Thermochemical stability and nonstoichiometry of erbia-stabilized bismuth oxide

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A phase study has been performed of high oxygen ion conducting erbia-stabilized bismuth oxide $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$ (BE100x) using thermal analysis and X-ray powder diffraction. Investigation of the effect of a long-time (500 h) anneal of samples at 650°C in air revealed that the minimum amount of erbia needed to stabilize the high-temperature cubic $\delta\text{-Bi}_2\text{O}_3$ phase is 27.5 at%. This boundary value is much larger than the one usually reported in literature where the sluggishness of the transformation from cubic to hexagonal at high Bi contents is not taken into account. Changes in nonstoichiometry of solid solutions $\text{Bi}_{2-2x}\text{Er}_{2x}\text{O}_{3+\delta}$ between 550°C and 850°C upon varying the ambient oxygen partial pressure are minimal for samples with 27.5 at% erbia, increasing with increasing erbia content. The parameter δ in pure oxygen increases from 0.0044 for BE27.5 to 0.022 for BE50 taking the composition in nitrogen ($P_{\text{O}_2} \approx 10^{-4}$ atm) as stoichiometric reference ($\delta=0$).

1. INTRODUCTION

Erbia and yttria stabilized phases of cubic $\delta\text{-Bi}_2\text{O}_3$ are among the best oxygen ion conductors known [1–7].

Phase analysis by Watanabe and Kikuchi [8] showed a fast polymorphic transition from hexagonal (rhombohedral) to the high-temperature cubic fcc structure related to the δ -phase in the system $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Y}_2\text{O}_3$ (BY100x) at about 720°C. Since the reverse transition was found to be very slow the cubic phase is easily obtained by quenching. The homogeneity region of the hexagonal phase as obtained by accurate determination of the structural parameters using X-ray diffraction is relatively narrow and ranges from about $x=0.215$ to $x=0.235$. Above and below this region two-phase regions will appear.

In a previous paper [9] we reported the minimum amount of yttria necessary to stabilize the cubic phase in $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Y}_2\text{O}_3$ even after annealing over long periods ($> 500\text{h}$) at 650°C to be 32 at%, which is much larger than found in literature where the cubic

to hexagonal phase transition is not taken into account [4,6].

The operating temperature of stabilized bismuth oxides as solid electrolyte is between 400°C and 750°C. Structural instabilities may limit the prospects of using them in devices such as fuel cells, sensors etc., of which the life-span should be as long as possible. As measured for yttria-stabilized bismuth oxide the cubic to hexagonal phase transition has a detrimental effect on the ionic conductivity [4,5]. Determination of the minimum amount of dopant oxide to stabilize the cubic phase is of importance, since the ionic conductivity is known to decrease with increasing dopant concentration [2,4].

According to literature the cubic phase in $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$ (BE100x) is stabilized between 17.5 and 45 mol.% erbia [2,10]. However, as described previously [11] the cubic phase gradually transforms into a hexagonal one during annealing of a sample of composition BE25 at 650°C. Therefore we started a phase study on the system $\text{Bi}_2\text{O}_3\text{-Er}_2\text{O}_3$ using combined TG, DTA and X-ray measurements of which the results are presented in this paper.

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2. EXPERIMENTAL PROCEDURES

Solid solutions of bismuth oxide containing 20 - 50 mol% erbia were prepared by the coprecipitation technique described elsewhere [12]. High purity raw materials (99.9%) were used to obtain samples of various compositions. After synthesis and drying the samples were calcined at 760°C to complete the solid solution formation. The effect of calcination on solid solution formation was investigated by applying different calcination times, 3h, 8h and 20 h, respectively. Powders thus obtained were annealed in air at 650°C during 500h.

Structure analysis was performed before as well as after the anneal by X-ray powder diffraction (XRD) using Cu K α radiation. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were both performed on a Du Pont 990 model thermal analyzer.

TGA was performed on powder samples calcined during 8h. A small piece of a sintered dense disk of BE25 was also measured to investigate whether weight changes originate from surface and/or bulk processes. The relative density of the dense ceramic was more than 98% as determined on the basis of the cell parameters from XRD. The surface area was found to be about 10^{-4} times smaller than that of a powder sample with equal weight.

In the TGA experiments the sample was first equilibrated in nitrogen ($pO_2 \approx 10^{-4}$ atm) at 850°C. The atmosphere was then changed from nitrogen to pure oxygen. After reaching constant weight (no weight changes within 1h) the sample was cooled under oxygen to 420°C. This temperature was maintained until no further weight change was observed ($\approx$ 20h). Finally, the atmosphere was changed to nitrogen again and the temperature raised to 850°C. Heating and cooling rates were 10°C/min. Gas flow rates were about 15 ml/min.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

Before annealing at 650°C all samples within the range of composition BE20 - BE35 possess the cubic structure as shown by X-ray analysis and DTA measurements (see below).

After annealing at 650°C during 500h samples containing less than 27.5 at% Er (BE27.5) showed the presence of an additional hexagonal phase. These observations agree with earlier results described elsewhere [11]. From peak intensity changes it is concluded that the amount of hexagonal phase present decreases strongly with increasing erbia content and with increasing calcination time.

The hexagonal phase could not be observed in annealed samples with erbia contents equal to or larger than 27.5 at%. Diffraction lines in powder patterns of samples calcined during 3h at 760°C were generally broadened in comparison to those in powder patterns of samples calcined during 8h or 20h. The anneal treatment of the former samples even led to a further broadening. This may indicate poor homogeneity upon calcination. No broadening of the diffraction lines by the anneal at 650°C was observed for samples calcined during 8h or 20h. Powder patterns of samples with 27.5 at% erbia already showed sharp diffraction lines after 3h calcination.

3.2. Differential thermal analysis

The hexagonal to cubic phase transition is fast and accompanied by a large endothermic heat effect [9,11,13]. For this reason DTA can be applied to trace the presence of the hexagonal phase. Prior to annealing no heat effects were observed during DTA measurements, indicating all samples to have the cubic structure.

After annealing in air at 650°C during 500h samples containing less than 27.5 at% erbia showed two consecutive endothermic heat effects in DTA (Fig. 1). The corresponding temperatures depend on composition as shown in Fig. 2.

The phase transformation from hexagonal to cubic in the system Bi_2O_3 - Y_2O_3 is accompanied by a single endothermic heat effect [9]. The present results indicate that the corresponding phase transformation in Bi_2O_3 - Er_2O_3 proceeds in two steps. It is suggested that ordering processes might play a role.

As shown in Fig. 3 the magnitude of the heat effects decreases with increasing erbia content becoming zero for BE27.5. This implies that the amount of hexagonal phase introduced by the anneal at 650°C decreases with increasing erbia content. A similar behaviour was found for yttria stabilized δ -bismuth oxide [9].

Fig. 1 DTA heating curve of annealed BE20 showing the hexagonal to cubic phase transformation to proceed in two steps.

Fig. 2 Compositional dependence of the transition temperature, T_c , observed in DTA of samples $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$ calcined during 8h and subsequently annealed in air at 650°C during 500h. Lowest and highest transition temperature as shown in Fig. 1 are denoted by symbols (o) and (Δ), respectively.

No heat effects were observed in DTA of annealed samples in the range of BE27.5 - BE35 calcined during 8h or longer. If, however, the calcination time was only 3h a single endothermic heat effect was observed. This is attributed to slow kinetics during calcination. As noted before no heat effect was observed in these samples prior to annealing. The calcination time of 3h probably is too short and may lead to an inhomogeneous product.

Fig. 3 Compositional dependence of heat effects of transitions observed in DTA of samples $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$ calcined during 8h and subsequently annealed in air at 650°C during 500h. Values given are relative to BE20. Lowest and highest transition temperature as shown in Fig. 1 are denoted by symbols (o) and (Δ), respectively.

The combined results of DTA and X-ray analysis of samples calcined during 3 h suggest the growth of hexagonal domains into larger ones during the long-time anneal at 650°C.

3.3. Thermogravimetric analysis

Typical TGA data of powder samples as measured between 420°C and 850°C are shown in Fig. 4. Points (a) through (d) were monitored until the weight remained constant during at least 1h.

At 850°C a rapid oxygen uptake occurs upon changing the ambient gas atmosphere from nitrogen to pure oxygen (a→b in Fig. 4). Cooling results in a further weight increase between 550°C and 420°C (c→d'). The equilibration under oxygen at 420°C (d'→d) is a slow process and takes about 20h. The last mentioned temperature was selected because preliminary experiments showed that the maximum uptake of oxygen occurs at this temperature. Upon changing the gas atmosphere from oxygen to nitrogen again and increasing the temperature a weight loss is observed between 420°C and 550°C. Between 550° and 850°C no further weight losses are observed. At 850°C point (a) is reached again.

These results indicate that erbium stabilized bismuth

Fig. 4 Schematic TGA diagram of a sample $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$ upon heating in nitrogen gas and cooling in pure oxygen as denoted by arrows. For explanation, see text.

oxide reversibly exchanges oxygen with the ambient gas atmosphere. The oxygen exchange is a function of temperature and oxygen partial pressure.

The results of TGA measurements of dense ceramics above 550°C are equal to those of powders. On the contrary the oxygen uptake by the dense ceramics is significantly less than that of powders below 550°C . From these observations it is concluded that weight changes are only due to bulk processes above 550°C , while below this temperature adsorption of oxygen on the surface of the material is partly responsible.

In Fig. 5 the departure from stoichiometry, δ , in pure oxygen is plotted versus the compositional parameter x . This departure is calculated from the weight increase $[W(b)-W(a)]$ according to equation

$$\delta = \frac{M_s}{M_o} \times \frac{[W(b) - W(a)]}{W(a)} \quad (1)$$

where M_s is the mean molar weight of the solid solution and M_o the molar weight of atomic oxygen. The composition, explicitly written as $\text{Bi}_{2-2x}\text{Er}_{2x}\text{O}_{3+\delta}$ in nitrogen is taken as stoichiometric reference ($\delta = 0$). From Fig. 5 it is seen that above composition BE28, δ increases with erbium content to 0.022 for BE50. Note that the composition BE28 at which the anomaly occurs in Fig. 5 is within experimental error equal to BE27.5 below which composition the hexagonal phase is formed during the 500h anneal at 650°C in air (see above).

Fig. 5 Compositional dependence of the departure from stoichiometry, δ , of samples $\text{Bi}_{2-2x}\text{Er}_{2x}\text{O}_{3+\delta}$ in pure oxygen obtained from TGA data above 550°C (a-b in Fig. 4). The composition in nitrogen is taken as stoichiometric reference ($\delta = 0$).

Fig. 6 gives the analogous quantity $M_s/M_o \times [W(d)-W(c)]/W(c)$ which expresses the total relative oxygen uptake between 550°C and 420°C (c-d in Fig. 4) as a function of x in $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$. In both Figs. 5 and 6 the oxygen uptake by the specimen increases with increasing erbium content.

Fig. 6 Compositional dependence of the total relative oxygen uptake between 550°C and 420°C in pure oxygen (c-d in Fig. 4) by samples $\text{Bi}_{2-2x}\text{Er}_{2x}\text{O}_{3+\delta}$ as measured by TGA. For sake of comparison with Fig. 5 the quantity along the vertical axis is expressed as the departure from stoichiometry, δ .

The small but measurable change in non-stoichiometry of $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$ upon varying the oxygen partial pressure indicates the presence of electronic defects. Their presence is due to the equilibration of the lattice with the atmosphere involving valency changes probably of the bismuth ion. Recent oxygen permeation experiments confirm an additional electronic contribution to the conductivity. The oxygen semi-permeability flux of a sintered dense disk of BE25 of thickness 0.7 mm at 810°C is $7.8 \cdot 10^{-5} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ in pure oxygen (versus nitrogen), which is about four orders of magnitude larger than the value observed for yttria-stabilized zirconia extrapolated to the same temperature [14]. A full discussion of these results will be reported elsewhere [15].

The nonstoichiometry of solid solutions $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$ as deduced from Figs. 5 and 6 is influenced by the erbia content though no weight changes were observed during TGA measurements of pure erbia.

3.4. Sample colour

The anneal at 650°C in air led to a noticeable change in colour.

Prior to annealing all specimens were orange. During the anneal the colour shifted to yellow in proportion to the amount of hexagonal phase formed. No colour change was observed for compositions equal to or larger than BE27.5.

Similar colour changes were induced by changing the atmosphere to lower oxygen partial pressures. As an example, a sample of composition BE30 turns out to be orange before and after the anneal in air at 650°C during 500h. Subsequent equilibration under oxygen at 420°C for 20h intensifies the orange colour, while shifting to yellow if equilibration is performed in nitrogen. From this it is concluded that the cubic to hexagonal phase transition leads to a change in nonstoichiometry.

The colour change during the anneal in air of samples with compositions above BE27.5 calcined during 3h was taken as additional evidence of the formation of the hexagonal phase. Such a colour change for instance was not observed if the calcination time was increased to 8h or 20h.

4. CONCLUSIONS

The phase study on the system $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$ on the basis of combined TG, DTA and X-ray measurements has provided the following information.

(a) Cubic solid solutions of $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$ with less than 27.5 at% of erbia are meta-stable below about 740°C, gradually transforming to the hexagonal phase during long-term (500h) annealing at 650°C in air. The amount of hexagonal phase present after the anneal increases in proportion to the deviation from the boundary composition BE27.5. The latter composition therefore corresponds with the minimum amount of stabilizing agent needed to stabilize the cubic phase.

(b) The hexagonal to cubic phase transition apparently proceeds in two steps as established by DTA and is characterized by a change in colour, viz., from orange to yellow. It is inferred that the latter is due to a change in oxide nonstoichiometry since similar colour changes are induced in stabilized cubic phases (above composition BE27.5) by lowering the oxygen partial pressure.

(c) Varying the oxygen partial pressure leads to a small but measurable change in nonstoichiometry of samples $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{Er}_2\text{O}_3$. Above 550°C the oxygen uptake by samples upon changing the atmosphere from nitrogen to pure oxygen is only due to bulk processes. Above composition BE27.5 the oxygen uptake increases with erbia content whereas a minimum is observed at composition BE27.5. Below 550°C adsorption of oxygen on the surface of the material is partly responsible for the weight gain.

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