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Thermal Expansion and Electrical Conductivity of $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$ Solid Electrolytes

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Abstract

The thermal expansion and electrical conductivity of $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$, *where* $x = 0{\cdot}2$, $0{\cdot}3$, $0{\cdot}4$ *and* $0{\cdot}5$, *were studied in the temperature range 100–800°C. Identification of the phases formed was performed by X-ray diffraction at room temperature. The β-type rhombohedral phase was confirmed for the samples with* $x = 0{\cdot}2$, $0{\cdot}3$, *and the LaOF-type rhombohedral phase for* $x = 0{\cdot}5$. *A mixture of the two phases was observed for* $x = 0{\cdot}4$. *A jump in both the thermal expansion and the electrical conductivity curves for* $x = 0{\cdot}2$, $0{\cdot}3$ *and* $0{\cdot}4$, *at around 700°C, indicated the occurrence of a phase transition. The thermal expansion coefficient of the substituted compositions in the low temperature range was in all cases higher than that of pure* Bi_2O_3, *but it decreased linearly with increasing* $Pr_2O_{11/3}$ *content. The LaOF-type structure exhibited higher conductivity and lower activation energy values compared with the β-type structure. The conductivity of the high temperature phase decreased with increasing* $Pr_2O_{11/3}$ *content. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Solid electrolytes based on Bi_2O_3 are characterized by high oxide ion conductivities, which are one to two orders of magnitude higher than those of conventional oxide ion conductors based in stabilized zirconia.[1,2] However, their use is limited because they are reduced under reducing atmosphere at high temperatures.[3] Therefore, they may be considered for use under high oxygen partial pressures.[1]

Pure Bi_2O_3 has two thermodynamically stable polymorphs:[4,5] the α-form, which is stable below 730°C, having a monoclinic structure, and the δ-form, which is stable above 730°C, having a face centered cubic (fcc) structure. The high temperature modification (δ-phase) is the one with the high ionic conductivity. The high conductivity phase can be stabilized down to room temperature, by suitable additives, such as di-, tri-, penta- and hexavalent metal oxides.[1] Most of these systems show fcc or rhombohedral structure.

The addition of Pr_6O_{11} to Bi_2O_3 has been previously investigated by various authors.[6–9] An interesting property of this system, originally reported by Esaka and Iwahara,[6] is the appearance of electronic (hole) conductivity as well as oxide ion conductivity when more than 40 mol% $Pr_2O_{11/3}$ was added. This is possible due to the ability of Pr to be present in both trivalent and tetravalent oxidation states in the system. Mixed conducting oxides display attractive features when used as electrode materials, or as membranes for the electrochemical separation of oxygen from air.[10]

Although the structural and electrical properties of the oxides in the system Bi_2O_3–Pr_6O_{11} have been previously examined, there is little published information concerning their thermal expansion behavior. The knowledge of the thermal expansion coefficient of these oxides is necessary before they are considered for practical application. Moreover, the electrical conductivity data published so far are not always consistent among the various examinations. The purpose of this investigation was to study the thermal expansion behavior and electrical conductivity of the oxides in the system $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$, where $x = 0{\cdot}2$, $0{\cdot}3$, $0{\cdot}4$, $0{\cdot}5$. Identification of the phases formed was also performed at room temperature.

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2 Experimental

The powders in the $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$ system were prepared by the coprecipitation method.[11] The required amounts of Bi_2O_3 and Pr_6O_{11} (Aldrich, 99·9% pure) were separately dissolved in concentrated HNO_3, and the solutions were mixed. The final nitrate solution and a 4 M NH_3 solution were added simultaneously, with constant stirring, to a buffer of 0·1 M NH_3 solution at 45–50°C and pH = 8–9. As a result, bismuth and praseodymium were coprecipitated as hydroxides. The precipitate was washed five times with water and dried at 100°C. The powders were calcined at 900–1000°C for 24 h, and wet milled with acetone for 24 h using zirconia balls as the grinding media. The oxides were compacted in the shape of cylindrical rods (approximate dimensions: 0·4 cm diameter and 4 cm length) by cold isostatic pressing at 300 MPa. The samples were then sintered in air at temperatures ranging from 1000 to 1150°C (the temperature was increased with increasing $Pr_2O_{11/3}$ content) for 15 h, and with a heating and cooling rate of 1°C min^{-1}.

The structure of the synthesized oxides at room temperature was examined by powder X-ray diffraction (XRD) on a SIEMENS D5000 diffractometer using CuK_α radiation. The thermal expansion was measured in air on the sintered rods using a quartz dilatometer. The data were collected upon cooling in the temperature range 100–800°C (cooling rate: 5°C min^{-1}). Electrical conductivity measurements were carried out in air by the 4-point DC method. Platinum wire contacts were made, which were painted with silver paint. The sample was then fired at 500°C for 1 h to allow complete adhesion of the electrodes and reduction of the contact resistance. The sample was placed in an horizontal tube furnace, and its electrical conductivity was measured upon heating in the temperature range 100–800°C (heating rate: 5°C min^{-1}).

3 Results and Discussion

3.1 Structure

The XRD patterns of the oxides in the system $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$ are shown in Fig. 1. The compositions with $x = 0{\cdot}2$ and 0·3 show the β-type[12,13] rhombohedral structure, in agreement with previous works.[6–9] For $x = 0{\cdot}5$ another rhombohedral phase is formed, which corresponds to the LaOF-type structure.[14] This phase is a distorted defect fluorite-type structure, and as can be seen from its XRD pattern, it is more symmetrical than the rhombohedral phase that is formed for low x values. The composition containing 40 mol% $Pr_2O_{11/3}$ appears to be composed of a mixture of the two phases.

As can be seen from Fig. 1, the addition of $Pr_2O_{11/3}$ up to the level of 50 mol% was not able to stabilize the fcc phase. This can be attributed to the close ionic radii values of Bi^{3+} (1·17 Å)[15] and Pr^{3+} (1·126 Å).[15] The small difference between the size of these two cations results in a small distortion of

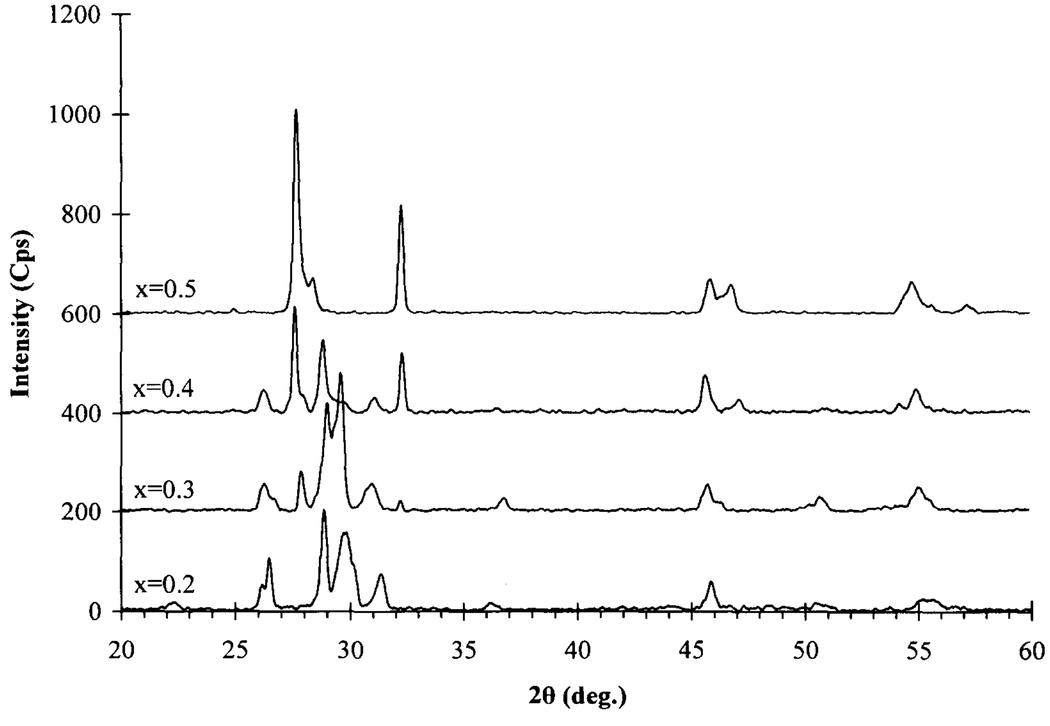

Fig. 1. Room temperature X-ray powder diffraction patterns of $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$.

the host lattice, and a large amount of substituent is required for the stabilization of the fcc phase.[2] It has been reported[6] that samples having more than 80 mol% $Pr_2O_{11/3}$ have the fcc structure.

3.2 Thermal expansion

The linear thermal expansion curves of $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$ oxides are shown in Fig. 2. The curves for the compositions containing 20, 30 and 40 mol% $Pr_2O_{11/3}$ are almost linear, but they exhibit a jump in the temperature range 700–750°C. The magnitude of the jump is reduced with increasing $Pr_2O_{11/3}$ content, and for $x=0{\cdot}5$, no jump can be observed. The length increase in the range 700–750°C is still linear, but the slope of the line is considerably greater. Above 750°C the slope of the thermal expansion curve is reduced, and it is somewhat greater than that corresponding to the low temperature range. The thermal expansion jump may be attributed to a phase transition, as will be confirmed in the next section by electrical conductivity measurements.

The linear thermal expansion coefficients (TEC), calculated from the thermal expansion curves of Fig. 2 by simple linear regression, in the temperature range 100–650°C, are drawn in Fig. 3. The TEC of pure Bi_2O_3 in the same temperature range (corresponding to α-Bi_2O_3), taken from literature,[4,16] is also incorporated in Fig. 3, for reference. As can be seen, the TEC of the $Pr_2O_{11/3}$-substituted Bi_2O_3 is considerably greater than that of pure Bi_2O_3. However, increasing the $Pr_2O_{11/3}$ content results in a linear decrease of the TEC of $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$.

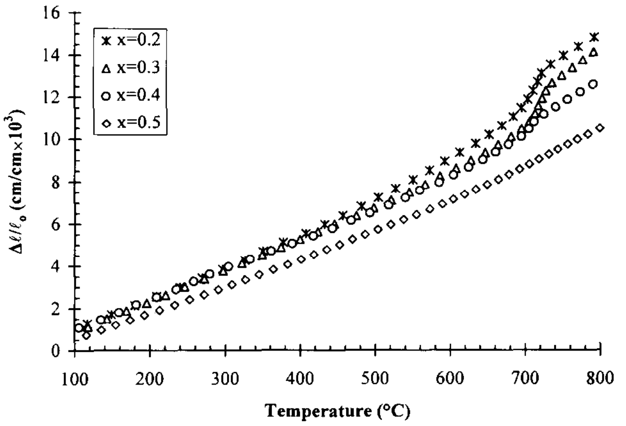

Fig. 2. Linear thermal expansion curves for $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$ in air.

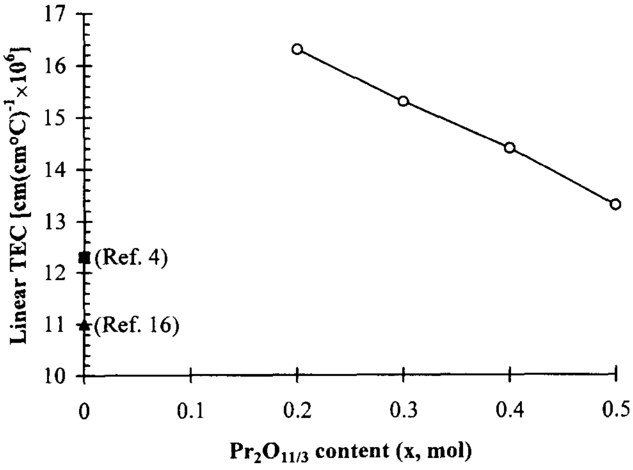

Fig. 3. Linear thermal expansion coefficient (TEC) values of $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$ in the temperature range 100–650°C as a function of $Pr_2O_{11/3}$ content (x, mol) in air.

3.3 Electrical conductivity

The logarithm of electrical conductivity of $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$ versus reciprocal temperature (Arrhenius plot) in air, is shown in Fig. 4 for the temperature range 200–800°C. The electrical conductivity curve of pure Bi_2O_3[17] is also included in the graph, for reference. Pure Bi_2O_3 shows an abrupt conductivity jump at 730°C, where the phase transition from the monoclinic to the fcc modification occurs. Similar, but far less abrupt, conductivity jumps can be observed at 650–700°C for the substituted samples containing 20, 30 and 40 mol% $Pr_2O_{11/3}$. The magnitude of the jump decreases with increasing $Pr_2O_{11/3}$ content, while no jump can be noticed for $x=0{\cdot}5$. This behavior is analogous with that described above for the thermal expansion curves, and it can be ascribed to some configurational change in relative position of atoms within the rhombohedral crystal lattice.[18] It is believed that a phase transition occurs to a more symmetrical rhombohedral structure with superior conductivity. For $x=0{\cdot}5$, the structure is of the LaOF-type at room temperature as described above, and since both the thermal expansion and conductivity curves exhibit no jump, the structure remains unchanged in the whole examined temperature range. It has been stated[1] that the minimum

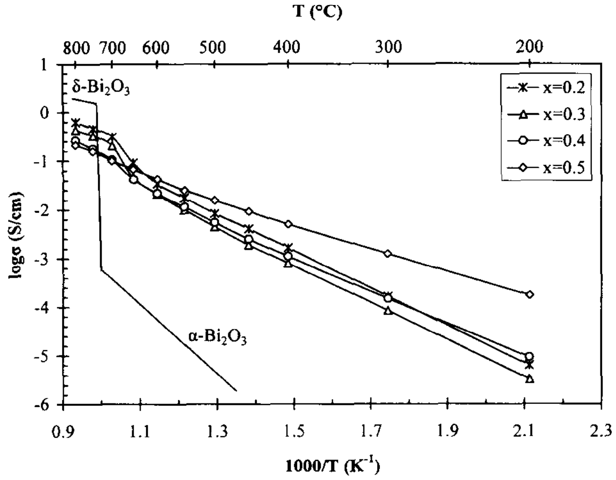

Fig. 4. Logarithm of electrical conductivity versus reciprocal temperature for $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$. The curve for pure Bi_2O_3 is also included.[6]

Table 1. Activation energies (E_a) for the Arrhenius plots of the conductivity of $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$

x (mol)	*Temperature range (°C)*	*E_a*	
		kJ mol⁻¹	*eV*
0·2	200–650	75·2	0·78
0·3	200–650	75·7	0·79
0·4	200–650	67·4	0·70
0·5	200–650	47·6	0·49

content of added oxides that gives no jump in conductivity, corresponds to the lowest content for forming the high conductivity phase in the low temperature region. From the results of this study it is evident that this minimum lies between 40 and 50 mol% $Pr_2O_{11/3}$, which is in agreement with the results of Esaka *et al.*[6]

The conductivity of the high temperature phase decreases with increasing $Pr_2O_{11/3}$ content. This is a general trend, which has also been observed for other trivalent dopant cations.[1,19] This behavior suggests that it is the interaction between the oxide ion vacancies and the doped cations that most probably affects the conductivity lowering.[1] The activation energy of the $Pr_2O_{11/3}$-substituted compositions, above 700°C, is almost concentration independent, and only slightly greater than that of δ-Bi_2O_3. This may indicate that the conduction mechanism in the high temperature phase remains the same, regardless of the level of dopant concentration.

In the low temperature range, the conductivity of the substituted compositions is considerably higher than that of α-Bi_2O_3. Among the two rhombohedral phases, the LaOF-type exhibits higher conductivity values. At 200°C, the conductivity of the sample with 50 mol% $Pr_2O_{11/3}$ is about 1·5–2 orders of magnitude higher than that of the samples with 20 or 30 mol% $Pr_2O_{11/3}$. Moreover, the activation energy of the LaOF-type structure is lower than that of the β-type structure (Table 1). This may indicate a higher degree of disorder in the former, more symmetrical, rhombohedral phase.

4 Conclusions

The formation of the β-type rhombohedral structure was confirmed for the $(Bi_2O_3)_{1-x}(Pr_2O_{11/3})_x$ samples with $x = 0·2$, 0·3, and that of the LaOF-type for $x = 0·5$. The composition with 40 mol% $Pr_2O_{11/3}$ is composed by a mixture of the two phases. The thermal expansion and electrical conductivity curves for $x = 0·2$, 0·3 and 0·4 showed a jump at around 700°C, which was attributed to a phase transition. The magnitude of the jump decreases with increasing $Pr_2O_{11/3}$ content, while no jump was observed for $x = 0·5$. The thermal expansion coefficient (TEC) in the low temperature range decreases linearly with increasing $Pr_2O_{11/3}$ content in the range $x = 0·2$–$0·5$. However, the TEC of all examined substituted compositions is greater than that of pure Bi_2O_3.

The conductivity of the high temperature phase decreases with increasing $Pr_2O_{11/3}$ content, while its activation energy is almost concentration independent. In the low temperature range the conductivity of the $Pr_2O_{11/3}$ containing compositions is higher than that of pure Bi_2O_3. The LaOF-type structure exhibits higher conductivity and lower activation energy values than the β-type rhombohedral structure in the low temperature region.

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