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Novel composition above the limit of Bi:Zr solid solution; synthesis and physical properties of $Bi_{1.33}Zr_{0.67}O_{3+\delta}$

Iratxe de Meatza^a, Jon P. Chapman^a, Fabrice Mauvy^b, José I. Ruiz de Larramendi^a, María I. Arriortua^c, Teófilo Rojo^{a,*}

^aDepartamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain

^bInstitut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS), 33608 Pessac Cedex, France ^cDepartamento de Mineralogía y Petrología, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain

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Abstract

This paper presents an increase to x = 0.67 of the zirconium content in the conductive $Bi_{2-x}Zr_xO_{3+\delta}$ solid solution. Complete incorporation of Zr in the β_{III} -Bi₂O₃ structure, confirmed by X-ray powder diffraction, has produced a phase with a lower volume and superior conductivity than those predicted by an earlier study. The observed β_{III} - δ Bi_{2-x}Zr_xO_{3+ δ} phase transition around 730 °C has been characterised for the first time and shows a segregation of a mixture of predominantly γ -Bi₂O₃ and approximately 30% of the ZrO₂, before total reincorporation of the Zr in the high temperature δ -phase.

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1. Introduction

The high oxide ion conductivity observed in Bi_2O_3 and related systems has led to a considerable number of publications regarding these phases [1,2], mainly due to their potential application in gas sensors and solid oxide fuel cells (SOFC). Among the polymorphs of Bi_2O_3 , the fluorite related, cubic

^{*} Corresponding author. Tel.: +34-946012458; fax: +34-946013500.

E-mail address: qiproapt@lg.ehu.es (T. Rojo).

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 δ -phase shows high oxide ion conductivity (1 Ω⁻¹cm⁻¹ at 800 °C) but limited to a range from 730 to 825 °C (melting point) with the disadvantage of its instability against reduction. This highly conducting phase can be obtained below 730 °C by solid solution formation with other oxides [3,4].

Due to the stability and well known high conductivity of zirconia, several papers have been published regarding the Bi₂O₃–ZrO₂ system [5–9]. The phase diagram by Levin et al. [6] indicated a narrow solid solution range for a high temperature cubic phase, with phase separation at room temperature, indicating a small solubility of ZrO₂ in the various forms of Bi₂O₃. Phase diagrams presented by Hund [7] suggested a solid solution range of x = 0-0.70 ZrO₂ with tetragonal Bi₂O₃ structure but have not, to the authors' knowledge, been confirmed experimentally. Contrarily, Sorokina and Sleight [8] reported that, despite Hund's assertation, at temperatures above 750 °C only ZrO₂ and β -Bi_{1.84}Zr_{0.16}O_{3.08} are stabilised. A recent study of Abrahams et al. [9] on the Bi₂O₃-rich end of the Bi₂-_xZr_xO_{3+x/2} system sets the limit of solid solution at x = 0.17 despite their x = 0.15 simultaneous X-ray and neutron refinement clearly showing a second phase. Here we report the synthesis of a single phase sample of composition above that limit as suggested by Hund. The compound Bi_{1.33}Zr_{0.67}O₃₊₈, prepared after high temperature calcination (800 °C), shows tetragonal β_{III} -structure [9] and higher conductivity than predicted for this large fraction of Zr.

2. Experimental

A sample of nominal composition $Bi_{1.33}Zr_{0.67}O_{3+\delta}$ was prepared by solid state techniques from analytical grade Bi_2O_3 and $ZrO(NO_3)_2$ instead of conventional zirconia. The starting materials were ground with acetone in an agate mortar, pelleted, placed in an alumina crucible and heated in air at 500 °C for 5 h then 800 °C for 60 h with one intermediate grinding. Fast cooling of this sample results in an orange polycrystalline powder. X-ray powder diffraction data, collected using a Philips X'Pert-MPD diffractometer (Bragg-Brentano geometry; Cu K α ; secondary monochromator; range 10–115° 2 θ ; step 0.01° 2 θ ; 15 s per step), were fitted by the Rietveld method using GSAS [10]. A variable temperature Xray study, from 200 to 800 °C for every 5 °C was also carried out using the above mentioned diffractometer with an Anton Paar Physica TCU2000 variable temperature chamber. The experimental density was measured by Archimedes method using a Mettler Toledo AG135 analytical balance with density kit. A sample for impedance measurements was prepared as a circular pellet with thickness, L =0.118 cm and surface area, S = 0.7014 cm², sintered at 800 °C for 2 h and slow cooled (12 °C/h). The pellet density was 95.8% of the theoretical density. AC impedance data were collected using an Eco-Chemie Autolab PGSTAT30 system, in the frequency range 10 mHz to 1 MHz over several temperatures ranging from 300 to 745 °C in air and over one cycle of heating and cooling.

3. Results and discussion

The use of ZrO(NO₃)₂ as reagent, in addition to a fast cooling of the sample, appears to be an important factor in the attainment of a meta-stable single phase sample of Bi_{1.33}Zr_{0.67}O_{3+ δ}. The room temperature X-ray powder diffraction pattern, fitted with a single tetragonal phase (see Fig. 1), is consistent with the *P4₂/nmc* structure of β_{III} -Bi_{1.85}Zr_{0.15}O_{3.075} refined from neutron powder diffraction data by Abrahams et al. [9] yielding refined parameters of *a* = 7.7113(2) Å, *c* = 5.6325(2) Å and *V* = 334.93(2) Å³. Contrary to



Fig. 1. Fitted diffraction profile for $Bi_{1.33}Zr_{0.67}O_{3\pm\delta}$ at 298 K showing observed (crosses), calculated (line) and difference (lower) profiles. Markers indicate reflection positions. Inset: detail of $27.80^{\circ} < 2\theta < 28.30^{\circ}$ showing absence of ZrO₂.

the tendency of their parameters to increase from values of a = 7.7206(8) Å, c = 5.6370(6) Å and V = 336.0(1) Å³ for x = 0.15 with increasing zirconium (and therefore oxygen) content, ours are more comparable to those for their x = 0.11 sample. The fitted profile also confirms the absence of any Zr impurity. In addition, the measured density of 7.90(7) g cm⁻³ is in agreement with a density value of 7.922(4) g cm⁻³ obtained from X-ray diffraction. This result represents a significant increase (x = 0.67) of the Zr content in the Bi_{2-x}Zr_xO_{3+ δ} solid solution, contrary to the published results that limited the solid solution to x = 0.17 [9].

The variable temperature X-ray diffraction is shown in Fig. 2. On raising the temperature of the single phase $Bi_{1.33}Zr_{0.67}O_{3+\delta}$, there are small additional diffraction peaks which are consistent with the $P4_2/nmc$ symmetry but are not seen in the room temperature diffraction pattern. Around 450 °C there appears a minute fraction (<1.9%) of an I4/mmm polymorph of $Bi_2O_{2.3}$ (PDF no. 76-2477). At 550 °C the $P4_2/nmc$ $Bi_{1.33}Zr_{0.67}O_{3+\delta}$ begins to decompose yielding the meta-stable γ -Bi₂O₃ (PDF no. 74-1375). Further decomposition leads to a mixture of ZrO_2 , γ -Bi₂O₃ and a further orthorhombic phase (*o*-Bi₂O_{2.3}, space group *Immm*) related to the above mentioned tetragonal polymorph of $Bi_2O_{2.3}$, with part of the Zr still incorporated in the Bi_2O_3 phases. The phase segregation and solubility limit change with temperature can be described as a chemical reaction:

$$\mathrm{Bi}_{1.33}\mathrm{Zr}_{0.67}\mathrm{O}_{3+\delta} \xrightarrow{650^{\circ}} C0.30\mathrm{Zr}\mathrm{O}_{2} + 0.70\,\gamma - \mathrm{Bi}_{1.64}\mathrm{Zr}_{0.36}\mathrm{O}_{3} + 0.10\,o - (\mathrm{Bi}, \mathrm{Zr})_{2}\mathrm{O}_{2.3}$$

Above 730 °C, a single cubic phase, isostructural with δ -Bi₂O₃ is observed. No additional reflections are observed, indicating complete incorporation of x = 0.67 Zr in this structure. Another measurement after fast cooling the sample to room temperature shows the initial β_{III} single phase, indicating the



Fig. 2. Temperature dependant X-ray diffraction patterns for Bi_{1.33}Zr_{0.67}O_{3+δ}.

reversibility of this transition. The low temperature β_{III} and high temperature δ -structures are both able to accommodate a Zr substitution of x = 0.67 with the intermediate γ -structure unable to incorporate more than x = 0.36.

The impedance spectra in both low and high temperature regions are shown in Fig. 3. For low temperatures the Nyquist plots are characterised by a slightly depressed semi-circle for the high frequency contribution and straight lines at lower frequencies (see Fig. 3a). The high frequency part represents the bulk contribution from the Bi_{1.33}Zr_{0.67}O_{3+ δ} with the straight line being associated with interfacial processes at the platinum blocking electrodes. The bulk contribution was fitted with a simple parallel combination of a resistance, *R*, and a capacitance, *C*. The mean value of the calculated bulk capacitance was 4×10^{-11} F, in good agreement with that usually found for bulk response [11] meaning that the resistance, *R*, of the high frequency curves represents the intra-granular response of the ceramic. The bulk conductivity, σ , is then calculated from the bulk resistance *R* according to the relation, $\sigma = (1/R) \cdot (L/S)$.

At higher temperatures the electrode impedance becomes more significant than the bulk contribution. The high frequency part represents bulk impedance associated with the inductive contribution of the platinum wires used as current collectors. Medium and low frequency contributions can be attributed to the complex electrode processes (charge transfer, oxygen exchange, solid state diffusion, gas-phase diffusion) (see Fig. 3b).

The Arrhenius plot of the conductivity is shown in Fig. 4. There are two regions in the plot, separated by a large increase in conductivity for temperatures above 700 °C corresponding to the δ - and β_{III} -polymorphs of Bi_{1.33}Zr_{0.67}O_{3+ δ} observed in the variable temperature X-ray diffraction. The obtained



Fig. 3. Complex plane plots of $Bi_{1.33}Zr_{0.67}O_{3+\delta}$ at (a) T = 347 and (b) T = 745 °C.

conductivity values were $\sigma_{745} = 0.026 \ \Omega^{-1} \ cm^{-1}$ and $\sigma_{300} = 1.18 \times 10^{-6} \ \Omega^{-1} \ cm^{-1}$ for lower temperatures. The activation energy observed in the low temperature range is 0.91 eV and is almost equal to that of yttrium stabilised zirconia ($\approx 1.0 \ eV$). In the high temperature domain, δ -Bi₂O₃, the activation energy of the conductivity seems to decrease as previously observed by Shuk et al. [1]. As the oxygen partial pressure of the surrounding atmosphere is high, it can be assumed that the conductivity is mainly ionic [1]. The σ_{300} conductivity is comparable with the highest value reported by Abrahams et al. [9] in their entire solid solution and is also far superior to that predicted in his work for higher zirconium contents.



Fig. 4. Arrhenius plot of total conductivity for Bi_{1.33}Zr_{0.67}O_{3+δ}.

4. Conclusions

In conclusion, a single phase sample of composition $Bi_{1.33}Zr_{0.67}O_{3+\delta}$ was synthesised using both reagents and thermal treatments different from those previously used in the literature. The limit of solid solution, x = 0.17 of Zr, previously reported in β_{III} -Bi₂O₃ has been increased. The existence of this elevated level of Zr substitution is also evidenced in the cubic, high temperature δ -Bi₂O₃ structure seen above 720 °C. The intermediate, meta-stable γ -Bi₂O₃ is unable to accommodate more than x = 0.36substitution of Zr, leading to a segregation of phases during the transition. The high conductivity of Bi_{1.33}Zr_{0.67}O_{3+ δ} can be explained by a high density with respect to the theoretical crystallographic density, which is itself higher than predicted by a previous study. This highlights the importance of sample processing conditions when preparing materials for use as components of solid oxide fuel cells.

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