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Electrical Conductivity and Thermal Expansion of Bi_2O_3 Doped with Pr

Ch. Ftikos[a] & B. C. H. Steele[b]

[a] Laboratory of Inorganic Materials Technology, Department of Chemical Engineering, NTU of Athens,
9 Iroon Polytechniou Str., Zografou Campus, Athens 15773, Greece
[b] Centre of Technical Ceramics, Department of Materials, Imperial College,
Prince Consort Road, London, UK, SW7 2BP

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Abstract

Electrical conductivity and thermal expansion of Bi_2O_3 doped with 15 and 25 mol% prasoeodymia have been studied, named BP15 and BP25 respectively. The crystal phases formed in the sintered oxides and their lattice parameters were determined by X-ray diffraction (XRD). The electrical conductivity was measured in air by means of both impedance spectroscopy and the four-point DC technique within the temperature range 100–850°C. Thermal expansion coefficient measurements were carried out using the dilatometry technique. The results derived show the formation of a single rhombohedral phase in both cases which appears to be stable up to 680°C. The electrical conductivity is thermally activated exceeding 1·0 and 0·7 S/cm at 850°C for the compositions BP15 and BP25 respectively. The thermal expansion coefficient is highly non-linear and varies between 6 and 13 × 10^{-6} K, presenting an increase up to 500°C followed by a decrease above this temperature region.

Die elektrische Leitfähigkeit und die thermische Ausdehnung von Bi_2O_3, dotiert mit 15 und 25 mol% Praseodymoxid (BP15 und BP25), wurden untersucht. Die entstandenen Kristallphasen der gesinterten Oxide und ihre Gitterparameter wurden mit Hilfe der Röntgenbeugung (XRD) ermittelt. Die Bestimmung der elektrischen Leitfähigkeit erfolgte mittels Impedanzspektroskopie und Vierpunktgleichstromtechnik unter Luft in einem Temperaturbereich von 100–850°C. Die thermischen Ausdehnungskoeffizienten wurden dilatometrisch bestimmt. Die Ergebnisse zeigen in beiden Fällen die Bildung einer einzigen rhomboedrischen Phase, die bis zu 680°C stabil ist. Die elektrische Leitfähigkeit ist thermisch aktiviert und ist größer als 1·0 und 0·7 S/cm bei 850°C für BP15 bzw. BP25. Der thermische Ausdehnungskoeffizient ist stark nichtlinear und variiert zwischen 6 und 13 × 10^{-6} K, mit einer Zunahme bis 500°C und einer Abnahme oberhalb dieser Temperatur.

On a étudié la conductivité électrique et l'expansion thermique de Bi_2O_3 dopé avec 15 et 25 mol% de praséodyme, que nous appelerons BP15 et BP25 respectivement. Les phases cristallines présentes dans les oxydes frittés et leurs paramètres de maille ont été déterminés par diffraction X. On a mesuré la conductivité électrique sous air à la fois par spectroscopie d'impédances et mesures en quatre points en courant continu, ceci dans la gamme de temp'ratures 100–850°C. Les coefficients d'expansion thermique ont été déterminés par dilatométrie. Ces résultats montrent qu'il se forme une phase rhomboédrique dans les deux cas, et que cette phase est stable jusqu'à 680°C. La conductivité électrique est thermiquement activée, et dépasse 1·0 et 0·7 S/cm à 850°C pour BP15 et BP25 respectivement. Le coefficient d'expansion thermique n'est pas constant et varie de 6 à 13 × 10^{-6} K, il augmente jusqu'à 500 °C et diminue au-delà de cette température.

1 Introduction

Ceramic mixed oxide conductors have increasingly attracted technological interest due to their many practical applications. So far, these oxides, presenting mixed conductivity at elevated temperatures (800–1000°C) are potential materials for high-temperature fuel cells, oxygen pumps, oxygen sensors, etc.[1–4] For further applications, e.g. transport, lower temperature operation is desirable.

From this point of view, the scientific interest

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has been focused on oxides presenting high ionic/electronic conductivity at intermediate temperatures. Several Bi_2O_3-based fcc compositions are reported to be amongst the best oxide ion conductors known in this temperature range.[5–10] The properties of a variety of Bi_2O_3 solid solutions have been reviewed by Boivin & Thomas[11] and many of these solid electrolytes exhibit higher ionic conductivity values than $Zr_{0.9}Y_{0.1}O_{1.95}$. However, the redox stability of these compounds is very low, so that the oxygen partial pressure range over which the electrolyte exhibits negligible electronic conductivity is relativey small.[12–14] If a high ion conducting phase could be stabilised in the Bi_2O_3-based oxide system by adding some electron conducting oxide, a mixed ionic/electronic conductor might be obtained which could have applications as a cathode material. Pr_6O_{11} is suggested to be a suitable dopant, since it varies its oxygen content and exhibits electronic conduction at high temperatures.[5,6]

As a part of the author's extensive research programme intended to investigate and optimise ceramics presenting mixed ionic/electronic conductivity at intermediate temperatures, the authors have examined the crystal phase formed, electrical conductivity and thermal expansion of Bi_2O_3 solid solutions containing 15 and 25 mol% Pr_6O_{11} respectively.

2 Experimental

The starting materials used were Bi_2O_3 (99·9%) and Pr_6O_{11} (99·9%). Two samples were prepared by adding 15 and 25 mol% Pr_6O_{11}, named BP15 and BP25 respectively. The mixtures were homogenised by dispersing the powders in ethyl alcohol and milling thoroughly for 24 h. After drying, the samples were calcined at 900°C for 12 h. The calcined material was ground and milled, by dispersing it in alcohol for 15 h. After drying, pellets and bars were formed using a uniaxial compaction of 300 MPa. The specimens formed, referred to as BP15, were sintered at 930°C, whilst those referred to as BP25 were sintered at 1000°C. In both cases, the sintering time was 10 h, using a heating and cooling rate of 5°C/min.

The bulk density of all the specimens measured was found to be more than 92% of the theoretical density. XRD analysis was performed by using a computerised Philips IW1710 diffractometcr and $Cu_{K\alpha}$ radiation. The diffractometer was operated at 45 kV and 40 mA. XRD spectra were obtained by scanning continuously at a rate of $1°2\theta$/min. The cell parameters were calculated using a least squares refinement program.

Impedance spectroscopy (IS) was performed by using a Schlumberger SI 1286 impedance analyser controlled by a microcomputer. The AC signal had an amplitude of 100 mV and a frequency which varied from 1 to 10^6 Hz. Both sides of the pellet were covered with platinum (Pt) paste and fired at 850°C, in order to stabilise the Pt electrodes. Measurements were taken at various temperatures, in the range of 100–800°C, during the heating and cooling cycle, after the specimens were left at the specific temperature for 40 min. Electrical conductivity was also measured in bars prepared by means of the four-point DC technique. Thermal expansion measurements were carried out using the dilatometer technique.

3 Results and Discussion

The X-ray diffraction data for the sintered samples are shown in Fig. 1. Both samples contain the single rhombohedral phase, the structure of which corresponds to the β-phase studied by Boivin and coworkers,[11,15,16] in the system Bi_2O_3–SrO. The lattice parameters calculated using a least squares refinement program are given in Table 1. In the same table the composition of the samples is given, where the praseodymium oxide is indicated by $Pr_2O_{11/3}$ instead of Pr_6O_{11} in order to match the cation number of Bi_2O_3. By increasing praseodymium substitution from 15 to 25 mol%, a

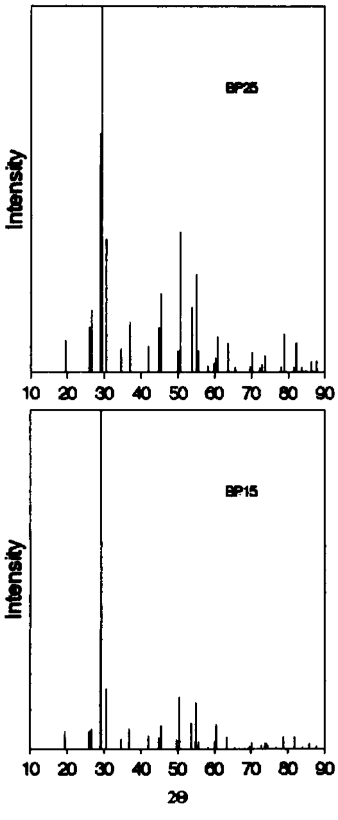

Fig. 1. XRD data of the compositions BP15 and BP25.

Table 1. Composition, crystal class and lattice parameters of the oxides prepared

Code	*Composition*	*Lattice parameter*		*Crystal class*
		a (Å)	*c (Å)*	
BP15	$(Bi_2O_3)_{85}(Pr_2O_{11/3})_{15}$	3·992 (1)	27·529 (5)	Rhombohedral
BP25	$(Bi_2O_3)_{75}(Pr_2O_{11/3})_{25}$	3·997 (1)	27·397 (4)	Rhombohedral

decrease of the *c* dimension of the unit cell is observed, due to stacking of the layered structure along the *c*-axis.[15]

The total electrical conductivity (σ) of the compositions prepared, measured in air, on bars by the four-point DC technique and on pellets by impedance spectroscopy, is presented in Fig. 2 as a function of the reciprocal absolute temperature. Electrical conductivity data for pure Bi_2O_3 reported by Esaka *et al.*[5] are also included in this figure, for a ready comparison between the doped materials and the pure material. Electrical conductivity data obtained during the heating procedure were very close to those taken during cooling of the samples, showing a very good reproducibility of the measurements. On varying the praseodymium content from 15 to 25 mol%, no significant difference is observed on the σ values. The electrical conductivity results obtained by the DC technique are in good agreement with those reported by Esaka *et al.*,[5] Mobius and coworkers[6] and Sammes & Gainford[17] for similar compositions.

When conductivity measurements were carried out by the DC technique, both samples reveal a conductivity jump which starts at about 680°C, while the conductivity data over this temperature region are almost one order of magnitude higher compared with those obtained by the AC technique. The apparent difference of the total conductivity noticed for the different measurement technique might be attributed to changes in the relative magnitudes of the electronic and ionic conductivity. A more detailed explanation must await determination of values of the ionic transference number.

Pure Bi_2O_3 also presents a similar conductivity jump which starts at 730°C, corresponding to the phase transition to the fcc system.[5] Namely, it appears likely that there is a phase transition at 680°C and the rhombohedral phase is stable only below this temperature region.

The conducting mechanism(s) appear to be thermally activated but the log (σ) versus $1/T$ curves are not linear throughout the entire temperature range. However, the apparent activation energies (E_a) calculated for the linear part of the curves, that is up to 680°C, are 81 and 89 kJ/mol for the samples BP15 and BP25 respectively.

Figure 3 presents the temperature dependence of the thermal expansion coefficient (η) for the compositions prepared. The dilatometric curves show that both the compositions have a nonlinear thermal expansion in the temperature range 100–850°C. An increase of the thermal expansion coefficient is observed up to 450 and 500°C for the samples BP25 and BP15 respectively followed by a remarkable decrease up to 850°C. This decrease is most likely to occur due to phase transition from the rhombohedral to the cubic

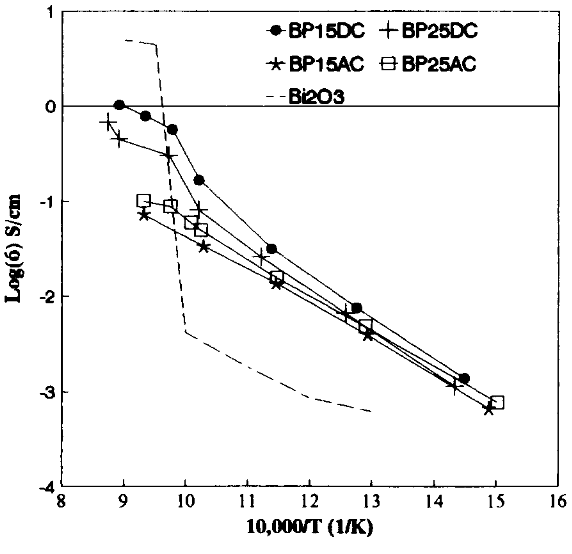

Fig. 2. Electrical conductivity (σ) versus reciprocal absolute temperature for pure Bi_2O_3 and for the compositions prepared.

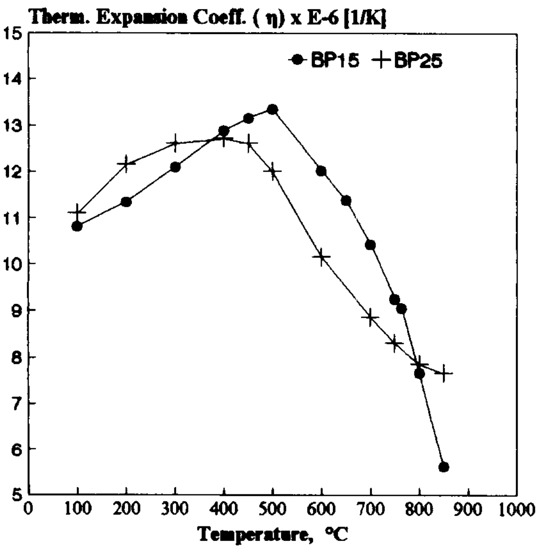

Fig. 3. Thermal expansion coefficient (η) of the oxides prepared versus temperature.

system which is followed by a significant volume decrease.[11]

However, the thermal expansion behaviour observed for the Bi–Pr oxides system examined could compromise their use as cathode materials for solid oxide fuel cells.

4 Conclusion

On doping Bi_2O_3 with 15 and 25 mol% praseodymia a single rhombohedral phase is formed, stable up to 680°C, while electrical conductivity and thermal expansion coefficient are not remarkably affected.

The electrical conductivity is thermally activated and exceeds 1·0 and 0·7 S/cm for the compositions BP15 and BP25 respectively. The thermal expansion coefficient is highly non-linear, presents an increase up to 500°C followed by a decrease above this temperature region and varies from 6 to 13 $\times 10^{-6}$/K.

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