technological use (Takahashi *et al* 1992). High ionic mobility in a crystalline solid is a primary requirement and it can only be achieved in the presence of disorder (Hagenmuller 1978). The materials with fluorite structure can be disordered either by thermal activation (intrinsic conductors) or by doping with trivalent ions (extrinsic conductors) such as lanthanides. These systems are therefore, excellent candidates for studies of mechanism of ion transport in crystalline materials. In recent years, the fluorite structured solid solutions have been the subject of numerous experimental studies focused on their fast ion conducting behaviour (Kilner 2000). An interesting subgroup of this class of materials are the oxides that display oxygen ion conductivity. There has been a continued drive towards the synthesis of new materials and their development because of the promise of important technological devices such as solid oxide fuel cells (SOFC), oxygen separation membrane etc (Harwig and Gerads 1978; Kilner 1997). All these devices offer the potential of enormous commercial and ecological benefits provided suitable high performance material can be developed.

Among the various types of oxygen ion conductors (Sethi and Gauer 1955), the anion deficient fluorite structured oxides such as calcia-stabilized zirconia and *d*-

Bi_2O_3 oxides are still the best known oxygen ion conductors. Moreover, the simplicity of the structure and bonding in fluorites makes them ideal systems for fundamental, theoretical and experimental studies. Bismuth oxide (*d*-phase) is known to have a defect fluorite type structure including large amounts of vacant sites in the oxide ion sublattice (Sethi and Gauer 1955). These materials show high oxide ion conductivity under ordinary atmosphere (Dutta and Mechan 1971). This phase, is, however, stable only in the narrow temperature range of 730–825°C. The conductivity falls remarkably below 730°C and the substance undergoes a phase transition to monoclinic structured *a*-phase. It is, therefore, interesting to stabilize the high conducting *d*-phase at low temperatures by doping bismuth oxide with *alio* or *iso* valent ions with the aim of stabilizing the *fcc* phase at low temperature. Although the phase diagrams of Bi_2O_3 – M_2O_3 are partly studied (Turkoglu *et al* 2002), the composition range studied are rather narrow and are limited to the Bi_2O_3 rich region (≥ 90 mole% of Bi_2O_3). In the present paper we report investigations that have been carried out on the synthesis and structural characterization of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$ and $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ systems. The exact range of dopant concentrations that stabilizes the fluorite phase has been identified. The results on other bismuth oxide based systems are reported elsewhere.

2. Experimental

Two series of samples having the composition, $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$ and $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$, for $x = 0.10, 0.20, 0.30$

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and 0.40 were prepared by using standard solid state reaction technique. Appropriate quantities of the required constituent oxides of high purity (99.99%) fine powders of Bi_2O_3 (Thomas Baker), Y_2O_3 and Gd_2O_3 (E Merck) were thoroughly dry mixed and ground using agate mortar and pestle. This mixture was heated in air at 725°C for 12 h in platinum crucibles to obtain homogeneous product. The material thus obtained after first heating was reground till a fine powder was obtained and it was again kept for second heating at 825°C for 12 h and slowly cooled at 5°C per min until room temperature was reached. The product thus obtained after second heating was then finally ground and cold pressed into pellets that were sintered in air from $800^\circ\text{--}1000^\circ\text{C}$. It was observed

that greater the content of doped oxide the higher was the sintering temperature. All these samples were prepared in carbolite furnace using Eurotherm temperature controller.

All the samples were characterized at room temperature by X-ray diffraction using CuK_α radiation. The XRD data were analysed to index the Bragg peaks and to identify the phases present. Unit cell parameters were evaluated from the positions of Bragg peaks.

3. Results and discussion

$(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$ system: All the samples were characterized at room temperature by X-ray diffraction using

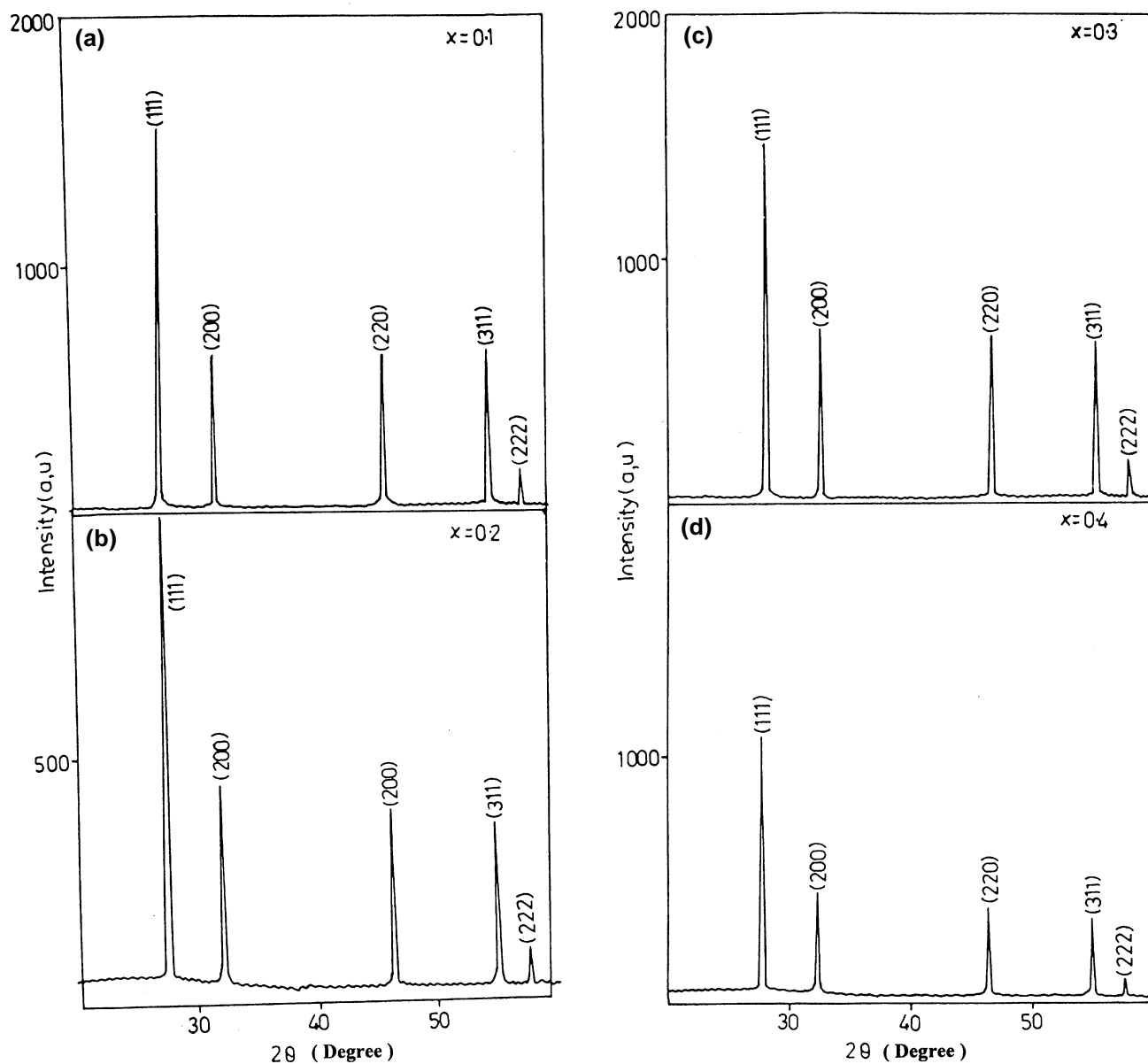


Figure 1. X-ray diffraction patterns of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$ for a. $x = 0.10$, b. $x = 0.20$, c. $x = 0.30$ and d. $x = 0.40$.

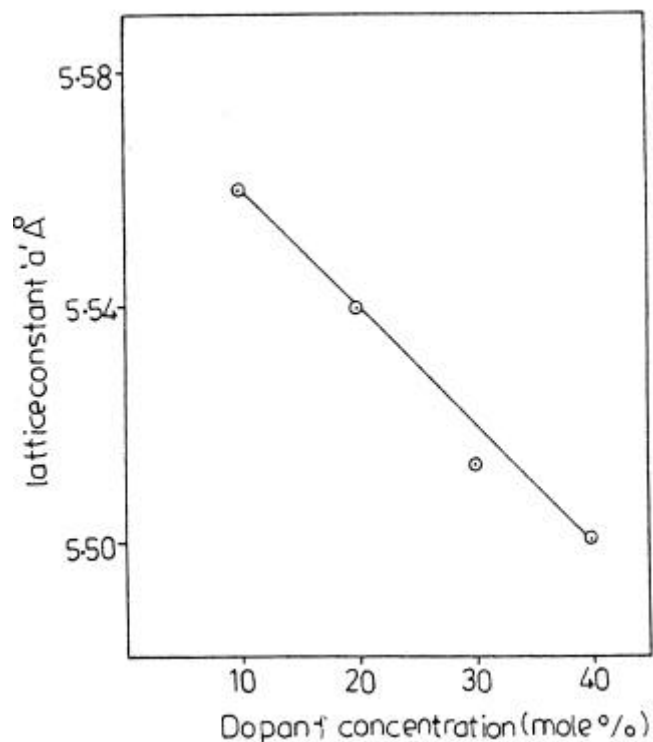


Figure 2. Variation of lattice parameter with dopant concentration for $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$.

CuK_α radiation. The X-ray analysis revealed that all samples were single phase as seen from the absence of extra peaks. The X-ray peaks were indexed and lattice parameters were evaluated using REFIDET least square programme. The observed X-ray diffraction patterns of all the samples of this series are shown in figures 1a–d. The lattice parameter and structural phases present are tabulated in table 1. It is observed that the values of lattice parameter 'a' decreases with increasing dopant concentration as shown in figure 2 and obeys Vegard's rule in the composition range 10–40 mole%. This implies that the system, $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$, forms a solid solution series over a wide range of compositions. Specimens containing < 10 mole% of Y_2O_3 showed mixed phases.

$(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ system: X-ray diffraction patterns of Gd_2O_3 doped samples are displayed in figures 3a–d. A series of compounds having the composition, $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$, for $x = 0.10, 0.20, 0.30$ and 0.40 were characterized by X-ray diffraction using PW 1700 (Philips make, Holland) X-ray diffractometer using Fe target. The observed XRD patterns were analysed and the refined unit cell parameters were calculated using the standard least square refinement programme. All the four Gd_2O_3 doped samples exhibited rhombohedral structure. The values of the unit cell parameters were obtained on hexa-

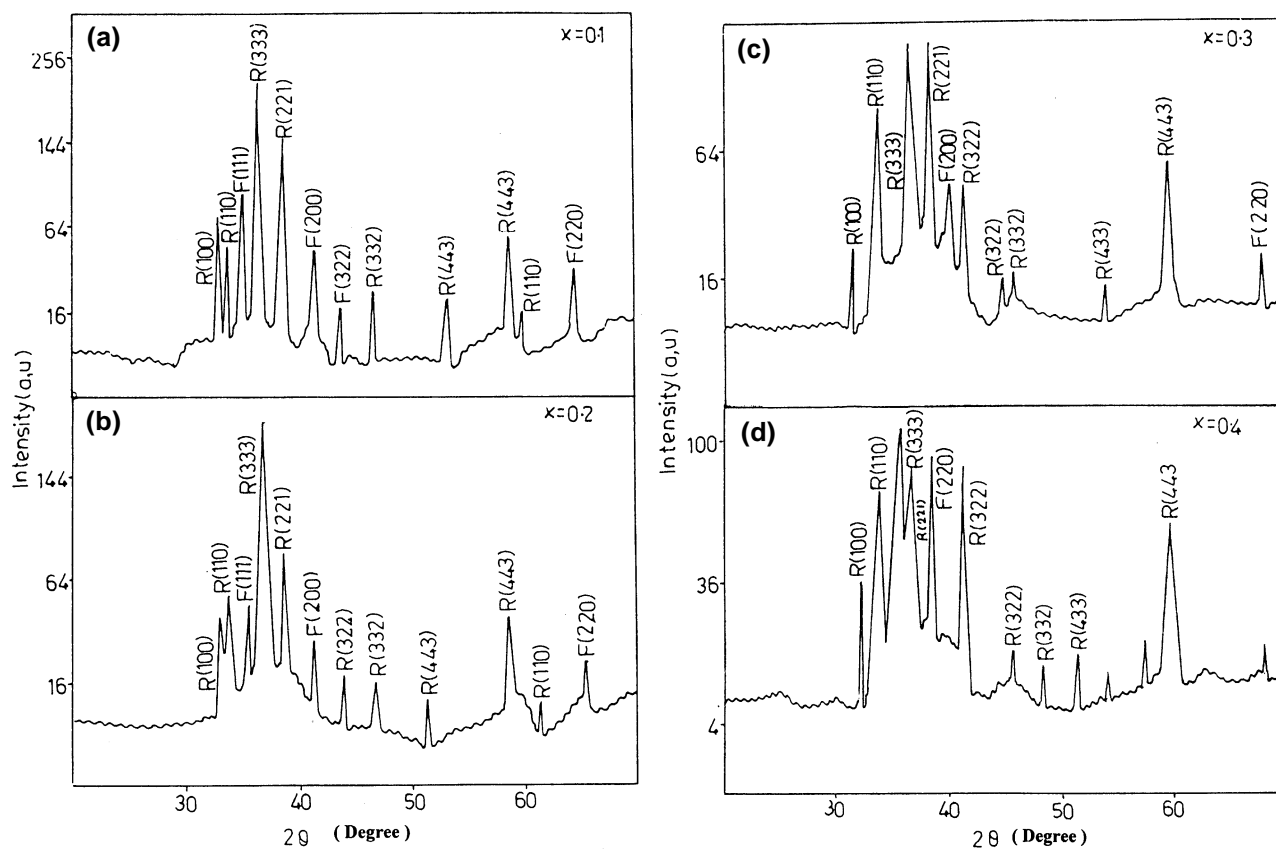


Figure 3. X-ray diffraction patterns of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ for **a.** $x = 0.10$, **b.** $x = 0.20$, **c.** $x = 0.30$ and **d.** $x = 0.40$.

Table 1. Unit cell parameter, unit cell volume and structural phases present in $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$.

Composition, X (mole%)	Unit cell parameter, $a(\text{\AA})$	Unit cell volume, $V = a^3 (\text{\AA})^3$	Structural phase present
10	5.560 ± 0.002	171.88	<i>fcc</i>
20	5.540 ± 0.002	170.03	<i>fcc</i>
30	5.520 ± 0.002	168.20	<i>fcc</i>
40	5.500 ± 0.002	166.38	<i>fcc</i>

Table 2. Unit cell parameter, unit cell volume and structural phase present in $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$.

Composition, X (mole%)	On rhombohedral lattice			Structural phase
	$a_R (\text{\AA})$	α°	$V_R (\text{\AA})^3$	
10	9.506	24.09	120.00	Rhombohedral
20	9.505	24.18	125.30	Rhombohedral
30	9.508	24.25	121.19	Rhombohedral
40	9.481	24.33	123.50	Rhombohedral + impurity peaks

gonal setting and tabulated in table 2. The results of present study reveal that the *fcc* phase is not stabilized in Gd_2O_3 doped samples within the range of dopant concentrations studied.

From the consideration of the cationic radius of the dopant oxides, it is expected that the oxide ion conductive phase in the system, $(\text{Bi}_2\text{O}_3)_{1-x}(\text{M}_2\text{O}_3)_x$, is rhombohedral in the case of a relatively large ionic radius of M^{3+}

and is *fcc* in the case of comparatively small ionic radius of M^{3+} . The rhombohedral phase is formed in the system doped with Gd_2O_3 , the cationic radius of Gd^{3+} (0.94 \AA) ions are comparatively large. The *fcc* phase is stabilized by doping with oxides with relatively small cationic radius Y^{3+} (0.90 \AA) than Bi^{3+} (1.03 \AA). The deviation in structural stabilization is due to the difference in electronic configuration of Y(5*d*) and Gd (5*f*).

4. Conclusions

From the results of the present study it is observed that fluorite structured *fcc* phase is retained for the dopant concentration (x) lying between 10 mole% and 40 mole% for Y_2O_3 doped systems. The rhombohedral phase is observed for Gd_2O_3 doped system for the dopant concentrations lying between 10 mole% and 40 mole% of Gd_2O_3 .

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