Preparation and ionic conductivity of new Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ phase

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1. Introduction

At present the stabilized bismuth sesquioxide is one of the promising materials to be used for ceramic oxygen generators, electrocatalic activity (for the interconversion of molecular O$_2$ and O$^{2-}$ ions) and as an electrolyte in full cells operated at lower temperatures (<1200 K) [1-10]. Pure bismuth sesquioxide has two thermodynamically stable crystallographic polymorphs. One is $\alpha$-Bi$_2$O$_3$, which is stable below 1000 K and has a monoclinic structure, which shows p-type conduction. The other is $\delta$-Bi$_2$O$_3$, which is stable above 1000 K up to its melting temperature of 1100 K and crystallizes in the fluorite (cubic, CaF$_2$) structure. The CaF$_2$-type $\delta$-Bi$_2$O$_3$ contains 25% of the anion sites (one oxygen site per formula) vacant, and as a result exhibits very high O$^{2-}$ ion conductivity. The conductivity is up to two orders of magnitude greater than that in stabilized zirconia. However, the high conductivity phase is stable over narrow range of temperature (1000-1100 K). Further, the volume change associated with the $\delta \rightarrow \alpha$ transition leads to cracking and severe deterioration of the materials. Thus, for application of Bi$_2$O$_3$ as a solid electrolyte in fuel cells, it is imperative that the high-temperature

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cubic phase is stabilized. A large number of studies has shown that the high conductivity δ - phase in Bi₂O₃ could be stabilized at lower temperature by the addition of dopants (by various di-, tri-, tetra-, penta-, or hexavalent cations).

At present ones of the best ionic conductors are materials of type BIMEVOX (ME = Cu, Fe, Cr, etc.) [3]. Their main disadvantages are low mechanical strength and easiness of vanadium reduction when high activity of hydrogen. From this point of view it seems to be appropriate to carry out the directed synthesis of solid electrolytes at lower temperatures with the following characteristics: 1) ionic conductivity close to BIMEVOX; 2) isotropic; 3) low thermal expansion coefficient; 4) without ions, which can oxidize or reduce in the operating regime of the fuel cells. The new compounds of general formula Bi₁₂.₅ReLnO₂₄.₅ (Ln = Y, Eu, Er, La, Nd) were discovered in 2006 by Prof. C. Greaves [1-2]. Their conductivity in the temperature range 600-900 K is practically the same like BIMEVOX but they are isotropic and have a low thermal expansion coefficient. In pioneer works of Prof. C. Greaves the structure and conductivity of compounds with Ln = Y, Eu, Er, La, Nd were investigated.

Here we report the synthesis of a new compound, Bi₁₂.₅Lu₁.₅ReO₂₄.₅, its structure, and conductivity measurements.

2. Experimental section

In literature [1-2] Bi₂O₃, NH₄ReO₄, and R₂O₃ were used to synthesize the compounds of general formula Bi₁₂.₅ReLn₁.₅O₂₄.₅ (Ln = Y, Eu, Nd, La, Er). The temperature, used for synthesis was 1070 K. The temperature was selected because the δ - Bi₂O₃ phase exists in the temperature range of 1000-1100 K.

We used the following compounds to prepare Bi₁₂.₅Lu₁.₅ReO₂₄.₅: Bi₂O₃ (99.999%, ABCR, Karlsruhe), Re₂O₇ (99.99%, Alfa Aesar), Lu₂O₃ (99.999%, ChemPur). Synthesis proceeds according to the reaction:

$$6.25\text{Bi}_2\text{O}_3 + 0.75\text{Lu}_2\text{O}_3 + 0.5\text{Re}_2\text{O}_7 = \text{Bi}_{12.5}\text{Lu}_{1.5}\text{ReO}_{24.5}$$
The samples were prepared as follows. Starting reagents were mixed in an agate mortar and ground for about 70 h with four intermediate reground in a planetary mill (FRITSCH pulverisette, analyseette Laborrette). All operations with Re$_2$O$_7$ were performed in a glove box under pure argon, because Re$_2$O$_7$ reacts with water immediately. Then samples were placed in the furnace (Carbolite) and held at 1070 K in air for 70 h. The same technique was used to prepare high quality samples of other complex oxides [11, 12].

The phase purity of the samples was analyzed with an X-ray diffractometer (STADI-P, Stoe diffractometer, Germany, Cu K$_{\alpha1}$ radiation). Impurities were determined by X-ray Fluorescence Spectrometer (ARL ADVANT’XP). A typical X-ray Spectrum is presented in Fig. 1.

X-ray power diffraction indicated that the sample is single phase and that the $\delta$-phase structure had been stabilized to room temperature.

Structural investigated were based on neutron powder diffraction data (collected at Studsvik, Sweden; 10 K; wavelength 1.4703 Å). A detailed description of structural determination is given in ref. [1-2]. Rietveld refinements were performed using the program GSAS with a starting model based on pure $\delta$-Bi$_2$O$_3$, space group Fm-3m, with the cations statistically distributed on the 4$a$(0,0,0) site and the oxygen atoms occupying the regular 8$c$ and interstitial 32$f$(x,x,x) site. The fitted profile for Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ (see, Fig. 2) 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.

| Atom  | $X$  | $y$  | $Z$  | $U_{i}/U_{e}\times10$ | Fractional occupancy |
|-------|------|------|------|------------------------|---------------------|
| Bi    | 0.0  | 0.0  | 0.0  | 4.54(3)                | 0.8333              |
| Lu    | 0.0  | 0.0  | 0.0  | 4.54(3)                | 0.10                |
| Re    | 0.0  | 0.0  | 0.0  | 4.54(3)                | 0.0667              |
| O(1)  | 0.25 | 0.25 | 0.25 | 11.5(1)                | 0.593(5)            |
| O(2)  | 0.364(1) | 0.364(1) | 0.364(1) | 11.5(1) | 0.060(1) |

Table 1. Refined Structural data for Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$
As mentioned before, the Bi$_{12.5}$ReLn$_{1.5}$O$_{24.5}$ (Ln = Y, Eu, Nd, La, Er) compounds have been reported in literature. In reference [1] the lattice parameters were given as follows: $a = 5.6456(3)$ Å (Bi$_{12.5}$La$_{1.5}$ReO$_{24.5}$), $a = 5.6184(4)$ Å (Bi$_{12.5}$Nd$_{1.5}$ReO$_{24.5}$), $a = 5.5689(5)$ Å (Bi$_{12.5}$Er$_{1.5}$ReO$_{24.5}$), $a = 5.575(1)$ Å (Bi$_{12.5}$Y$_{1.5}$ReO$_{24.5}$). For Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ we determined the lattice parameter $a = 5.5591(2)$ Å. With the ionic radii for the rare-earth elements taken from Shannon [13] ($\text{La}^{3+} = 1.032$ Å, $\text{Nd}^{3+} = 0.983$ Å, $\text{Y}^{3+} = 0.900$ Å, $\text{Er}^{3+} = 0.890$ Å, $\text{Lu}^{3+} = 0.861$ Å) it can be seen that the lattice parameters increased with increasing ionic radius. Fig. 3 shows that this increase is linear.

Impedance measurements were made on pellets (about 70% of theoretical density; gold contacts and wires) in the range 500-900 K using Hewlett-Packard 4192A and 4800A impedance analyzers. The conductivities (see, Fig. 4) were calculated from the overall resistance determined from the minima in the complex plane plots. In the article [1] the data of conductivity for BiCuVO$_{x}$, and Bi$_{12.5}$Ln$_{12.5}$ReO$_{24.5}$ (Ln = Eu, Er, La, Nd, Y) are presented. A comparison of the reported data with the conductivity of our sample shows that the Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ phase appears to be one of the best moderate temperature isotropic ion conductors known. For example, the conductivity of Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ at 800 K is equal to the conductivity of BiCuVO$_{x}$, Bi$_{12.5}$Ln$_{12.5}$ReO$_{24.5}$ (Ln = Eu, Er, La, Nd, Y) phases.

**Conclusions**

As a conclusion it is possible to say that new Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ phase has been synthesized and shown high ion conductivity at the moderate temperatures. Structural analysis shows that space group is Fm3m with lattice parameter $a = 5.5591(2)$ Å. The conductivity was measured in the temperature range of 600-800 K. The conductivity of Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ at 800 K is the same as the conductivity of BiCuVO$_{x}$, Bi$_{12.5}$Ln$_{12.5}$ReO$_{24.5}$ (Ln = Eu, La, Nd) phases. In this connection the Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ phase offers excellent potential for moderate temperature application.
Acknowledges

This work is supported by Karlsruhe Institute of Technology, DFG (grant LO 250/24-1), NATO programme (grant CBR.NR.NRCLG 982559) and Program of Fundamental Investigation of Siberian Branch of the Russian Academy of Sciences.

References

1. R. Punn, A.M. Feteira, D.C. Sinclair, C. Greaves, J. Amer. Chem. Soc., 128 (2006) 15386-15387.
2. R. Punn, I. Gameson, E. Berry, C. Greaves, J. Phys. Chem. Sol., 69 (2008) 2687-2690.
3. A.M. Azad, S. Larose, S.A. Akbar, J. Mater. Science, 29 (1994) 4135-4151.
4. M. Leszczynska, M. Holdynski, F. Krok, I. Abrahams, X. Liu, W. Wrobel, Solid State Ionics, 181 (2010) 796-811.
5. T. Takahashi, H. Iwahara, Y. Nagai, J. Appl. Electrochem., 2 (1972) 97-104.
6. X.P. Wang, G. Corbel, S. Kodjikian, Q.F. Fang, P. Lacorre, J. Solid State Chemistry, 179 (2006) 3338-3346.
7. Y.K. Taninouchi, T. Uda, T. Ichitsubou, Y. Awakura, E. Matsubara, Solid State Ionics, 181 (2010) 719-723.
8. M. Drache, P. Roussel, J.P. Wignacourt, Chem. Rev., 107 (2007) 80-96.
9. T. Takahashi, T. Esaka, H. Iwahara, J. Appl. Electrochem., 7 (1977) 303-308.
10. C.D. Ling, J. Solid State Chem., 148 (1999) 380-405.
11. Th. Zeiske, R. Sonntag, D. Hohlwein, N. H. Andersen, Th. Wolf, Nature 1991, 353, 542–544.
12. N.I. Matskevich, Th. Wolf, M.Yu. Matskevich, T.I. Chupakhina, Eur. J. Inorg. Chem., 2009, 1477-1482.
13. R.D. Shannon. Acta Cryst. A32(1976) 751-767.
Abstract

The substitution of Re into Bi$_2$O$_3$ allows stabilization of the $\delta$- Bi$_2$O$_3$ structure by additional substitution of lutetium ion to give phase of composition Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$. The phase was synthesized for the first time. Structural analysis performed by neutron diffraction showed that space group was Fm3m with lattice parameter $a = 5.5591(2)$ Å. The phase has been found to show high ion conductivity at moderate temperature. The conductivity was measured in the temperature range of 600-800 K. The conductivity of Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ at 800 K is the same as the conductivity of BiCuVO$_x$, Bi$_{12.5}$Ln$_{1.5}$ReO$_{24.5}$ (Ln = Eu, La, Nd) phases. In this connection the Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ phase offers excellent potential for moderate temperature application.

Keywords: A. Bismuth rhenium oxide; C. Neutron diffraction; D. Ion conductivity.
Fig. 1. X-ray diffraction of Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$ at room temperature
Fig. 2. Neutron diffraction data for Bi$_{12.5}$ReLu$_{1.5}$O$_{24.5}$ at 10 K
Fig. 3. Dependence of lattice parameters from ionic radii
Fig. 4. Variation of conductivity with temperature for Bi$_{12.5}$Lu$_{1.5}$ReO$_{24.5}$