Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 37 (2011) 3451–3455

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of Y_2O_3 and Er_2O_3 co-dopants on phase stabilization of bismuth oxide

Sepideh Arasteh [a], Amir Maghsoudipour [b,*], Masoud Alizadeh [b], Ali Nemati [c]

[a] *Department of Material Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran*
[b] *Materials and Energy Research Center, P. Box 14155-4777, Karaj, Iran*
[c] *Sharif University of Technology, Tehran 11365-9466, Iran*

Received 17 December 2010; received in revised form 17 March 2011; accepted 27 April 2011
Available online 12 June 2011

Abstract

Bi_2O_3 compositions were prepared to investigate the effect of rare earth metal oxides as co-dopants on phase stability of bismuth oxide. Compositions containing 9–14 mol% of Y_2O_3 and Er_2O_3 were synthesized by solid state reaction. The structural characterization was carried out using X-ray powder diffraction. The XRD results show that the samples containing 12 and 14 mol% total dopants had cubic structure, whereas the samples with lower dopant concentrations were tetragonal. Comparing the lattice parameters of the cubic phases of $(Bi_2O_3)_{0.88}(Y_2O_3)_{0.06}(Er_2O_3)_{0.06}$ and $(Bi_2O_3)_{0.86}(Y_2O_3)_{0.07}(Er_2O_3)_{0.07}$ revealed that lattice parameter decreases by increasing the dopant concentration. The XRD pattern and the powder density results indicated the formation of solid solution in the studied systems. After annealing samples with cubic phase at 600 °C for various periods of time, phase transformation to tetragonal and rhombohedral occurs.

Keywords: Bi_2O_3; Y_2O_3 Stabilization; Solid oxide fuel cell; Er_2O_3

1. Introduction

Solids with high oxide ion conductivity are currently subject of considerable research interests, because of their potential technological application as ceramic electrolytes in Solid Oxide Fuel Cell (SOFC). At present yttria-stabilized zirconia (YSZ) is the most common electrolyte material, which must be operated above 800 °C to gain high ionic conductivity. Number of oxides possess higher ionic conductivity than YSZ providing the possibility of operating SOFC at lower temperatures [1–3].

It is well known that the high temperature phase of Bi_2O_3, δ-Bi_2O_3, is one of the best ionic conductor. The conductivity of δ-Bi_2O_3 is two orders of magnitude higher than that of YSZ at the same temperature. The high temperature δ-Bi_2O_3 phase crystallizes in a fluorite structure having two vacant oxygen sites in oxygen sublattice. The large number of oxygen vacancies and high anion mobility of δ-Bi_2O_3 result in high ionic conductivity [4–6].

However, δ-Bi_2O_3 is stable only at the narrow temperature range of 730 °C to its melting point, 825 °C. Below 730 °C, the α-Bi_2O_3 phase (monoclinic structure) is stable and the electronic conductivity dominates. Instability of δ-Bi_2O_3 restricts its application as a solid electrolyte [1,7].

Several researchers have investigated the possibility of cubic phase stability by adding different metal oxides. It has been reported that the high temperature δ-Bi_2O_3 phase can be stabilized at room temperature by doping rare earth metal oxides [7–11].

During the investigation of Bi_2O_3–Ln_2O_3 systems, it was observed that in cubic solid solution, a time dependent transformation to phases with lower ionic conductivity occurs by annealing at temperatures below 730 °C. [8–11].

In recent years, several studies have been carried out on co-doping systems [4,12–16], indicated stabilization of the cubic phase over wide ranges of temperature [12].

Jiang et al. [13] showed that by combination of metal oxides (Dy_2O_3 and WO_3) they were able to obtain the cubic phase in sample containing lower dopant (11–17 mol%) with higher conductivity comparing to these single dopants.

Hsieh et al. [15] concluded that the formed phase is dependent upon dopant concentration in a Bi_2O_3–WO_3–Y_2O_3

---

* Corresponding author. Tel.: +98 261 6204131; fax: +98 261 6280030.
E-mail address: a_maghsoudipour@yahoo.com (A. Maghsoudipour).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.04.136

system based on the following observations: the as-sintered $(YO_{1.5})_{0.1}(WO_3)_{0.15}(BiO_{1.5})_{0.75}$ exhibited a single cubic at room temperature; samples formulated as $(YO_{1.5})_x(WO_3)_{0.15}(BiO_{1.5})_{0.85-x}$ ($x = 0.2$, 0.3, and 0.4) consisted of a cubic fluorite structure and rhombohedral Y_6WO_{12}. After heat treatment at 600 °C for 200 h, transformation from cubic to rhombohedral was observed in the sample formulated as $(YO_{1.5})_{0.2}(WO_3)_{0.15}$ $(BiO_{1.5})_{0.65}$.

Studies on Bi_2O_3–Er_2O_3–WO_3 system [4] indicated that δ-Bi_2O_3 phase transformed after several repetitive long-term heat treatment at 600 °C.

In the present study, we examined room temperature crystal structure and possibility of stable cubic phase based samples containing Er_2O_3 and Y_2O_3 co-dopants after annealing at 600 °C. Structural investigation was carried using X-ray diffraction (XRD).

2. Experimental procedure

2.1. Sample preparation

All samples were synthesized by solid-state reaction between Bi_2O_3 (Merck, 99.9%), Y_2O_3 (Merck, 99%) and Er_2O_3 (Aldrich, 99%).

The appropriate amounts of Y_2O_3 and Er_2O_3 dopants and Bi_2O_3 were weighed for six different samples as shown in Table 1. In all samples, a Er_2O_3/Y_2O_3 ratio of one was studied, but for the ones with dopant concentration of 10 mol%, the two additional ratios of 0.5 and 2 were also studied.

After ball milling with acetone for 20 min, the powder mixtures dried. Subsequently, the powder was pressed into disks by uniaxial die pressing at 80 Mpa. The green disks were sintered in air at 850 °C for 24 h.

The sintered samples with cubic phase were annealed at 600 °C for several hours (24–120 h) to characterize phase transformation.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of all samples were collected using Siemens D500 diffractometer with Cu-Kα radiation (λ = 1.5418 Å) to determine the phases present in both sintered and annealed samples. Lattice parameter was measured for sintered samples with cubic structure based on the data collected over the 2θ range from 20° to 80°.

Table 1
Mol percentage of the compounds used for six different compositions of Bi_2O_3–Y_2O_3–Er_2O_3 system.

Composition	Bi_2O_3 (mol%)	Y_2O_3 (mol%)	Er_2O_3 (mol%)
4.5Y4.5Er	91	4.5	4 .5
3.3Y6.7Er	90	3.3	6.7
5Y5Er	90	5	5
6.7Y3.3Er	90	6.7	3.3
6Y6Er	88	6	6
7Y7Er	86	7	7

Powder density was measured by a helium gas pycnometer (Micromeritics, Accupyc1330).

3. Results and discussion

Fig. 1 shows XRD pattern of sintered $(Bi_2O_3)_{0.91}(Y_2O_3)_{0.045}$ $(Er_2O_3)_{0.045}$ sample containing 9 mol% total dopants. The pattern corresponds to tetragonal and cubic phases. XRD pattern for the samples of $(Bi_2O_3)_{0.9}(Y_2O_3)_{0.1-x}(Er_2O_3)_x$ ($x = 0.033$, 0.05, 0.067), containing 10 mol% total dopants with different concentrations of Y_2O_3 and Er_2O_3 dopants, is given in Fig. 2. As shown in XRD pattern, broadening of the (2 0 0), (2 2 0) and (3 1 1) reflections and asymmetry of (2 0 0) peak in $(Bi_2O_3)_{0.9}(Y_2O_3)_{0.067}(Er_2O_3)_{0.033}$ is attributed to β-Bi_2O_3-type tetragonal structure. Indeed, in all samples, containing 10 mol% dopants with different Er_2O_3/Y_2O_3 ratios, the tetragonal phase formed.

The XRD patterns in Fig. 3 indicates that $(Bi_2O_3)_{0.88}$ $(Y_2O_3)_{0.06}(Er_2O_3)_{0.06}$ and $(Bi_2O_3)_{0.86}(Y_2O_3)_{0.07}(Er_2O_3)_{0.07}$ samples containing 12 and 14 mol% total dopants respectively exhibit cubic structure, which indicates that the duration and temperature of sintering are suitable for solid solution formation.

Table 2 shows the lattice parameters of samples containing cubic phase. According to Table 2, the lattice parameters of cubic phase in doped samples are lower than that of pure bismuth oxide (5.6595 Å [2]). Since the ionic radius of Er^{3+} and Y^{3+} are smaller than the ionic radius of Bi^{3+}, if the dopant cations are substituted in bismuth oxide lattice, the lattice shrinks and the lattice parameters reduces. From a comparison between the unit cell parameters of the given samples in Table 2, the lattice parameter decreases as the dopant concentration increases, which indicate the solid solution formation. These results agree with the observations from the work done by Ekheilikar et al. on Bi_2O_3–Y_2O_3 [17] systems.

Lattice shrinkage caused by smaller cations decreases the atomic movement and prevents the transformation from cubic phase to monoclinic which end the formation of cubic phase at room temperature.

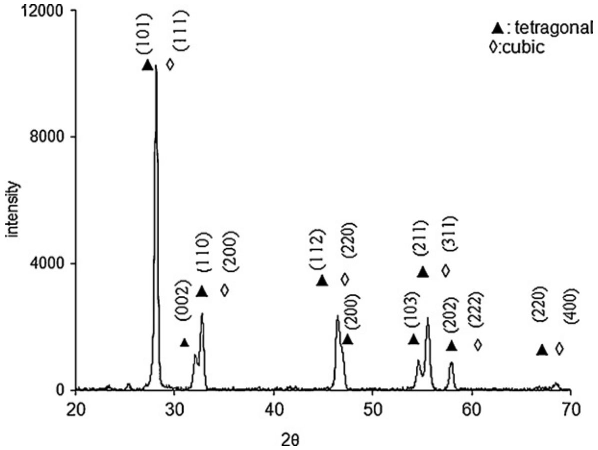

Fig. 1. XRD patterns of cubic and tetragonal phases for the sample containing 9 mol% total dopants.

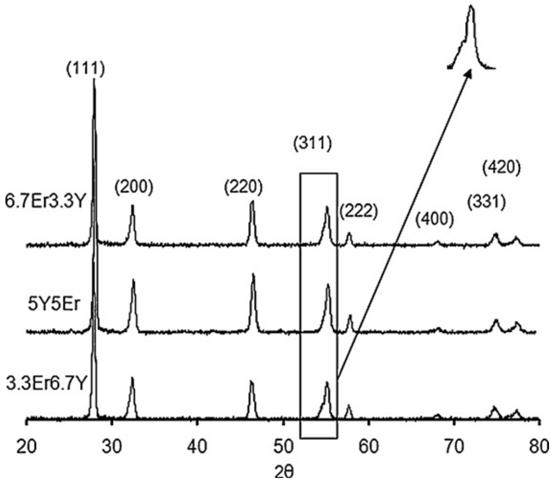

Fig. 2. XRD Pattern of samples containing 10 mol% total dopant content.

Dopant cations can be substituted or placed in interstitial sites of bismuth oxide lattice. The two possible models that can be suggested are:

All cations (Er^{3+}, Y^{3+} and Bi^{3+}) occupy their normal sites in the fluorite structure

$$M_2O_3 \xrightarrow{B_2O_3} 2M_{Bi}^{x} + 3O_{O}^{x} \quad M = Er, Y$$

$$Bi_{4(1-x)}M_{4x}O_6 \tag{1}$$

All Bi^{3+} ions occupy their normal sites in the fluorite structure and Er $^{3+}$ and Y^{3+} ions occupy interstitial sites.

$$M_2O_3 \rightarrow 2M_i^{\bullet\bullet\bullet} + 2V_M^{'''} + 3V_O^{\bullet\bullet} + 3O''_i \quad M = Er, Y$$

$$Bi_4M_{4x/(1-x)}O_{6/(1-x)} \tag{2}$$

In order to calculate the theoretical densities of samples for the characterization of solid solution, the Eqs. (1) and (2) are used for the calculation of mass and the lattice volume obtained from lattice constant.

Table 2
Lattice parameter of Bi_2O_3–Y_2O_3–Er_2O_3 system.

Composition	Lattice parameter (Å)
7Y7Er	5.505
6Y6Er	5.513

Table 3
Theoretical densities of interstitial and substitutional solid solutions of $(Bi_2O_3)_{0.88}(Y_2O_3)_{0.06}(Er_2O_3)_{0.06}$.

Model	Calculated density (g/cm^3)
1	8.853
2	9.962

Comparison between the calculated densities (given in Table 3) and the powder density (8.932 g/cm^3) of 6Y6Er indicates that model 2 is quite improbable and Er^{3+} and Y^{3+} cations substitute in bismuth oxide lattice.

Samples with cubic phase, $(Bi_2O_3)_{0.88}(Y_2O_3)_{0.06}(Er_2O_3)_{0.06}$ and $(Bi_2O_3)_{0.86}(Y_2O_3)_{0.07}(Er_2O_3)_{0.07}$, were annealed at 600 °C to investigate stability of the cubic phase.

As shown in Fig. 4, in the sample $(Bi_2O_3)_{0.88}(Y_2O_3)_{0.06}$(-$Dy_2O_3)_{0.06}$, the cubic phase transformed to tetragonal after 24 h and rhombohedral phase is formed after 120 h. According to research on bismuth oxide doped with rare earth metal oxides [8,11], cubic to rhombohedral phase transformation is diffusional transformation which is thermally activated and depends on time. Consequently, cubic phase transforms to rhombohedral phase after 120 h heat treatment.

XRD pattern of $(Bi_2O_3)_{0.86}(Y_2O_3)_{0.07}(Er_2O_3)_{0.07}$ annealed at 600 °C for 24 and 48 h is given in Fig. 5. The XRD pattern corresponds to cubic and rhombohedral phases after 24 h (Fig. 5a), whereas after 48 h (Fig. 5b) the intensity of rhombohedral peak increased.

The volume fraction of transformed phase for annealed samples was estimated by the intensity peak of rhombohdral

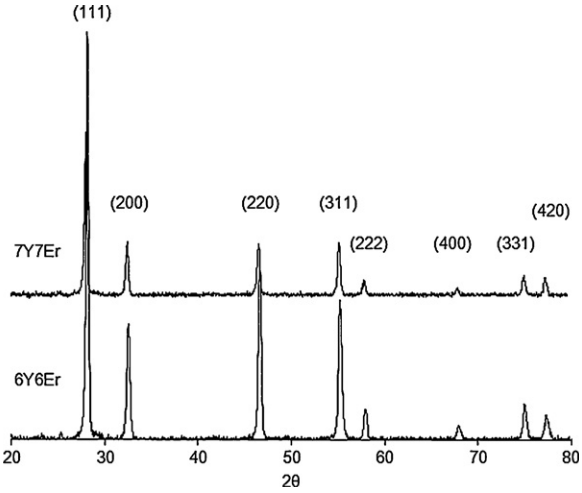

Fig. 3. XRD Pattern of cubic stabilized bismuth oxide with 12 and 14 mol% total dopant content.

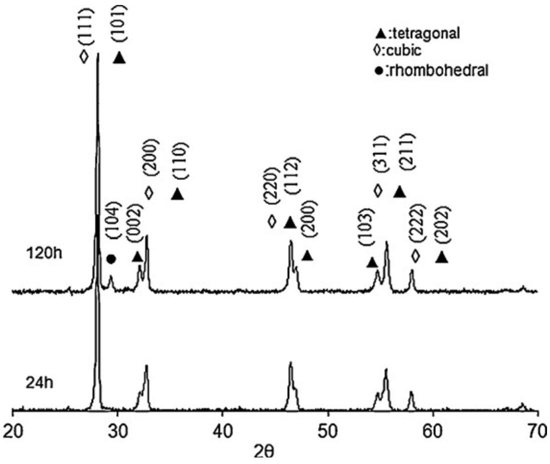

Fig. 4. XRD pattern of $(Bi_2O_3)_{0.88}(Y_2O_3)_{0.06}(Er_2O_3)_{0.06}$ after annealing at 600 °C after 24 h and 120 h.

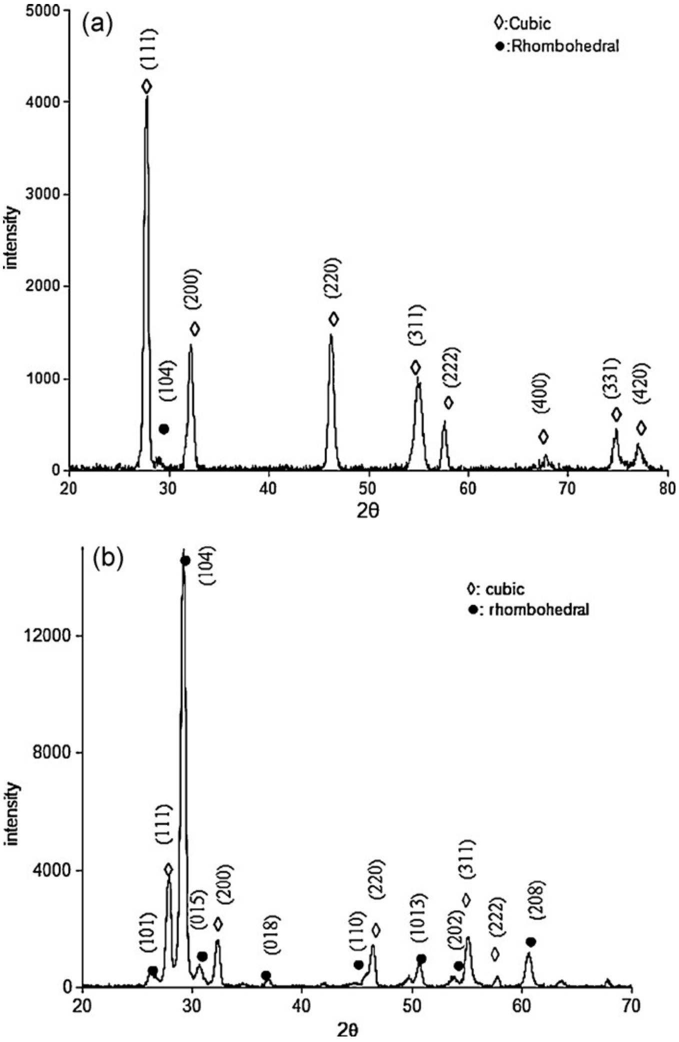

Fig. 5. XRD pattern of $(Bi_2O_3)_{0.86}(Y_2O_3)_{0.07}(Er_2O_3)_{0.07}$ after annealing at 600 °C for a) 24 h and b) 48 h.

phase (I_R) and tetragonal phase (I_t) as follows:

$$V_2 = \frac{I_R}{I_R + I_t}$$

The calculated concentrations of transformed rhombohedral phase at different times (see Table 4) show a progressive transformation indicated by a reduction in cubic phase and an increase in rhombohedral concentration.

According to heat treatment results, the cubic structure is thermodynamically metastable and phase transformation occurs to reduce Gibbs free energy of system.

In doped Bismuth oxides, phase transformation is a diffusional process. Atomic movement and diffusion become difficult due to the lattice shrinkage by smaller dopant cations and need more time to diffuse, consequently cubic phase remains at room temperature metastably. Indeed adding dopants only affect the kinetics of phase transformation. Heat treatment under critical temperature supplies activation energy and facilitates the atomic movement and diffusion therefore transformation occurs.

Table 4
Concentrations of phases after heat treatment in $(Bi_2O_3)_{0.86}(Y_2O_3)_{0.07}$-$(Er_2O_3)_{0.07}$.

Phase	Annealing after 24 h	Annealing after 48 h
Cubic	97	81
Rhombohedral	3	19

4. Conclusion

Based on the investigation in the ternary Bi_2O_3–Y_2O_3–Er_2O_3 system, the δ-Bi_2O_3 phase formed in compositions containing 12 and 14 mol% of Y_2O_3 and Er_2O_3 total co-dopants at room temperature. In samples with lower dopant content including $(Bi_2O_3)_{0.91}(Y_2O_3)_{0.045}(Er_2O_3)_{0.045}$ and $(Bi_2O_3)_{0.9}$ $(Y_2O_3)_{0.1-x}$ $(Er_2O_3)_x$ ($x = 0.033$, 0.05, 0.067) tetragonal phase formed. Calculated lattice parameters of $(Bi_2O_3)_{0.88}$ $(Y_2O_3)_{0.06}(Er_2O_3)_{0.06}$ and $(Bi_2O_3)_{0.86}(Y_2O_3)_{0.07}(Er_2O_3)_{0.07}$ revealed that lattice parameters decreased compared to pure bismuth oxide. Comparing the powder density of $(Bi_2O_3)_{0.88}(Y_2O_3)_{0.06}(Er_2O_3)_{0.06}$ with theoretical densities implies that dopant cations are substituted in bismuth oxide lattice. Substitution of smaller cations Y^{3+} and Er^{3+} shrinks the cubic lattice and causes to formation δ-Bi_2O_3 at room temperature. Investigation on heat treatment at 600 °C on $(Bi_2O_3)_{0.88}(Y_2O_3)_{0.06}(Er_2O_3)_{0.06}$ and $(Bi_2O_3)_{0.86}(Y_2O_3)_{0.07}$ $(Er_2O_3)_{0.07}$ indicates that the room temperature formed δ-Bi_2O_3 phase is metastable and transformed to rhombohedral after heat treatment for periods of time. Indeed, substituting the smaller cations in bismuth oxide lattice inhibits diffusion of ions and it takes longer to diffuse. Heat treatment supplies the activation energy to diffuse and subsequently, phase transformation occurs.

References

[1] Fruth, A. Ianculescu, D. Berger, S. Preda, G. Voicu, E. Tenea, M. Popa, Synthesis, structure and properties of doped Bi_2O_3, Journal of the European Ceramic Society 26 (2006) 3011–3016.

[2] P. Shuk, H.-D. WiemhÖfer, U. Guth, W. GÖpel, M. Greenblatt, Review Oxide ion conducting solid electrolytes based on Bi_2O_3, Solid State Ionics 89 (1996) 179–196.

[3] Stephen Hull, S.T. Norberg, M.G. Tucker, S.G. Eriksson, C.E Mohnc, S. Stølen, Neutron total scattering study of the d and b phases of Bi_2O_3, Dalton Transactions (2009) 8737–8745.

[4] A. Watanabe, M. Sekita, Stabilized δ-Bi_2O_3 phase in the system Bi_2O_3–Er_2O_3–WO_3 and its oxide-ion conduction, Solid State Ionics 176 (2005) 2429–2433.

[5] E.D Wachsman, S. Boyapati, N. Jiang, Effect of dopant polarizability on oxygen sublattice order in phase-stabillized cubic bismuth oxides, Ionics 7 (2001).

[6] S. Boyapati, E.D Wachsman, N. Jiang, Effect of oxygen sublattice ordering on interstitial transport mechanism and conductivity activation energies in phase-stabilized cubic bismuth oxides, Solid State Ionics 140 (2001) 149–160.

[7] K.-Z. Fung, J. Chen, A. Virkar, Effect of Aliovalent Dopants on the kinetics of phase transformation and ordering in RE_2O_3–Bi_2O_3 (RE = Yb, Er, Y or Dy) solid solution, Journal of American ceramic Society 76 (1993) 2403–2418.

[8] A. Virkar, P. Su, K.-Z. Fung, Massive transformation bismuth oxide-based ceramics, Metallurgical and Materials Transactions A 334 (2002) 433–443.

[9] A.M. Azad, S. Larose, S.A. Akbar, Review bismuth oxide- based solid eledtrolyte for fuel cells, Journal of Materials Science 29 (1994) 4135–4151.

[10] M.J. Verkerk, A.J. Burggraaf, High oxygen ion conduction in sintered oxides of the Bi_2O_3 system, Journal of Electrochemical Society 128 (1) (1981).

[11] P. Su, A. Virkar, Massive transformation in Gd_2O_3–Bi_2O_3 ceramic, Journal of American Ceramic Society 79 (1996) 371–380.

[12] G. Meng, C. Chen, X. Han, P. Yang, D. Peng, Conductivity of Bi_2O_3-based oxide conductors with double stabilizers, Solid State Ionics (1988) 533–538.

[13] N. Jiang, E.D. Wachsman, S.-H. Jung, A higher conductivity Bi_2O_3 based electrolyte, Solid State Ionics 150 (2002) 347–353.

[14] M. Omari, M. Drache, P. Confant, J.C. Bovin, Anionic conduction properties of the fluorite type phase in the Bi_2O_3–Y_2O_3–PbO system, Solid State Ionics 40/41 (1990) 929–933.

[15] C.-Y. Hsieh, K.-Z. Fung, Crystal structure and electrical conductivity of cubic fluorite-based $(YO_{1.5})_x(WO_3)_{0.15}(BiO_{1.5})_{0.85-x}$ $(0 \leq x \leq 0.4)$ solid solutions, Journal of Solid State Electrochemistry 13 (2009) 951–957.

[16] K. Huang, M. Feng, J.B. Goodenough, Bi_2O_3–Y_2O_3–CeO_2 solid solution oxide-ion electrolyte, Solid State lonics 89 (1996) 17–24.

[17] S. Ekhelikar, G.K. Bichile, Synthesis and structural characterization of δ-Bi_2O_3 and Bi_2O_3–Er_2O_3–WO_3 solid solutions, Bulletin of Materials and Science 27 (1) (2004).