

PROPERTIES OF IONIC CONDUCTING β -Bi₂O₃ CONTAINING MIXED DOPANTS

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ABSTRACT

β -Bi₂O₃ compositions were prepared to evaluate the effect on properties of using mixed dopants. Baseline compositions containing 28 mol% of the alkaline earth oxides CaO, SrO, or BaO were used for comparison. When the alkaline earths were combined in pairs to dope the bismuth oxide, the resulting properties were intermediate between the baseline end members. Utilization of additional additives having different ionic size or valence charge compared to the alkaline earths resulted in no observed property changes that could be attributed to the additive alone. The most important variables influencing the conductivity level and phase transformation temperature of β -Bi₂O₃ were the type and amount of the alkaline earth dopant in the composition.

INTRODUCTION

Doped β -Bi₂O₃ exhibits oxygen ion conductivity that is much higher than yttria-stabilized ZrO₂ at lower operating temperatures.¹ The conductivity increases by nearly ten-fold due to a subtle phase change in the temperature range of 565°C to 745°C, depending upon the dopant used to form the β phase and the amount of dopant in the composition.¹⁻³ At the transformation temperature, the low-temperature β_2 phase transforms to the high-temperature β_1 phase. The β phase of Bi₂O₃ is formed by partial substitution for the bismuth atoms by divalent alkaline earth ions such as calcium, strontium, and barium. The general chemical formula for β -Bi₂O₃ is Bi_(1-x)M_xO_{(3-x)/2} where M = Ca, Sr, or Ba. The divalent cation substitutions change the structure and properties of Bi₂O₃ through the creation of oxygen-site defects and lattice distortions due to charge and ionic size effects. For such substitutions, it has been shown that the resulting single phase, randomly oriented ceramic is a very good ionic conductor with conductivities that are higher than well-known electrolytes such as zirconia at temperatures below

565°C. Above the phase transformation temperature, the ionic conductivity is increased by an order of magnitude. In the binary oxide systems, the transformation temperature depends both on the amount and type of solute ion.^{3,4} In the present study, mixed dopants were added to evaluate the effect on conductivity level and transformation temperature.

EXPERIMENTAL

Baseline compositions containing a single alkaline earth oxide dopant were prepared. The phase diagrams for the binary systems Bi₂O₃ – CaO, Bi₂O₃ – SrO, and Bi₂O₃ – BaO were examined to identify a single dopant level which would form β-Bi₂O₃ in all three systems.^{3,4} The range of β-Bi₂O₃ solid solution in these systems is shown in Table I.

Table I. The range of beta-phase solid solution for alkaline earth doped bismuth oxide.

Alkaline Earth Dopant	Solid Solution Range ³		
	x*	mol. %	wt. %
CaO	0.120-0.183	21.5-31	3.2-5.1
SrO	0.093-0.274	17-43	4.4-14.4
BaO	0.146-0.170	25.5-29	10.1-11.0

*General Formula: Bi_(1-x)M_xO_{(3-x)/2} (M = Ca, Sr, or Ba)

A dopant level of 28 mol% was chosen for this study. Mixed dopant compositions were also prepared. The alkaline earth oxides were combined in pairs and added in equal molar amounts, again with a total of 28 mol% dopant. Additional compositions were prepared in which the ionic size of the additive was smaller (Mg) or where the size was similar to the alkaline earths but the valence charge was greater (La). Also, compositions containing a lower mol% alkaline earth were made for comparison. The compositions that were prepared and the starting raw materials are shown in Table II. The starting powders were milled in a small attritor using 3-mm yttria-stabilized zirconia milling media and isopropyl alcohol as the solvent. After milling, the slurry was poured through a sieve into a glass tray and dried under low heat to evaporate the alcohol. The dried cake was crushed into loose powder using a mortar and pestle. The powder was then placed in a crucible and heated to 625°C for 12 hr. to decompose the carbonate and hydroxide raw materials and to react the constituents to form the desired compounds. The calcined material was again crushed to form a loose powder. Samples were fabricated by uniaxially pressing the calcined powder into disks and bars. The pressed shapes were then sintered at 700°C for 48 hr. to fully react the constituents and to densify the samples.

Table II. Compositions of the samples evaluated in this study.

Composition Mole %	Raw Material Addition, Wt. %					
	Bi ₂ O ₃	CaCO ₃	SrCO ₃	BaCO ₃	La(OH) ₃	MgCO ₃
Bi ₂ O ₃ 28CaO	92.29	7.71				
Bi ₂ O ₃ 28SrO	89.03		10.97			
Bi ₂ O ₃ 28BaO	85.86			14.14		
Bi ₂ O ₃ 14CaO 14SrO	90.66	3.86	5.49			
Bi ₂ O ₃ 14CaO 14BaO	89.08	3.86		7.07		
Bi ₂ O ₃ 14SrO 14BaO	87.45		5.49	7.07		
Bi ₂ O ₃ 25.6CaO 1.4La ₂ O ₃	91.66	6.91			1.43	
Bi ₂ O ₃ 25.6SrO 1.4La ₂ O ₃	88.74		9.87		1.39	
Bi ₂ O ₃ 23.2SrO 2.8La ₂ O ₃	88.46		8.78		2.76	
Bi ₂ O ₃ 21CaO 7MgO	92.57	5.80				1.63
Bi ₂ O ₃ 21SrO 7MgO	90.09		8.33			1.58
Bi ₂ O ₃ 22CaO	94.29	5.71				
Bi ₂ O ₃ 18SrO	93.50		6.50			

Powder and sintered samples were examined by x-ray diffraction analysis (XRD) to determine the phases present. Both room temperature and elevated temperature measurements were made using Cu K α radiation. Selected samples were cycled through the phase transformation temperature to examine the reversibility of the phase change in air.

Differential thermal analysis (DTA) measurements were made on a small fragment of sintered ceramic. Data were recorded while the samples were heated from room temperature to 800°C at a rate of 5°C/min. Data were also recorded on cooling from the peak temperature, again at a rate of 5°C/min.

The DC conductivity was measured in both 4-point and 2-point mode using a Hewlett Packard 4194A Impedance Analyzer. Small bars, which measured approximately 38mm long by 4mm by 3mm, were used for the conductivity measurements. The conductivity of the samples was measured over a temperature range from ambient to 700-900°C, depending upon the composition.

RESULTS AND DISCUSSION

All of the compositions formed the single-phase compound β -Bi₂O₃ after calcining and sintering. The lattice parameters of the compounds varied with dopant addition due to the differences in the ionic radii. XRD data taken at high temperatures showed an abrupt change in the lattice dimensions that is associated with the β_2 - β_1 phase transformation. This transformation was also observed in the DTA measurements, which showed hysteresis in the transformation temperature. A sample of the DTA characterization is shown in Fig. 1. The β_1 -to- β_2 phase transformation (cooling) always occurred at a lower temperature than the β_2 -to- β_1

transformation (heating). The phase transformation temperatures varied with sample composition and are tabulated in Table III.

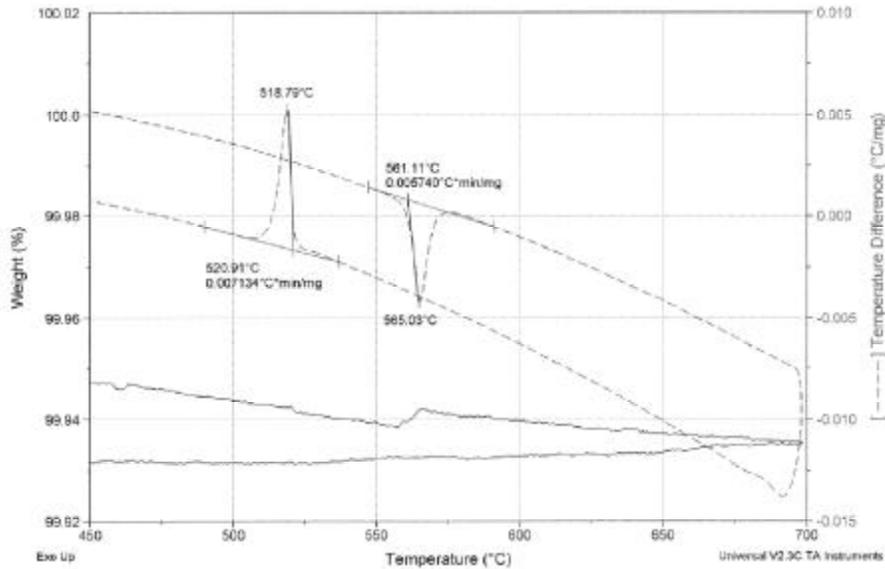


Fig. 1 DTA/TGA results for Bi_2O_3 -28 mol% BaO showing the reversible b2-b1 phase transformation. The endothermic transformation on heating (upper curve) occurs at a higher temperature than the exothermic transformation on cooling (second curve).

Table III. Transformation temperatures determined by differential thermal analysis (DTA).

Composition Mol%	Transformation Temperature, °C		Temperature Difference, °C
	Heating	Cooling	
28 CaO	750.8	725.3	25.5
28 SrO	708.0	674.2	33.8
28 BaO	565.0	518.8	46.2
14 CaO / 14 SrO	730.8	707.8	23.0
14 CaO / 14 BaO	655.2	624.4	30.8
14 SrO / 14 BaO	637.8	600.0	37.8
25.6 CaO / 1.4 La_2O_3	771.4	751.6	19.8
25.6 SrO / 1.4 La_2O_3	729.7	695.8	33.9
23.2 SrO / 2.8 La_2O_3	742.0	706.0	36.0
21 CaO / 7 MgO	731.8	700.6	31.2
21 SrO / 7 MgO	692.8	662.0	30.8
18 SrO	664.0	625.8	38.2

The conductivity of the baseline samples as a function of temperature is shown in Fig. 2. The conductivity of yttria stabilized zirconia (YSZ) is shown in

the figure for comparison. As seen in the figure, the three β - Bi_2O_3 baseline compositions show an abrupt increase in conductivity at the β_2 - β_1 phase transformation temperature. The conductivity increases by approximately an order of magnitude and is substantially greater than that of YSZ.

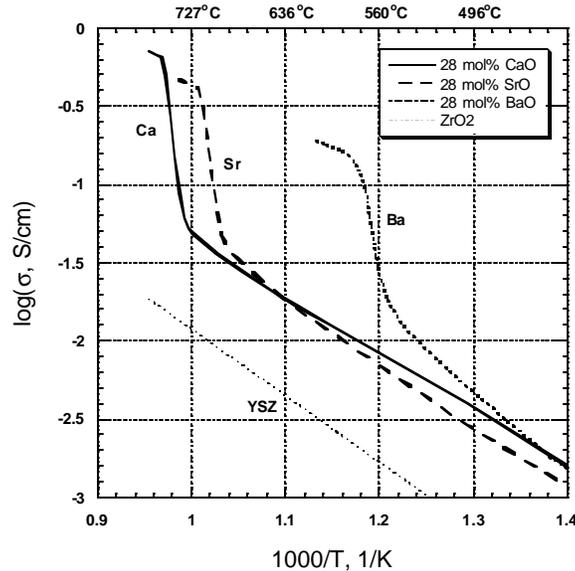


Fig. 2. Conductivity measurements for the baseline samples (28 mol% alkaline earth dopant). The step increase in conductivity occurs at the β_2 - β_1 phase transformation temperature. The plot for yttria stabilized zirconia (YSZ) is shown for comparison.

The conductivity of the mixed alkaline earth compositions is shown in Fig. 3. The shape of the curves is similar to the baseline compositions. Comparison of Fig. 2 and Fig. 3 reveals that for the mixed pair compositions both the phase transformation temperature and the peak conductivity are intermediate between the two baseline end members.

The phase transformation temperature and the peak conductivity of the compositions containing La and Mg are shown in Table IV. While most of these compositions exhibit an increase in conductivity over the baseline samples, the increase cannot be attributed to the presence of the additives. Compositions simply having a lower amount of alkaline earth dopant (22 mol% CaO and 18 mol% SrO) also show the higher conductivity values. The reason for the increase in conductivity at lower dopant levels is not yet understood. Tests of these materials are continuing in an effort to clarify the conduction mechanisms.

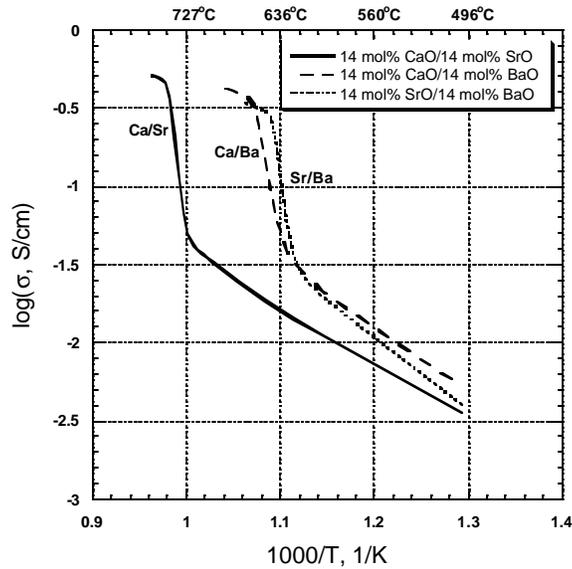


Fig. 3. Conductivity of the mixed alkaline earth compositions showing transformation temperatures and conductivity values that are intermediate between the baseline alkaline earth doped end members.

Table IV. Summary of the effect of additives on the phase transformation temperature and conductivity of b-Bi₂O₃.

Additive and Amount mol%	Temperature for Complete Transformation °C	Conductivity After Complete Transformation S/cm
28 CaO	765	0.673
28 SrO	725	0.429
28 BaO	590	0.164
14 CaO / 14 SrO	760	0.573
14 CaO / 14 BaO	675	0.404
14 SrO / 14 BaO	660	0.330
25.6 CaO / 1.4 La ₂ O ₃	785	0.789
25.6 SrO / 1.4 La ₂ O ₃	765	0.527
23.2 SrO / 2.8 La ₂ O ₃	770	0.598
21 CaO / 7 MgO	750	0.780
21 SrO / 7 MgO	720	0.392
22 CaO	755	0.930
18 SrO	685	0.662

CONCLUSIONS

β - Bi_2O_3 compositions were prepared to evaluate the effect on properties of using mixed dopants. Baseline compositions containing 28 mol% of the alkaline earth oxides CaO, SrO, or BaO were used for comparison. When the alkaline earths were combined in pairs to dope the bismuth oxide, the resulting properties were intermediate between the baseline end members. Utilization of additional additives having different ionic size or valence charge compared to the alkaline earths resulted in no observed property changes that could be attributed to the additive alone. The most important variables influencing the conductivity level and phase transformation temperature of β - Bi_2O_3 were the type and amount of the alkaline earth dopant in the composition.

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