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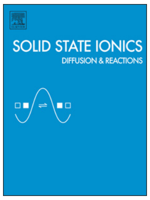

Phase formation and electrical properties of Bi_2O_3-based compounds in the Bi_2O_3-La_2O_3-MoO_3 system☆

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The ternary system Bi_2O_3–La_2O_3–MoO_3 is shown to contain a wide range of $(Bi_2O_3)_x(La_2O_3)_y(MoO_3)_z$ $(x + y + z = 1)$ compounds isostructural with the cubic phase δ-Bi_2O_3, stable at room temperature: $0.65 \le x \le 0.93$. In addition, the ternary system contains two tetragonal phases (β at $x = 0.96$ and β′ in the region $0.50 \le x \le 0.61$, $0.14 \le y \le 0.21$, and $0.22 \le z \le 0.31$) and a rhombohedral phase in a narrow composition range ($0.60 \le x \le 0.64$) on the Bi_2O_3–La_2MoO_6 join. When heated to 1000–1100 °C, the rhombohedral and β′ tetragonal compounds undergo one phase transition, to the cubic phase with the δ-Bi_2O_3 structure. The samples with the β-Bi_2O_3 structure exhibit a more complex polymorphism. The electrical conductivity of the samples increases with Bi_2O_3 concentration. The conductivity of the cubic materials with $x = 0.8$ reaches 0.6 S/cm at 800 °C. The high-temperature (350–800 °C) conductivity of such samples follows the Vogel–Fulcher–Tammann law. At lower temperatures, their conductivity exhibits Arrhenius behavior with an activation energy near 0.8 eV.

1. Introduction

Bi_2O_3-based oxide phases stand out among oxygen ion conductors in that they have high oxygen ion conductivity. These materials can be used in gas sensors, as solid electrolytes in fuel cells, and as gas separation membranes. The polymorphism and special conductive properties of bismuth oxide have been the subject of many reports and reviews [1–4]. The high conductivity of Bi_2O_3 was first mentioned by Takahashi et al. [5].

At room temperature, bismuth oxide has a monoclinic (α) structure (sp. gr. $P2_1/c$). On heating, this phase transforms into a cubic (δ) phase, which exists in a rather narrow temperature range: 730–825 °C. The δ-phase was shown to have space group Fm–$3m$ [6,7]. In its fluorite structure, a quarter of the anion sites are vacant, being responsible for its high conductivity.

On cooling, it transforms into the α-phase, passing through metastable phases: tetragonal (β) and cubic (γ). Replacing bismuth by a rare-earth element (Y, Dy, or Er), Iwahara et al. [8] were able to stabilize the δ-phase. According to Watanabe [9], however, firing at a temperature on the order of 600 °C causes the stabilized phase to decompose. The binary systems Bi_2O_3–Ln_2O_3 with large rare earths (La, Pr, and Nd) contain rhombohedral phases [1]. In addition to the rhombohedral compounds, the Bi_2O_3–Ln_2O_3 systems contain other phases with a cubic, tetragonal, orthorhombic, or monoclinic structure, depending on synthesis conditions [1,2,10].

As shown in a number of studies [11–13], tungsten and molybdenum also stabilize the δ-phase. The Bi_2O_3–MoO_3 binary has been the subject of several studies [14–16]. It was shown to contain many phases. The tetragonal compound $Bi_{14}MoO_{24}$ stands out among them [17].

δ-Bi_2O_3 can be successfully stabilized by so-called codoping, e.g. with tungsten and a rare earth [18–22]. Watanabe and Sekita [18] investigated the ternary system Bi_2O_3–Er_2O_3–WO_3 and showed that codoping prevented the compound from decomposing on heating. The formation and conductive properties of the δ-phase codoped with dysprosium and tungsten have been the subject of several studies [19–21]. The conductivity of such compounds reaches 0.1–1 S/cm at 800 °C.

The effect of molybdenum on the stabilization of δ-Bi_2O_3 in the case of codoping has not yet been studied in sufficient detail. Kharitonova et al. [23,24] investigated the Nd_2MoO_6–Bi_2O_3 and Pr_2MoO_6–Bi_2O_3 joins in the ternary systems Bi_2O_3–Nd_2O_3–MoO_3 and Bi_2O_3–Pr_2O_3–MoO_3 and identified both cubic and tetragonal phases with high conductivity.

In this paper, we describe the formation and electrical properties of conductive phases in the ternary system Bi_2O_3–La_2O_3–MoO_3 (Bi_2O_3 codoped with lanthanum and molybdenum).

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2. Experimental

Polycrystalline Bi_2O_3–La_2O_3–MoO_3 samples were prepared by solid-state reactions in air, using appropriate mixtures of 99.9%-pure Bi_2O_3, La_2O_3, and MoO_3. Before weighing, the La_2O_3 was calcined at 1000 °C for 1 h to remove water and carbon dioxide. The compositions of the samples were $(Bi_2O_3)_x(La_2O_3)_y(MoO_3)_z$, with $x + y + z = 1$. The starting reagents were weighed on a Sartorius E1200S balance with an accuracy of ± 0.001 g. The total weight of the resultant ceramics was 3.5 g. The initial composition of the samples was determined with an accuracy (Δx, Δy, and Δz) in the range $\pm$ 0.0001–0.005.

The samples were fired in two steps, with intermediate grinding and pressing at 0.1 GPa. In preliminary syntheses of polycrystalline samples in the system under consideration, we tested firing in two to five steps at various temperatures. The duration of each step was varied from 12 h to a week. The results showed that two 12-h steps were sufficient to reach equilibrium. In the first step, the firing temperature was 750–800 °C. The density of the ceramics was found to increase with firing temperature, so the firing temperature in the second step was chosen to be near the melting point of the material: 820–1300 °C, depending on the composition of the ceramics. For the samples containing >85 mol% Bi_2O_3 ($x > 0.85$), this temperature was 820–850 °C. Most of the samples containing 50–85 mol% Bi_2O_3 were prepared at temperatures from 900 to 1000 °C. The materials containing 30–60 mol% Bi_2O_3 and a large excess of La_2O_3 relative to MoO_3 were prepared by firing between 1100 and 1300 °C. To avoid the formation of metastable Bi_2O_3-based phases, all of the samples were cooled slowly. The heating and cooling rates in our syntheses were 5 K/min. To assess the effect of quenching, presynthesized samples were heated to a preset temperature (690–1050 °C), held there for 30 min, and then quenched in cold water.

To ascertain whether the intended compositions were obtained, we evaluated bismuth and molybdenum volatility in our samples by thermogravimetry using a Netzsch STA 449C system. Heating the samples to their melting points was found to cause a weight change no >0.1%, indicating that none of their components vaporized. Thus, we are led to conclude that the final composition of the ceramics produced by firing below their melting points was near the intended composition: $(Bi_2O_3)_x(La_2O_3)_y(MoO_3)_z$ with $x + y + z = 1$.

The phase analysis of ground polycrystalline samples was performed by X-ray diffraction (XRD) on a DRON-2.0 diffractometer (Cu K_α radiation, $2\theta = 20°$–$60°$, 0.05° scan step). Their unit-cell parameters were evaluated by least squares fitting using the Powder 2.0 program. Ground SiO_2 single crystals were used as an external standard.

The density of some of the polycrystalline samples was determined by hydrostatic weighing in toluene.

The samples were characterized by differential scanning calorimetry (DSC) in air using the Netzsch STA 449C (30–1150 °C, heating/cooling rate of 10 K/min, platinum crucibles). To verify DSC data reproducibility, two or three heating/cooling cycles were performed for each sample.

The conductivity of the samples was measured at 1 MHz between 30 and 850 °C by a two-probe technique using a Tesla BM 431E bridge. The measurements were made during heating and cooling at 10 K/min. In addition, $(Bi_2O_3)_{0.80}(La_2O_3)_{0.1}(MoO_3)_{0.1}$ and $(Bi_2O_3)_{0.61}(La_2O_3)_{0.17}(MoO_3)_{0.22}$ samples were characterized by two-probe impedance spectroscopy at frequencies from 0.01 Hz to 1 MHz, temperatures from 50 to 700 °C, and an applied sinusoidal voltage of 0.1 V peak, using a Novocontrol Alpha AN impedance analyzer. In the conductivity measurements, we used platinum electrodes made by firing platinum paste at 800 °C for 15 min (the samples were heated and cooled at 5 K/min). In the case of the $(Bi_2O_3)_{0.96}(La_2O_3)_{0.02}(MoO_3)_{0.02}$ sample, which was obtained as the α-phase, electrodes were produced by firing at 650 °C, i.e. below the temperature of the $\alpha \rightarrow \delta$ phase transition, to avoid the formation of the tetragonal metastable phase β- Bi_2O_3.

3. Results and discussion

3.1. Formation of Bi_2O_3-based compounds in the ternary system Bi_2O_3-La_2O_3-MoO_3

Fig. 1 shows powder XRD patterns of ground polycrystalline $(Bi_2O_3)_x(La_2O_3)_y(MoO_3)_z$ samples. Fig. 2 indicates the compositions of the samples in the ternary system Bi_2O_3–La_2O_3–MoO_3 and presents XRD results. A slight increase in La and Mo dopant concentrations allows the tetragonal phase with the β-Bi2O3 structure to be stabilized at room temperature ($(Bi_2O_3)_{0.96}(La_2O_3)_{0.02}(MoO_3)_{0.02}$ sample, Fig. 1a). Higher doping levels lead to the formation of a cubic phase isostructural with the high-temperature cubic phase δ-Bi_2O_3 (in the composition region $0.65 \le x \le 0.93$, $0.03 \le y \le 0.175$, and $0.015 \le z \le 0.22$; Fig. 1b). Further changes in composition and a decrease in bismuth content to $0.50 \le x \le 0.61$ ($0.14 \le y \le 0.21$ and $0.22 \le z \le 0.31$) lead to distortion of the cubic (δ-Bi_2O_3) structure and the formation of another tetragonal phase (β'-phase) (Fig. 1c). The present results on the formation of the cubic phase (δ) and two tetragonal phases (β and β') are similar in many respects to previously reported data for the Nd_2MoO_6–Bi_2O_3 join in the corresponding ternary system [23], but in the La system the stability fields of the δ- and β'-phases are displaced from the Bi_2O_3-La_2MoO_6 join to higher MoO_3 concentrations (Fig. 2). Another distinction from the Nd system is the formation of a rhombohedral phase on the Bi_2O_3-La_2MoO_6 join in a narrow range of Bi_2O_3 concentrations: $0.60 \le x \le 0.64$ (Fig. 1d). The strongest reflections in the XRD patterns in Fig. 1d correspond to $Bi_2La_4O_9$ [27], but according to the present XRD data $Bi_2La_4O_9$ does not form solid solutions with any of the observed rhombohedral compounds.

Fig. 3 shows the composition dependence of the unit-cell parameter for the cubic phase. The cubic cell parameter and volume increase sharply with decreasing bismuth oxide concentration and increasing codoping level. At a constant Bi_2O_3 concentration, the unit-cell parameter decreases with increasing lanthanum concentration. Note that the unit-cell parameter of the cubic phase was also observed to increase with decreasing bismuth oxide content in the neodymium system [23], but in the lanthanum system the increase is much greater. Given that the ionic radius of trivalent bismuth exceeds those of lanthanum, neodymium, and molybdenum, this behavior of the unit-cell parameter cannot be understood in terms of cation geometry and seems to be caused by changes in oxygen stoichiometry in response to changes in the composition of the samples.

The unit-cell parameters of the tetragonal and rhombohedral compounds are presented in Table 1. Like in a previous study [23], for the convenience of comparison with the unit-cell parameters of the δ- and β'-phases we used the same setting as Sillen [6,28] in calculating the unit-cell parameters of $(Bi_2O_3)_{0.96}(La_2O_3)_{0.02}(MoO_3)_{0.02}$ (β-Bi_2O_3 phase). Like in the Nd system, the tetragonal phases β and β' differ in unit-cell geometry ($a > c$ in the β'-phase and $a/2 < c$ in the β-phase). Note that the tetragonal distortion of the structure of the β'-phase increases with decreasing bismuth concentration and increasing molybdenum content, i.e. as the composition moves farther away from the stability region of the cubic phase. Like in the case of the cubic materials, the unit-cell volume increases with codoping level. The unit-cell parameters of the rhombohedral compounds vary little with composition (Table 1).

Comparison of the X-ray density, d_x, and the density determined by hydrostatic weighing, d_{meas}, allowed us to evaluate the relative density of the ceramics, which was found to be high, on the order of 97–98%, for the cubic (δ) and tetragonal (β') materials. For example, the cubic material $(Bi_2O_3)_{0.9}(La_2O_3)_{0.05}(MoO_3)_{0.05}$ had $d_x = 8.35$ g/cm^3 and $d_{meas} = 8.18 \pm 0.02$ g/cm^3.

3.2. Polymorphism

The DSC heating curve of the tetragonal material $(Bi_2O_3)_{0.96}(La_2O_3)_{0.02}(MoO_3)_{0.02}$ (β-Bi_2O_3 phase) has two endothermic

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