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Fluorite-like compounds with high anionic conductivity in $Nd_2MoO_6 - Bi_2O_3$ system

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ABSTRACT

A wide range of $(Bi_2O_3)_x(Nd_2O_3)_{(1-x)/2}(MoO_3)_{(1-x)/2}$ solid solutions with the structure of the anion-conducting bismuth oxide was found in the Bi_2O_3–Nd_2MoO_6 join of ternary Bi_2O_3–MoO_3–Nd_2O_3 system at $0.5 \leq x \leq 1$. In said concentration range the compounds with large ($0.92 \leq x \leq 0.98$) and small ($0.5 \leq x < 0.6$) bismuth content are tetragonal at room temperature. In the intermediate concentration range ($0.67 \leq x \leq 0.9$) cubic δ-Bi_2O_3 structure is stabilized at room temperature. It is shown that two tetragonal phases observed at different bismuth concentrations differ from each other in their polymorphism and behavior of the unit cell parameters. All the obtained compounds show high conductivity that reaches 0.1 S/cm (for a cubic sample with $x = 0.8$ at 800 °C).

Introduction

The search for new materials with high oxygen conductivity for new electrochemical power sources is an actual problem. These materials are used as solid electrolytes in fuel cells, in the gas sensors in the gas separation membranes and other devices. For a long period of time there were numerous articles and reviews devoted to polymorphism and properties of bismuth oxide [1–3].

From the all known anionic conductors the cubic high-temperature δ-Bi_2O_3 phase with fluorite structure has the highest oxygen conductivity of about 1 S/cm at 730 °C [4]. The high oxygen conductivity of this phase is attributed to intrinsic oxygen vacancies [5]. The authors [5] showed that δ-Bi_2O_3 phase crystallizes in a cubic cell with space group Fm−3m and unit cell parameter $a = 5.66$ Å at 750 °C. However, the temperature range of the existence of this phase is narrow and extends from 730 °C to the melting point of 825 °C. Below 730 °C the phases with a lower conductivity exist: room-temperature monoclinic α-phase, tetragonal β and cubic γ phases. The sequence of phase transitions depends on the speed of cooling [1,2].

Takahashi et al. [6] were the first to find the stabilization of the high-temperature δ-phase to room temperature by doping of rare-earth elements in the Bi_2O_3–Ln_2O_3 systems. The best results were obtained for Y, Dy, Er as a dopants. However, some studies have shown that so-called "stabilized" solid solutions are metastable and decay over time at a annealing temperature of about 600 °C [7]. The effect of impurity on the conductivity depended on the ionic radius of the rare earth element and its polarizability [8]. In binary Bi_2O_3–Ln_2O_3 systems the cubic δ-Bi_2O_3 phase was obtained for Ln = Dy, Ho, Y, Er, Tm, Yb [6]. Rhombohedral phases were formed with large

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rare-earth elements (Ln = La, Pr, Nd) [9]. A number of studies have shown that tungsten also stabilizes the δ-Bi_2O_3 cubic structure [6,10,11]. Takahashi et al. [6] first attempted to stabilize δ-Bi_2O_3 phase by doping the tungsten. The authors found that the $(Bi_2O_3)_{0.78}(WO_3)_{0.22}$ compound has cubic structure over a wide temperature range, wherein the oxygen conductivity was 2.8×10^{-2} S/cm at 600 °C, which is higher than that of the yttrium-stabilized ZrO_2. The binary Bi_2O_3–MoO_3 system is widely investigated [12–14]. A large number of phases in a bismuth-rich region were found, in particular, the $Bi_{14}MoO_{24}$ compound with tetragonal structure [14].

In a number of works so-called codoping was used to stabilize δ-Bi_2O_3, in other words two dopants were used. In Ref. [15] twice doped Bi_2O_3 was studied in Bi_2O_3–Y_2O_3–MO_x systems (M = Nb, Gd, Sm, Pr). Codoping with rare earth and tungsten was successfully used by Watanabe et al. [16] and Wachsman et al. [17,18]. Watanabe [16] have investigated the ternary Bi_2O_3–Er_2O_3–WO_3 system and have shown that δ-Bi_2O_3 phase is not degrade in ternary systems in contrast to the doping with single rare earth element, when the stabilized δ-Bi_2O_3 phase decays during prolonged annealing. Wachsman et al. [17,18] studied the phase formation and conductive properties of compounds with the structure of δ-Bi_2O_3 in Bi_2O_3–Dy_2O_3–WO_3 system. The conductivity of these compounds was high and reached 0.1–1 S/cm at 800 °C.

Although molybdenum is similar to tungsten in its crystallochemical properties, there are no data in the literature about double doping of bismuth oxide with rare-earth elements and molybdenum in the literature. In this work the phase formation in the Bi_2O_3–Nd_2MoO_6 join of ternary Bi_2O_3–Nd_2O_3–MoO_3 system is investigated to find the compounds with the structure of Bi_2O_3, to study their polymorphism and conductivity.

Materials and methods

Polycrystalline $(Bi_2O_3)_x(Nd_2O_3)_{(1-x)/2}(MoO_3)_{(1-x)/2}$ ($0 \le x \le 1$) samples have been prepared by solid–state reactions in air between 99.9%-pure Bi_2O_3, Nd_2O_3, MoO_3. Neodymium oxide was precalcined for 1 h at 1000 °C to remove water and carbon dioxide. The two-step firing of the samples with intermediate grinding and pressing under a pressure of 0.1 GPa was used. The duration of each firing step was 12 h. The first firing step was carried out at 750–800 °C, the temperature of the second firing step was limited to melting point of the samples and varied between 750 and 1200 °C depending on the ceramic composition. The heating/cooling rate was 5 K/min. To study the quenching effect previously synthesized samples were heated to a predetermined temperature (800–1000 °C), held for 30 min, and then quenched in cold water.

The phase composition of ground samples was determined by XRD with a DRON-2.0 diffractometer (CuK_α-radiation, $2\theta = 20–60°$, scan step 0.05°). Differential scanning calorimetry (DSC) curves were obtained in air using a NETZSCH STA 449C thermal analyzer (Pt crucibles, 30–1200 °C). The heating and cooling rates were 10 K/min. Dilatometry of samples was carried out by NETZSCH TMA 202 thermomechanical analyzer in the temperature range of 20–600 °C, the heating and cooling rates were 5 K/min.

The dielectric permittivity and conductivity of the solid solutions were measured at 1 MHz between 20 and 1000 °C by a two-probe technique using a Tesla BM 431E bridge. Electrophysical studies of several polycrystalline samples were carried out by two-probe measurements at frequencies from 0.01 Hz to 3 MHz, temperatures from 300 to 950 °C, and an applied sinusoidal voltage of 0.5 V peak using a Novocontrol Beta-N impedance analyzer and NorECs ProboStat ceramic cell. In electrical measurements, we used polycrystalline samples with platinum electrodes, applied to the sample by burning of platinum paste at temperatures of 750–800 °C for 30 min, the rate of heating and cooling of the samples in this case was 5 K/min.

Results and discussion

The powder XRD patterns of $(Bi_2O_3)_x(Nd_2O_3)_{(1-x)/2}(MoO_3)_{(1-x)/2}$ samples are shown in Fig. 1. X-ray studies showed that in the Bi_2O_3–Nd_2MoO_6 join there is a wide range of solid solutions on the basis of Bi_2O_3 in the concentration range of $0.5 \le x \le 1$. Three polymorphic modifications of bismuth oxide were revealed in the samples depending on the composition. The XRD patterns of the samples with $0.6 \le x \le 0.9$ coincide with that of high-temperature δ-Bi_2O_3 phase [19,20]. We used the indices given in Refs. [19,20] to calculate the unit cell parameters (Fig. 2). Vegard's law is realized for unit cell parameters of cubic samples in the $0.67 \le x \le 0.85$ range. The a_{cubic} unit cell parameter decreases slightly with increasing concentration of bismuth. The samples with $x = 0.6$ and $x = 0.9$ demonstrate smaller unit cell parameter than the rest of the cubic samples closer to the unit cell parameters of tetragonal phase. The latter may be due to the peculiarities of the transition from cubic to tetragonal structure in the indicated concentration range.

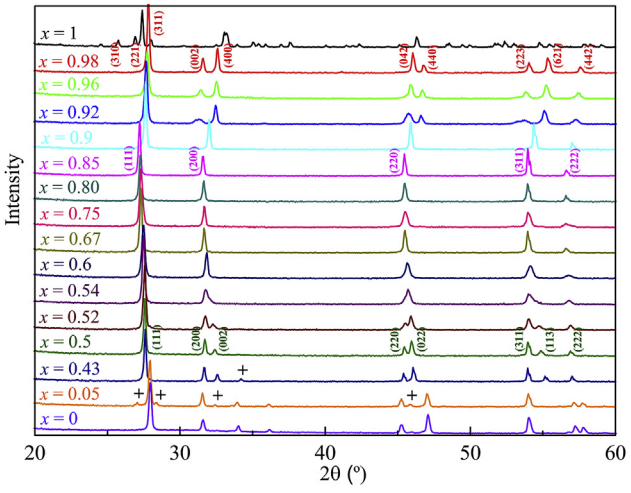

Fig. 1 – XRD patterns of $(Bi_2O_3)_x(Nd_2O_3)_{(1-x)/2}(MoO_3)_{(1-x)/2}$ polycrystalline samples. Symbol "+" denotes reflexes from impurity phases.