Synthesis and characterization of *b* type solid solution in the binary system of Bi_2O_3–Eu_2O_3

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Abstract. We have investigated Bi_2O_3–Eu_2O_3 binary system by doping with Eu_2O_3 in the composition range from 1 to 10 mole% via solid state reactions and succeeded to stabilize *b*-Bi_2O_3 phase which is metastable when pure. Stability of *b*-Bi_2O_3 polymorph was influenced by heat treatment temperature. Tetragonal type solid solution was obtained in 3–6 mole% addition range when annealed at 750°C and the range was 2–7 mole% when annealed at 800°C. We have also carried out investigations on lattice parameters, microstructural properties and elemental compositions of this *b* type solid solution for each doping ratio. Lattice parameters increased with amount of Eu_2O_3 addition. Our experimental observations strongly suggested that oxygen deficiency type non-stoichiometry is present in doped *b* type solid solutions.

Keywords. Bismuth trioxide polymorphs; solid solution; Bi_2O_3–Eu_2O_3 binary system.

1. Introduction

Bismuth trioxide has four polymorphs: monoclinic (or pseudo-orthorhombic) *a*-form, face centred cubic (*fcc*) *d*-form, tetragonal *b*-form and body centred cubic (*bcc*) *g*-form. Of these polymorphs, only *a*-Bi_2O_3 is a stable phase of pure Bi_2O_3 at room temperature (Takahashi *et al* 1977; Chiodelli *et al* 1994; Oniyama and Wahlbeck 1998). When pure *a* phase is heated to about 730°C, transition to the *d*-Bi_2O_3 occurs and this phase is stable only between 730°C and melting point of 825°C. Large thermal hysteresis effects are present upon cooling, and *d* phase transforms to one of the two intermediate phases which are *b*-form (formed at 650°C) and *g*-form (formed at 639°C). The *g* phase can be obtained by controlled cooling of *b*-Bi_2O_3. The last two phases are metastable and they usually transform to the *a* phase in the temperature range 650–500°C (Harwig and Gerards 1978; Miyayama and Yanagida 1986; Oniyama and Wahlbeck 1998). The *g* and *b* forms can only be obtained as stable phases at room temperature by addition of small amounts of other dopant oxides, i.e. Y_2O_3, MoO_3, CoO, Sb_2O_3, WO_3, SrO, CaO, La_2O_3, V_2O_5 and Gd_2O_3 (Takahashi *et al* 1977; Miyayama *et al* 1982; Miyayama and Yanagida 1986; France *et al* 1997; Ling *et al* 1998; Turkoglu *et al* 1998, 1999; Turkoglu and Soylak 2002).

b-Bi_2O_3 type crystal structure is a two-dimensional superstructure of the *d*-Bi_2O_3 structure. *b*-$Bi_2O_{2.5}$ has been reported as a non-stoichiometric phase in the space group $P42_1c$ with lattice constants of $a = 7.75$, and $c = 5.63$ Å, while the lattice parameters of the stoichiometric *b*-Bi_2O_3 phase which is also in the same space group are $a = 7.74$ and $c = 5.63$ Å. The locations of the bismuth ions in the crystal structures are nearly identical but large differences for the locations of oxygen ions have been reported (Harwig 1978; Medernach and Snyder 1978). Gattow and Schütze (1964) have observed that the *b*-$BiO_{1.5}$ and *b*-$BiO_{1.75}$ phases prepared by quenching maintain their structures in non-stoichiometric compositions. Lattice parameters of non-stoichiometric *b*-$BiO_{1.5}$ and *b*-$BiO_{1.75}$ phases are $a = 10.95$, $c = 5.63$ Å and $a = 10.96$, $c = 5.64$ Å, respectively (Gattow and Schütze 1964). It has been reported in the references mentioned above that the non-stoichiometric *b* phases have oxygen ion vacancies while for stoichiometric compounds of this type, all particular cationic and anionic sites are fully occupied.

In the present work, we intended to stabilize the metastable *b* phase of Bi_2O_3 at room temperature by addition of Eu_2O_3 and to investigate the range of addition ratio and heat treatment temperature for stabilization. Moreover, some crystallographic and microstructural properties of the obtained single *b* phase samples were examined.

2. Experimental

The powder samples were prepared by mixing appropriate amounts of *a*-Bi_2O_3 (99·99% Merck) and Eu_2O_3 (99·99% Merck) without further purification. The solid

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oxide mixtures that contained increasing amounts of Eu_2O_3 from 1 to 10 mole% were prepared by mixing and homogenizing in an agate mortar. These oxide mixtures were calcined at 650°C for 48 h. The calcined powders were ground and heat-treated at 700°C for 48 h. These oxide powders were further heat treated for 48 h at 750 and 800°C with an intermediate grinding. Heat treatments were performed as loose powders, in gold crucibles, in air. At the end of each heat treatment procedure, annealed powders were slowly cooled in the furnace by switching off (uncontrolled). Following the heat treatment step at 800°C, powder samples were heated to 830°C in a vertical tube furnace, kept at that temperature for 15 min in air then quenched by dropping the sample into ice-water mixture.

X-ray powder diffraction (XRD) patterns were taken after every heat treatment step in order to check phase formation. XRD data were collected with Bruker AXS D8 advanced diffractometer using a Bragg–Brentano geometry with graphite monochromator CuK$_a$ radiation ($l = 1.5405$ Å) 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 0.002° steps over the angle range of 10°–90° (2q). Diffracted beams were counted with a NaI(Tl) scintillation detector and the obtained XRD data were compared with the reference data.

Microstructural aspects and microprobe analysis of formed samples were studied employing a LEO 440 scanning electron microscope (SEM). Microprobe analysis data were taken from flat surface of the pressed samples. Ten analyses were made from different regions of each sample at high magnification and mean values from these measurements were used for calculations. SEM images of the prepared samples were taken from loose powders, free outer surfaces and fracture surfaces of the pressed and annealed samples.

The grain size of the crystallites (mean crystalline diameter, D) is calculated using Scherrer's equation which is given below (West 1998)

$$D = (0.9l)/(b \cos q),$$

where l is the wavelength of X-rays, q the Bragg's angle

of XRD and b the broadening of diffraction line measured at half its maximum intensity (radians). In this study, b values of the particular planes of the single phase samples were found by using Bruker AXS D8 TOPAS 2 software.

3. Results and discussion

In $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$ system, experimented solid solution region and obtained phases either single or heterogeneous, are presented in table 1, depending on the reaction temperature. Heat treatment temperatures below 750°C and quenching experiments produced the mixture of phase regions for all of the samples according to the XRD measurements. Annealing temperature also has an effect on formation of this phase, widening its formation range. When the heat treatment temperature is increased from 750°C to 800°C, composition range that b phase obtained widened from 3–6 mole% to 2–7 mole% addition. XRD patterns of 4 mole% Eu_2O_3 (after heating at 800°C and 750°C, for 48 h) were given in figure 1. XRD patterns of other samples in these solid solution ranges were quite similar to the pattern given in this figure. All of the XRD peaks of the single phase samples were indexed in the tetragonal crystal symmetry and unit cell parameters were calculated and are given in figure 2. XRD measurements revealed that doping with more than 6 or 7 mole% Eu_2O_3 and less than 2 or 3 mole% Eu_2O_3, depending on the heat treatment temperature, had produced the heterogeneous solid mixture of Bi_2O_3 polymorphs. These multi-phase samples were excluded from this study.

Figures 2a and b show dependence of lattice parameters a and c, respectively on addition ratio of Eu_2O_3. It is evident from XRD data that Eu ions are incorporated in the crystal structure of b-Bi_2O_3 since the lattice parameters display a systematic variation. Lattice parameters showed a slight but continuous increase with increasing Eu_2O_3 content. Therefore, we concluded that the solubility range for Eu_2O_3 in tetragonal type $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$ solid solution were $0.03 \le x \le 0.06$ at 750°C and $0.02 \le x \le 0.07$ at 800°C. The slight increase of lattice parameters with increasing Eu_2O_3 content was in good agreement with effective ionic radii considerations. Reported ionic radii

Table 1. The observed phases in the system $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$, x being $0.01 \le x \le 0.10$.

Temperature (°C)	Mole% Eu_2O_3 addition									
	1	2	3	4	5	6	7	8	9	10
700	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*
750	*a* + *b*	*a* + *b*	*b*	*b*	*b*	*b*	*a* + *d*	*a* + *d*	*a* + *d*	*a* + *b*
800	*a* + *b*	*b*	*b*	*b*	*b*	*b*	*b*	*d* + *g*	*d* + *g*	*d* + *g*
830 wq*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *b*	*a* + *d*	*a* + *d*	*a* + *d*

*Water quench.

are 0·102 nm for Bi^{3+}, 0·109 nm for Eu^{2+} and 0·095 nm for Eu^{3+} (West 1998; Misra and Andronenko 2000). When Eu^{2+} ions replace Bi^{3+} ions, lattice parameters should enlarge (Bi^{3+} ion has smaller ionic radii than Eu^{2+} ions) and this enlargement should be about 0·069% for 1% replacement. These figures are consistent with our observations on lattice parameter changes. Elongation of a when addition of Eu_2O_3 is increased from 2 mole% to 7 mole% is about 0·62%, on the other hand elongation of c under the same conditions is almost half being about 0·36%. This indicates the possibility of localization of oxygen deficiency defects on a–a related planes in the crystal structure since the enlargement along the c axis is closer to the value obtained through ionic radii considerations. When lattice parameters in figure 2 are considered, ratio of the lattice parameters (a/c) is increased with increasing addition ratio showing an enhanced tetragonality. Further, evidence for oxygen non-stoichiometry is discussed later in the text.

On the other hand, formation of tetragonal type $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$ solid solution was a very slow process requiring a long heat treatment duration. It was concluded from this fact that diffusion rate for europium ions into bismuth trioxide was quite low. Through this slow diffusion mechanism, Eu cations preferentially substituted bismuth cations in the crystal structure. Although valence number of Eu cation is + 3 in pure Eu_2O_3, these incorporated Eu ions would probably be reduced to bivalent state in the structure of obtained tetragonal type solution. When the charge balance is considered, as the addition of Eu_2O_3 increased, O^{2-} ions should spontaneously be oxidized to O_2 molecules. As a result of this possible mechanism, some oxygen ion vacancies should occur at
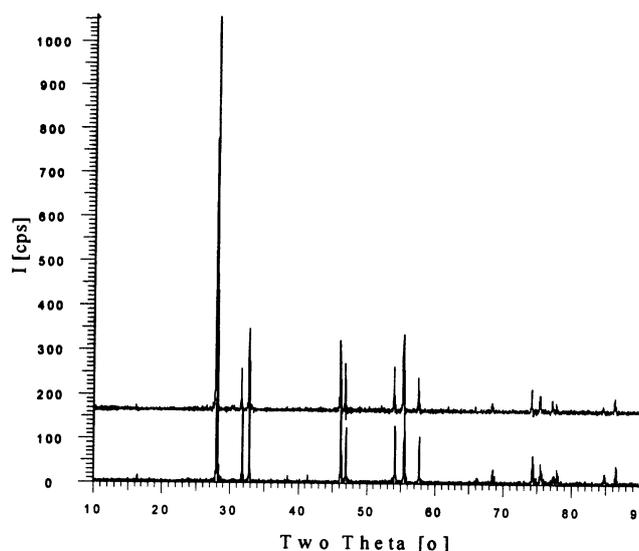
the O^{2-} sublattices in the tetragonal $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$ solution. At the end of this, obtained solid solution should have the non-stoichiometric character and defect tetragonal structure. The non-stoichiometry for formed samples in this study can be regarded as an oxygen deficiency type as seen in the phases prepared by Gattow and Schütze (1964), Harwig (1978) and Medernach and Snyder (1978). Therefore, the composition of the **b** type $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$ solution can be expressed as

$$Bi(III)_{2-2x}Eu(II)_{2x}O_{3-x},$$

where x denotes oxygen ion vacancy. x values are $0·03 \leq x \leq 0·06$ for 750°C and $0·02 \leq x \leq 0·07$ for 800°C annealing temperatures.

The calculated weight ratio values obtained using the approximations outlined above are given in table 2, together with values obtained from SEM microprobe analysis. The values of wt% Bi and wt% Eu were calculated according to non-stoichiometric formula. These measured values are
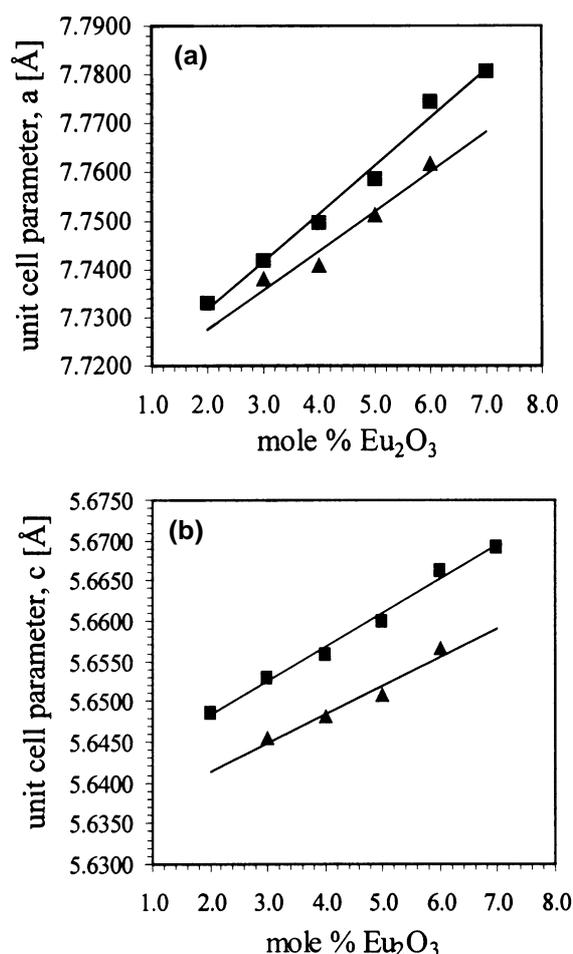
Figure 1. XRD pattern of **b**-Bi_2O_3 doped with 4 mole% Eu_2O_3 (above pattern: after heating at 750°C, below pattern: after heating at 800°C).

Figure 2. The relationship between the amount of Eu_2O_3 doping, and the lattice parameter of **b**-Bi_2O_3: **(a)** Unit cell parameter, a and **(b)** unit cell parameter, c (■, after heating at 750°C; ▲, after heating at 800°C).

in good agreement with the calculated ones. Cation concentrations higher than the expected stoichiometric values indicate oxygen deficiency in the crystal structure. Although this is not a solid proof for oxygen deficiency, it nevertheless is in agreement with the literature cited in the introduction. This oxygen deficiency may lead to variations in the electrical conductivity properties of these doped samples. When the data given in table 2 for samples annealed at two different temperatures (750°C and 800°C) were compared, no significant or systematic difference was present.

The colour of our annealed samples had a systematic change depending on the amount of europium trioxide addition. The colour of the sintered powder specimens was light yellow for 1%, 8% and 9% additions where single b phase is not obtained. As b type solid solution is formed with increasing addition ratio, the colour of the powder changed to red brown which is a darker colour. The observed colour change phenomenon provides further support for non-stoichiometry in our samples since non-stoichiometry causes darkening.

Table 3 shows the results of the grain size calculations from XRD data. There is a general tendency that grain size becomes smaller with increasing addition ratio. These peaks used for calculations were sharpest and symmetrical, (201) having the highest intensity. We have also observed that grain sizes of the samples annealed at 800°C are slightly smaller than the samples annealed at 750°C.

SEM investigation of the ground powders and fracture surfaces showed that grain size distribution was not uniform. We observed sub micron grains (finely ground powder) as well as grains above even 10 μ (fracture surfaces). XRD patterns were taken from finely ground powder which mostly had sub micron grain size. Connectivity of the grains is improved when Eu_2O_3 addition is increased. Outer free surfaces of the samples annealed at 750°C in air were examined and shown in figure 3. Outer surface of the sample with 1% Eu_2O_3 addition had smoother appearance and sharper grain boundaries. Sharpness of the grain boundaries gradually decreased while grain connectivity is improved as the addition ratio increased. At the same time, as the tetragonal b phase is formed, more voids appeared on the sample. Sample with higher Eu_2O_3 addition had more cracks on the surface and these cracks probably were due to shrinkage during heat treatment. As seen in SEM pictures (figure 4) of fracture surfaces of tablets annealed at 750°C, there are much more microcracks in 6% Eu_2O_3 added sample compared with 4% Eu_2O_3 added sample. Deterioration of the microstructure of the 6% Eu_2O_3 added sample is also apparent

Table 2. The microprobe analysis for the tetragonal (b) type solid solution of $(Bi_2O_3)_{1-x}$ $(Eu_2O_3)_x$ system.

	After heating at 750°C		After heating at 800°C		Calculated	
x	wt% Bi	wt% Eu	wt% Bi	wt% Eu	wt% Bi	wt% Eu
0·02	(–)*	(–)*	88·72 ± 0·26	1·25 ± 0·12	88·40	1·31
0·03	87·63 ± 0·36	1·92 ± 0·07	88·14 ± 0·22	1·82 ± 0·15	87·74	1·97
0·04	87·34 ± 0·19	2·48 ± 0·10	87·42 ± 0·29	2·44 ± 0·11	87·08	2·64
0·05	86·84 ± 0·13	3·01 ± 0·11	86·65 ± 0·16	3·10 ± 0·12	86·42	3·31
0·06	86·37 ± 0·31	3·65 ± 0·23	85·73 ± 0·33	3·88 ± 0·16	85·75	3·98
0·07	(–)*	(–)*	85·42 ± 0·23	4·24 ± 0·22	85·08	4·66

*Single b phase could not be observed.

Table 3. Effect of doping ratio of Eu_2O_3 on grain size.

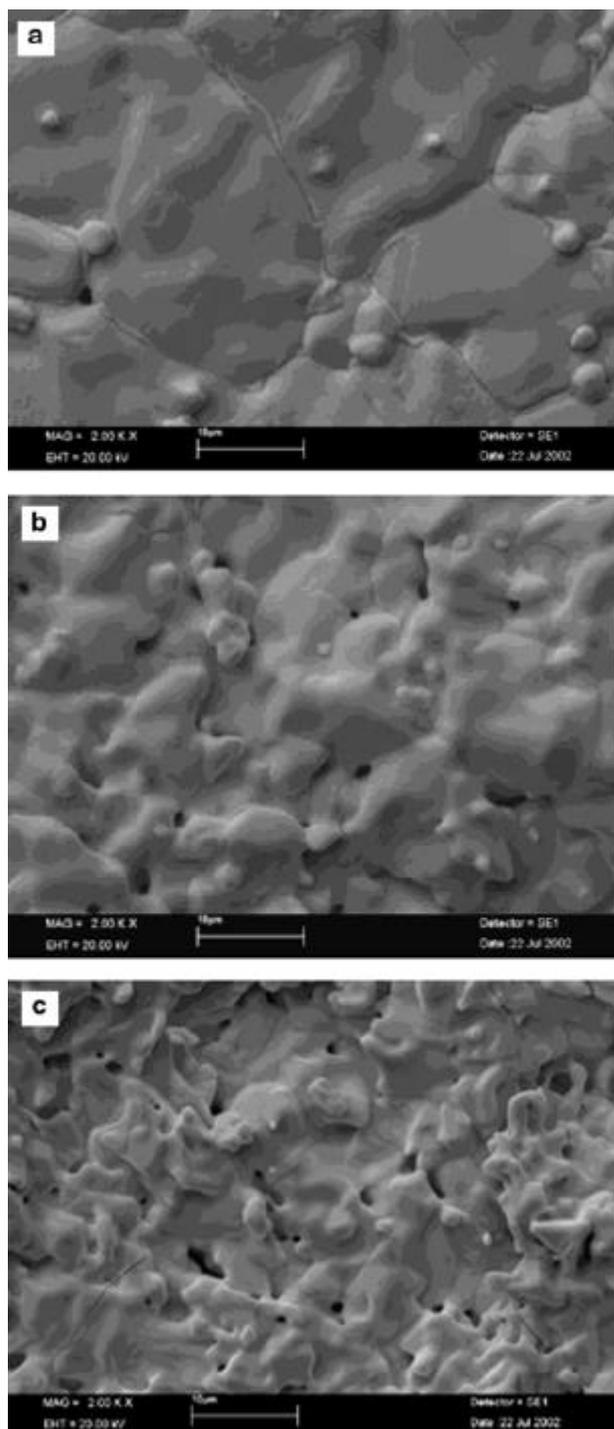|	Grain size for the planes (nm)							
	After heating at 750°C				After heating at 800°C			
x	(201)	(002)	(203)	(421)	(201)	(002)	(203)	(421)
0·02	(–)*	(–)*	(–)*	(–)*	208·6	178·3	157·8	169·6
0·03	242·0	187·3	228·4	192·0	204·4	170·3	148·1	137·4
0·04	226·2	174·0	215·8	181·5	200·6	153·9	122·4	135·5
0·05	213·1	161·2	146·8	151·2	197·0	141·9	111·4	113·8
0.06	193·8	148·8	113·1	135·2	188·7	134·3	88·8	88·3
0.07	(–)*	(–)*	(–)*	(–)*	179·2	99·1	64·1	80·7

*Single b phase could not be observed.

Figure 3. **a**, **b** and **c** show the outer free surface of the annealed samples (750°C) at the same magnification for 1, 3 and 5% Eu addition ratios, respectively.

Figure 4. Fracture surfaces of the samples with 4% Eu addition (**a**) and 6% Eu addition (**b**).

in this figure. This 6% Eu_2O_3 addition ratio is the limit for the formation of **b** phase for this annealing temperature. Very good grain connectivity is seen in the micrograph of the fracture surface of the 4% Eu_2O_3 added sample. Microvoids mentioned earlier are also seen in SEM pictures of the fracture surface of both samples.
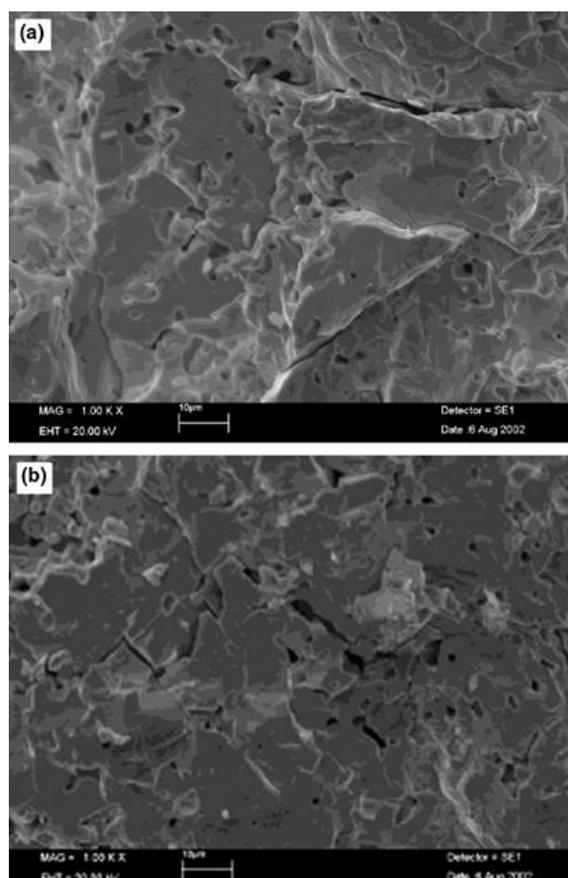
4. Conclusions

Metastable **b** phase of Bi_2O_3 polymorph and related solid solution have been obtained through solid state reaction techniques at room temperature stable phases by doping pure monoclinic **a**-Bi_2O_3 material with Eu_2O_3. Heat treatment temperature, annealing duration and amount of Eu_2O_3 are effective factors in synthesis of this polymorph. Eu^{2+} cations substituted Bi^{3+} cations in the crystal structure of **b** phase. We concluded that the synthesized phase was non-stoichiometric for oxygen content. Higher doping rates introduce more defects into the structures and tetragonality is enhanced. The most predominant defects may be oxygen vacancies which increase with increasing amount of Eu_2O_3. We presume that oxygen non-stoichiometry of this material may lead to an interesting electrical conductivity behaviour.

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