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Enhanced Oxide Ion Conductivity in Stabilized δ-Bi_2O_3

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Bismuth oxides have important potential for ceramic oxygen generators (e.g., for portable oxygen supplies) because of their potential to exhibit at low temperatures (300−500 °C) both high oxide ion conductivity and electrocatalytic activity for the interconversion of molecular O_2 and O^{2-} ions.[1] Here we report conductivity and structural data on some new materials that are related to cubic δ-Bi_2O_3 but have low-temperature (<400 °C) oxide ion conductivities that are significantly higher than previously reported for δ-Bi_2O_3 phases and comparable to those of BIMEVOX materials. However, in contrast to the two-dimensional properties of BIMEVOX, the new phases are isotropic and thermal expansion effects should be advantageous for applications involving thermal cycling. Our materials are synthesized by doubly doping Bi_2O_3 with rhenium and a rare earth cation. The substitution of rhenium produces two important consequences: the δ-Bi_2O_3 phase can be stabilized using even the largest lanthanides, a phenomenon not previously reported, and some compositions show significantly higher conductivities at low temperatures (<400 °C) than other δ-Bi_2O_3 phases.

δ-Bi_2O_3 exists only above 730 °C, and its oxygen deficient fluorite structure[2] provides exceptionally high oxide ion conductivity: $\sim$1 S cm^{-1} at 750 °C,[3] 2−3 orders of magnitude greater than that of Ca- or Y-stabilized zirconias.[4] The structure can be retained at room temperature by doping with 15−42 mol % isovalent or aliovalent cations.[3−12] Unfortunately, the substitutions reduce the conductivity, especially at low temperatures. Stabilizing δ-Bi_2O_3 with the smaller rare earth cations has been studied widely, and 20% Er substitution provides conductivities at $\sim$530 °C that are comparable to stabilized zirconias at 830 °C.[13,14] However, a structural transformation and decrease in conductivity occur when annealed for prolonged periods at 600 °C.[5,15,16] The basic structure of δ-phases (Figure 1) contains two partially occupied O sites: 8*c* ($^1/_4$,$^1/_4$,$^1/_4$) and 32*f* (*x*,*x*,*x*) with $x \approx 0.3$.[17] Aging has been reported to increase local vacancy order with increased occupancy of the 32*f* sites.[16,18,19]

The observation[20] of reasonably high oxide ion conductivity in a bismuth oxide ($Bi_{14}ReO_{24.5}$) containing discrete ReO_x oxyanions led to the current study in which we have explored the influence of isovalent cation substitutions for Bi in this phase. The materials discussed here were synthesized by reacting stoichiometric amounts of high purity Bi_2O_3, RE_2O_3 (RE = La, Nd, Eu, Er, and Y), and NH_4ReO_4 (Bi/RE/Re cation ratio of 12.5:1.5:1) at 800 °C in air for a total of 36 h with intermediate grinding. X-ray powder diffraction indicated that the δ-phase structure had been stabilized to room temperature for all the rare earth cations, and the unit cell size varied in accordance with the size of the RE cation.[21] Impedance measurements were made on pellets ($\sim$70% of theoretical density; gold contacts and wires) in the range 200−600 °C using Hewlett-Packard 4192A LF and 4800A impedance analyzers.

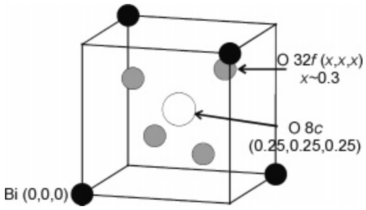

Figure 1. Part of δ-Bi_2O_3 unit cell showing O positions.

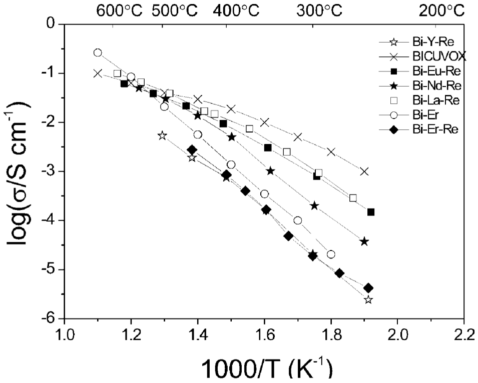

Figure 2. Variation of conductivities with temperature. The legend indicates the metals in the samples for $Bi_{12.5}RE_{1.5}ReO_{24.5}$; Bi−Er corresponds to $(Bi_2O_3)_{0.8}(Er_2O_3)_{0.2}$[22] and BICUVOX is the layered phase $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$.[1]

Low-temperature complex plane impedance plots consisted of a single semicircle and a Warburg-type impedance from electrode kinetic effects. The data were modeled on a single parallel resistor-capacitor (RC) element in series with a Warburg element. The conductivities were calculated from the overall resistance determined from the minima in the complex plane plots. Conductivity data (Figure 2) reveal that the low-temperature activation energies (E_{act}) for samples containing the larger lanthanides are lower than those for conventionally stabilized phases (e.g., 0.81 eV for $Bi_{12.5}La_{1.5}ReO_{24.5}$, 1.17 eV for $Bi_{1.6}Er_{0.4}O_3$) and provide exceptionally high conductivities at low temperatures. O^{2-} transport numbers were calculated for the Nd- and Y-containing samples (0.96(4) and 0.95(5), respectively) from voltages across O_2 | air concentration cells at 400 °C and confirmed predominantly ionic conductivity in non-reducing atmospheres. The phases appear to be the best low-temperature isotropic oxide ion conductors known, e.g., at 300 °C the conductivity of $Bi_{12.5}La_{1.5}ReO_{24.5}$ is *ca.* an order of magnitude higher than for phases stabilized by joint Dy/W substitutions, which were previously reported to exhibit the highest conductivities.[23] The conductivities of these nonoptimized phases approach that of the best low-temperature conductor, the 2-dimensional BICUVOX ($Bi_2V_{0.9}Cu_{0.1}O_{5.35}$), Figure 2.

Structural investigations were based on neutron powder diffraction data from samples containing La, Nd, Er, and Y (collected at Studsvik, Sweden; 10 K; wavelength 1.4703 Å). Rietveld refinements were performed using the program GSAS[24] with a starting

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Table 1. Refined Structural Data for $Bi_{12.5}Nd_{1.5}ReO_{24.5}$ (10 K)

atom	position	x	$U_{iso} \times 100$ /Å^2	fractional occupancy
Bi/Nd/Re	$4a$ (0,0,0)	–	4.01(7)	0.833/0.1/0.067
O1	$8c$($^1/_4$,$^1/_4$,$^1/_4$)	–	10.7(3)	0.615(10)
O2	$32f$(x,x,x)	0.379(3)	10.7(3)	0.047(2)
	$\chi^2 = 1.58$, $R_{wp} = 5.26\%$; $a = 5.6000(7)$; O occupancies imply $Bi_{12.5}Nd_{1.5}ReO_{24.1(5)}$.			

Table 2. Summary of Structural and Conductivity Data

	Bi–La–Re	Bi–Nd–Re	Bi–Er–Re	Bi–Y–Re
σ (S cm^{-1}; 300 °C)	1.10×10^{-3}	2.04×10^{-4}	1.95×10^{-5}	1.95×10^{-5}
E_{act} (eV; 250−400 °C)	0.81	0.94	1.08	1.08
Unit cell size (Å; 25 °C)	5.6456(3)	5.6184(4)	5.5689(5)	5.575(1)
$32f$ x	0.356(4)	0.379(3)	0.367(3)	0.367(3)
$32f$ occupancy	0.064(4)	0.047(2)	0.049(3)	0.051(3)

model based on pure δ-Bi_2O_3,[17,25] space group $Fm\bar{3}m$, with the cations statistically distributed on the $4a$ (0,0,0) site and the oxygen atoms occupying the regular $8c$ and interstitial $32f$ (x,x,x) site. The fitted profile for $Bi_{12.5}Nd_{1.5}ReO_{24.5}$ (see Supporting Information) is typical and indicates good agreement between observed and calculated profiles; an undulating background reflects the high level of disorder. The refined parameters are shown in Table 1.

Studies by Battle et al.[17] and Boyapati et al.[19] suggested that in doped δ-Bi_2O_3 structures, the cations may shift from the $4a$ site to a $24e$ (x,0,0) site and a small amount of oxygen may occupy a second interstitial site, $48i$, ($^1/_2$,x,x).[17,26−28] No strong evidence for occupancy of these sites was found in the present study, although the high cation temperature factor is consistent with small displacements. For all samples, the sum of the oxygen occupancies agrees well with the overall composition $Bi_{12.5}RE_{1.5}ReO_{24.5}$, consistent with the presence of Re(VII). The high thermal parameters for both cation and anion sites reflect the high level of disorder and the oxygen ions appear to be distributed over a range of similar sites. Notwithstanding the uncertainty relating to the local structure, there appears to be a significant structural difference between the samples studied here and simple RE-stabilized phases. Because all samples showed very similar structures, data for only the Nd-containing material are presented in Table 1, although a summary of structural and conductivity data is given in Table 2. The $32f$ oxygen interstitial sites (x,x,x) with $x \approx 0.37$ are significantly closer to the vacant octahedral site in the center of the unit cell and, in fact, are approximately midway between the $8c$ ($^1/_4$,$^1/_4$,$^1/_4$) site and the ($^1/_2$,$^1/_2$,$^1/_2$) site. The refined values contrast with reported values of: $x = 0.319$ for $(Bi_2O_3)_{0.73}(Y_2O_3)_{0.27}$;[17] $x = 0.309$ for $(Bi_2O_3)_{0.80}$-$(Er_2O_3)_{0.20}$;[18] $x = 0.354$ for Bi_2O_3 at 750 °C;[17] $x = 0.335$ for Bi_2O_3 at 778 °C.[25] Although the $32f$ site is generally thought to be important for the O^{2-} migration, the increased displacements observed here cannot alone explain the conductivity data: the displacement appears similar for all samples studied, yet the conductivities of the Y and Er containing phases are similar to those of samples with no Re substitution. The size of the lanthanide substituent may also be important, and for the first time, the largest of the lanthanides have been incorporated into this structure; indeed, the highest conductivities are observed for the larger ions La, Nd, and Eu.

δ-Bi_2O_3 phases comprising Re and rare earth substitutions have therefore been synthesized, and some show exceptionally high oxide ion conductivities at low temperatures. Structural analysis shows a significant difference between these materials and other δ-Bi_2O_3 phases, although it is not yet clear how important this is in determining the conduction properties. Further studies of the long-term stability of these materials at low temperatures are required, but since the conductivity decay is reported[5] to be reduced for large lanthanide dopants, and the highest conductivity observed by us is for the La containing phase, these materials offer excellent potential for low temperature applications in non-reducing conditions.

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Supporting Information Available: Neutron powder diffraction plot for $Bi_{12.5}Nd_{1.5}ReO_{24.5}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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