**IONIC CONDUCTIVITY OF Bi\(_{12}(V,Bi)O_{20} + \delta\)** Single Crystal (\(\delta = 0.27\)) with a Sillenite-Type Structure

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Abstract—The ionic conductivity of nonstoichiometric Bi\(_{12}(V_{0.89}Bi_{0.03})O_{20.27}\) single crystal with a sillenite-type structure has been investigated by impedance spectroscopy; its conductivity at 673 K is \(2 \times 10^{-3}\) S/cm, which is about two orders of magnitude higher than the conductivity of oxide superionic conductor single crystal Zr\(_{0.88}\)Y\(_{0.12}\)O\(_{1.94}\). As follows from crystallochemical analysis, ion transport in Bi\(_{12}(V_{0.89}Bi_{0.03})O_{20.27}\) is due to additional O\(^{2-}\) ions, which arise due to oxygen nonstoichiometry.

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**INTRODUCTION**

Individual Bi\(_{12}MO_{20}\) (\(M^{4+} = Si^{4+}, Ge^{4+}, Ti^{4+}\)) compounds with a sillenite-type structure are formed as a result of interaction of bismuth oxide with oxides of elements that can be tetrahedrally coordinated by oxygen. Bi\(_{12}MO_{20}\) crystals are isostructural to the metastable body-centered cubic phase \(\gamma\)-Bi\(_2\)O\(_3\) (sp. gr. \(I\bar{2}3\)), have dielectric properties, and are characterized by a variety of physical effects (piezoelectric, electrooptical, magneto-optical, optical activity, photoconductivity, and photorefraction) [1]. In Bi\(_{12}MO_{20}\) crystals, tetrahedral positions of \(M\) ions can be statistically occupied by isomorphic mixtures of \(M^{4+}\) cations (\(n = 2–5\)) with strongly differing ionic radii, which leads to a wide class of nonstoichiometric Bi\(_{12}M_{x}O_{20+\delta}\) sillenites (solid solutions).

At the atomic level the mechanisms of unusually wide isomorphism with respect to \(M\) cations in Bi\(_{12}M_{x}O_{20+\delta}\) crystals were considered in [2]. It was shown that the bismuth-oxygen sublattice plays a decisive role in the existence of a wide class of isomorphic sillenite-type compounds. Features of sillenite structure are determined by the oxidation state of \(M\) cations. Replacement of one type of cations (\(M^{4+}\)) by isomorphic mixtures of \(M^{2+}, M^{3+}, M^{4+}\), and \(M^{5+}\) cations leads to oxygen nonstoichiometry of Bi\(_{12}M_{x}O_{20+\delta}\) compounds due to the formation of oxygen vacancies in the \(8c\) positions of the sp. gr. \(I\bar{2}3\) or occupation of \(6b\) positions by additional oxygen.

Structural models of different nonstoichiometric crystals of the sillenite family in the Bi\(_2\)O\(_3\)—V\(_2\)O\(_5\) system were considered and the fundamental possibility of occupying the centers of [BiO\(_4\)] tetrahedra by Bi atoms was established in [3]. The single oxygen-excess Bi\(_{12}(V_{0.89}Bi_{0.03})O_{20.27}\) Solid solution is of special interest among the investigated vanadium-containing sillenites; its crystal structure was studied in details by precise neutron diffraction in [4]. Neutron diffraction made it possible to reliably establish the structural parameters of oxygen atoms and determine the percentage of V and Bi cations in the tetrahedral position of the structure with a high accuracy. It was found that trivalent bismuth cations are located in partially occupied tetrahedral positions \(M\), and the effective averaged valence of \(M\) cations is 4.54+.

The purpose of this study was to analyze the conductivity of nonstoichiometric Bi\(_{12}(V_{0.89}Bi_{0.03})O_{20.27}\) single crystal and reveal the relationship between the conduction process and atomic structure of this crystal.

**EXPERIMENT DETAILS AND DISCUSSION OF THE RESULTS**

Single crystals are obtained by hydrothermal synthesis through interaction of V\(_2\)O\(_3\) and Bi\(_2\)O\(_3\) (from alkaline solutions) at 300°C and pressure of \(5 \times 10^7\) Pa, with subsequent recrystallization of spontaneously nucleating crystals onto a seed. The orange color of the grown single crystals is due to V\(^{5+}\) ions. Single crystals were structurally attested by neutron diffraction analysis [4] at the Institute of Crystallography, Russian Academy of Sciences. They belong to the sillenite structure type (sp. gr. \(I\bar{2}3\)) with the unit-cell parameter \(a = 10.245(1)\) Å [4] and pycnometric density \(\rho = 8.89\) g/cm\(^3\) [5] (for comparison, the corresponding characteristics of \(\gamma\)-Bi\(_2\)O\(_3\) are \(a = 10.245(1)\) Å and \(\rho = 9.239\) g/cm\(^3\)). The structurally refined [4] composition of single crystals, Bi\(_{12}(V_{0.89}Bi_{0.03})O_{20.27}\) (complete...
were carried out in vacuum (residual pressure measurements did not exceed 5%. Dag-580 graphite paste BM-507). The relative error of the impedance dependences of the complex impedance in the frequency range 5 Hz–500 kHz (impedance meter Tesla BM-507). The relative error of the impedance measurements did not exceed 5%. Dag-580 graphite paste was used to form electrodes. Electrical measurements were carried out in vacuum (residual pressure $10^{-1}$ Pa) in a temperature range of 488–723 K. The $\sigma$ value was determined by extrapolating the impedance hodograph on the active resistances axis with allowance for the sample geometry. The electrode polarization observed at low frequencies in the impedance spectra of the C[crystal]C electrochemical cell with irreversible electrodes indicates the ionic nature of the conductivity in the crystal studied.

A sample in the form of a rectangular parallelepiped with a height of 2.5 mm and a base area of 15 mm$^2$ was prepared for electrical measurements. The sample was not oriented with respect to the crystallographic axes, because it belongs to the cubic system. The conductivity $\sigma$ was found by analyzing the frequency dependences of the complex impedance in the frequency range 5 Hz–500 kHz (impedance meter Tesla BM-507). The relative error of the impedance measurements did not exceed 5%. Dag-580 graphite paste was used to form electrodes. Electrical measurements were carried out in vacuum (residual pressure $10^{-1}$ Pa) in a temperature range of 488–723 K. The $\sigma$ value was determined by extrapolating the impedance hodograph on the active resistances axis with allowance for the sample geometry. The electrode polarization observed at low frequencies in the impedance spectra of the C[crystal]C electrochemical cell with irreversible electrodes indicates the ionic nature of the conductivity in the crystal studied.

Figure 1 shows the temperature dependence $\sigma$ of Bi$_{12}$(V$_{0.89}$Bi$_{0.03}$)O$_{20.27}$ single crystal and (for comparison) the data of [5] on the ionic conductivity of a single crystal of oxide superionic conductor Zr$_{0.88}$Y$_{0.12}$O$_{1.94}$. For the Bi$_{12}$(V$_{0.89}$Bi$_{0.03}$)O$_{20.27}$ crystal at $673$ K ($400^\circ$C), $\sigma = 2 \times 10^{-3}$ S/cm, a value that is approximately two orders of magnitude larger than the conductivity of the Zr$_{0.88}$Y$_{0.12}$O$_{1.94}$ single crystal. Kinks are not observed on the curve $\sigma(T)$, and it is described by an Arrhenius-type equation $\sigma = A/\exp(\Delta H/kT)$, where the preexponential conductivity factor is $A = 8.1 \times 10^8$ S K/cm and the activation enthalpy of charge carrier migration is $\Delta H = 0.91$ eV.

A structural model of Bi$_{12}$(V$_{0.89}$Bi$_{0.03}$)O$_{20.27}$ crystal [6] is shown in Fig. 2. Bi(1) atoms are in the 24$/$f position with the coordinates $x, y, z$ ($x \sim 0.17$, $y \sim 0.32$, $z \sim 0.01$), while Bi(2) and V atoms are in the 2$\alpha$ position with the coordinates 0, 0, 0. Oxygen atoms occupy four different regular systems of points: O(1) in the 24$/$f position with the coordinates $x, y, z$ ($x \sim 0.13$, $y \sim 0.25$, $z \sim 0.49$); O(2) and O(3) in the 8$e$ position with the coordinates $x, x, x$ with $x \sim 0.2$ and $x \sim 0.9$, respectively; and O(4) in the 6$b$ position with the coordinates 0.5, 0, 0. Oxygen atoms are bound with Bi and V atoms through ionic covalent bonds because of the high electronegativity of oxygen atoms. The structure of the Bi$_{12}$(V$_{0.89}$Bi$_{0.03}$)O$_{20.27}$ solid solution is of the framework type. The framework is formed by dimers from [Bi(V)O$_3$] (distorted half-octahedron), which is connected via [VO$_4$] and [Bi(2)O$_4$] tetrahedra. These tetrahedra contain oxygen atoms O(3), which are located around the tetrahedral position $M$ (Fig. 2). An additional O(4) atom occupies the center of the cavity formed by two dimers. The distance from the oxygen atom O(4) to the four nearest Bi atoms is 2.58 Å; the neighboring O atoms are spaced at distances larger than 2.88 Å. The vacancies in the tetrahedral positions $M$ of the structure compensate for the stresses arising near the additional O(4) atoms.

Neutron diffraction analysis [4] showed almost complete occupancy of the tetrahedral position by vanadium in the sillenite structure under study, as well as the presence of additional oxygen. The incorporation of oxygen atoms O(4) into the structure leads to...