

Oxygen-Ionic Conductivity of Ceramics

La₂O₃ • 2MoO₃

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Abstract – Taking into account the relevance of obtaining environmentally friendly materials with desired properties and the need for ionic conductors, we present the results of the synthesis and studies of oxygen-conducting $La_2O_3 \cdot 2MoO_3$ ceramics. Ceramic samples were obtained by the solid-phase method from the initial lanthanum oxides La_2O_3 and molybdenum MoO_3 . Using the methods of dielectric spectroscopy, using AC bridges P5083 and E7-12, the conductive properties of single-phase solid solutions were studied, and the presence of a phase transition at a temperature of about $560^\circ C$ was established. Temperature hysteresis in the mode of heating - cooling showed that the phase transition of the first kind. The results of studies of the dielectric properties of the obtained ceramics at various frequencies and at direct current revealed that the high conductivity observed in molybdate is ionic in nature and occurs due to the movement of oxygen ions.

Keywords – oxygen-conducting ceramics; rare earth elements; perovskites; fluorites; new materials.

I. INTRODUCTION

In today's world, issues related to the environmental safety of various processes are very relevant. Therefore, an important task is to obtain environmentally friendly materials with desired properties. Interesting and promising in terms of use are compounds exhibiting high values of conductivity.

As is well known, electric current can occur due to the movement of positive holes, electrons or ions [1], and with the addition of all these components, the total conductivity arises:

$$\sigma = \sigma_p + \sigma_n + \sigma_i,$$

Where σ_p – hole, σ_n – electron, σ_i – ionic component of conductivity.

$$\sigma = \sigma_p + \sigma_n + \sigma_i,$$

Moreover, ionic conductivity can occur due to the movement of cations and anions, and have different ion transport mechanisms. The movement of ions can proceed through the vacancy and tunnel mechanism. In ordinary solids, under standard conditions, the conductivity values are insignificant — on the order of 10^{-10} to $10^{-12} \text{ Ohm}^{-1} \text{ cm}^{-1}$. In superionic conductors, the conductivity reaches $10^{-1} \text{ Ohm}^{-1} \text{ cm}^{-1}$, which is comparable to the conductivity of liquid electrolytes and melts [2, 3].

The Arrhenius equation can express the dependence of ionic conductivity on temperature:

$$\sigma \cdot T = \sigma_0 \cdot e^{-\frac{E_a}{kT}}$$

where σ – ion conductivity, k – Boltzmann constant, T – temperature, determined by the choice of charge transfer model [1].

It is known that compounds with a fluorite, perovskite structure and their derivatives have high ionic conductivity.

The ancestor of the perovskite family, the most important class of inorganic compounds, is perovskite $CaTiO_3$. The structure of $CaTiO_3$ consists of 8 formula units (Fig. 1).

Despite the fact that the real structure of perovskites has different distortions and is different from cubic. The perovskite crystal structure is considered as the densest package of the cubic type. The perovskite structure can be considered as a three-dimensional framework. This framework consists of BO_6 octahedra, which are connected by vertices. The general formula for perovskites can be represented as ABX_3 , where position A is occupied by cations with an oxidation state of +1,

+2 or +3, and the charge of the cation in position B can be +5, +4 or +3 and is determined by the charge of the A-cation.

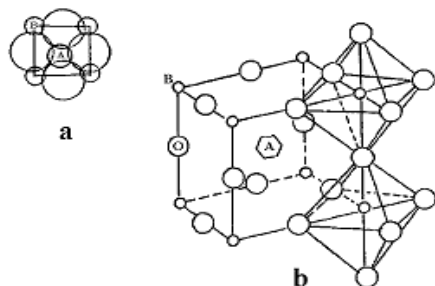


Fig. 1. Perovskite structure (a - the closest packing, b- in polyhedra).

In layered perovskites, there are layers in which the vertices of the octahedra are connected by type ReO_3 with atoms A. These layers can be combined into packets of 2, 3 and a larger number of layers, between which A and cations are separated by separate layers [4]. The structures of this type include the Aurivillius phases. They have the general formula $(Bi_2O_2)A_n-1B_nO_{3n+1}$, where n corresponds to the number of perovskite-like layers in packets. Between them are located Bi_2O_2 , in the form of corrugated square grids. These compounds can be attributed to the family of Bi-containing oxides.

Currently, active work is underway on the synthesis, the study of the structure, the study of the physicochemical characteristics of Bi-containing materials [5–8].

The results of the study of the dielectric and conductive properties of Bi_2WO_6 bismuth tungstate showed that high values of electrical conductivity in the temperature range from 400 °C to 730 °C are achieved due to the ionic component, are purely ionic in nature. The transfer of oxygen ions occurs by a vacancy mechanism. Ionic conductivity arises due to the infinite movement of oxygen along the crystal lattice [9]. The value of conductivity (at 730 °C) can reach $10^{-4} \text{ Ohm}^{-1}\text{cm}^{-1}$.

In bismuth tungstate Bi_2WO_6 , relaxation peaks were detected, which arise due to the reciprocating movement of oxygen ions within the nearest vacancies. Comparison of the characteristics of ionic conductivity and dielectric relaxation and their close energy values in Bi_2WO_6 suggest that the first process is the result of an infinite repetition of the second [9].

High ionic conductivity was found in gallates with the perovskite structure $(La, Sr)(Ga, Mg)O_{3-v}$. Systematic studies of the features of phase formation, structure and transport properties $(La_{0.9}Sr_{0.1})[(Ga_{1-x}Mx)_{0.8}Mg_{0.2}]O_{3-v}$ ($x = 0-1$, $M = Fe, Ni, Mn, Cr$), in as a result, the interconnection of ion-conducting, magnetic and transport properties with the characteristics of the structure parameters, the nature of bonds and charge states of transition elements was established, confirming the decisive role of the crystal-chemical factor in the formation of the properties of anion-deficient perovskite-like oxides [10].

The authors [11] have synthesized ternary molybdate $Na_{25}Cs_8Fe_5(MoO_4)_{24}$, determined the structure and identified the first-order phase transition. The method of dielectric impedance spectroscopy has established high values of the

conductivity of the high-temperature phase, which confirms the promise of this compound for the development of new materials with high ionic conductivity.

Another class of compounds interesting from the point of view of ionic conductivity is the fluorite CaF_2 and its derivatives. Representatives of this class have the general formula AB_2 . This structure is characterized by a face-centered cubic cell, in which calcium is surrounded by eight fluorine atoms, and there are 4 calcium atoms around the fluorine atom (Fig. 2) [1].

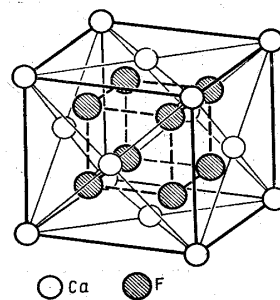


Fig. 2. The structure of fluorite.

This structural type includes fluorite derivatives with an excess or deficiency of anions. The most well-known and sought-after representative of this class, exhibiting high ionic conductivity in oxygen, is zirconium dioxide ZrO_2 , stabilized by oxides of calcium and yttrium. Stabilization of the high-temperature phase ZrO_2 with the addition of oxides CaO, Y_2O_3 , etc., occurs due to the formation of solid solutions of the type $(Ca_xZr_{1-x})O_{2-x}$. In these solutions, one oxygen vacancy is formed with the introduction of each calcium cation, as a result of which high oxygen-ionic conductivity occurs.

The study of the structure of complex oxides with the composition $(1-x)ZrO_2 \cdot xY_2O_3$ showed that they belong to the cubic system, pr.gr. $Fm\bar{3}m$ (225). However, at the local level, these compounds show significant differences (traces of the tetragonal phase are observed). [12].

As a result of comparing the quantitative characteristics of ionic conductivity and thermal conductivity of $M_{1-x}R_xF_{2+x}$ solid solutions ($M=Ca, Ba$) with the fluorite structure, it was found that these compounds can be attributed to three groups: cerium (tetrahedral clusters); yttrium (octahedral clusters); yttrium, sharply distinguished by mass from the rest of REE. [13].

II. METHODS AND MATERIALS

Synthesis of ceramic samples of $La_2O_3 \cdot 2MoO_3$ was carried out by the solid phase method from the starting oxides. [3].

Dielectric measurements were carried out using AC bridges P5083 and E7-12 (Fig. 3). Studies were conducted in the frequency range from 1 kHz to 1 MHz, at temperatures of 20–900 °C. Platinum electrodes were preliminarily applied to ceramic samples. Then they were placed in a quartz cell and electrodes were burned, gradually raising the temperature to 800 °C. Chromel was used - alumel thermocouple.

The value of conductivity σ was calculated directly during the experiment:

$$\sigma = \frac{d}{R \cdot S}$$

The value of d was determined by the distance between the electrodes [cm], R is measured by the device and is the sample impedance [Ohm], S is the surface area of the electrodes [cm²].

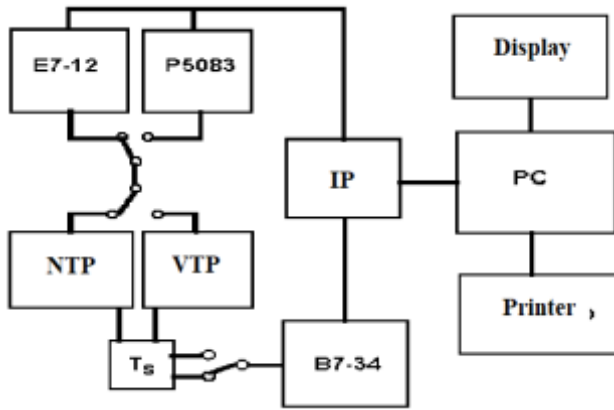


Fig. 3. Installation for dielectric measurements: AC bridges - E7-12 and P5083, thermostat - T_s , DC voltmeter - B7-34, low and high temperature attachments - NTP and VTP, interface device - IP, IBM PC - PC.

The studies were conducted on rectangular samples with a height of about 5 mm. The area of plane-parallel faces ranged from 5 to 10 mm². Platinum electrodes were deposited on the plane-parallel faces.

III. RESULTS

We synthesized lanthanum molybdate with the ratio of lanthanum oxides and molybdenum 1: 2 $\text{La}_2\text{O}_3 \cdot 2\text{MoO}_3$, and the dense ceramics of this sample was obtained. Phase composition and conductive properties of ceramics are studied.

Dielectric measurements of single-phase solid solutions of the composition $\text{La}_2\text{O}_3 \cdot 2\text{MoO}_3$ revealed that their conductivity at 800 °C reaches values of $7 \cdot 10^{-2} \text{ Ohm}^{-1} \cdot \text{cm}^{-1}$. It should be noted that in a sample containing a small amount of La_2MoO_6 impurity, the conductivity value is almost an order of magnitude lower than in single-phase ceramics.

The curves of the electrical conductivity of $\text{La}_2\text{O}_3 \cdot 2\text{MoO}_3$ ceramics as a function of the reciprocal temperature at various frequencies are shown in Fig. 4. With increasing frequency, the electrical conductivity of ceramics increases in accordance with the dependence $\sigma(\omega) = \sigma_0 (1 + \omega/\omega_0)$, where ω_0 is the frequency of oxygen ion jumps [14].

At a temperature of about 560 °C, a sharp increase in electrical conductivity is observed in the curves. This type is typical for compounds with a phase transition.

According to the equation of the Arrhenius law, we calculated the activation energy of conductivity. E_A takes values of 1.1 eV and 0.6 eV at temperatures of 200 – 500°C and 600 – 900°C, respectively.

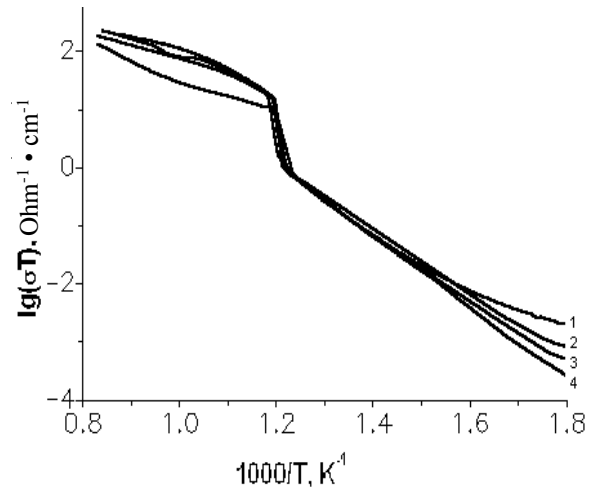


Fig. 4. Curves of the electrical conductivity of $\text{La}_2\text{O}_3 \cdot 2\text{MoO}_3$ ceramics versus the inverse temperature (1–1 kHz, 2–10 kHz, 3 - 100 kHz, 4 - 1 MHz).

The appearance of the curves obtained indicates that the conductivity has a predominantly ionic character.

To confirm the ionic nature of the conductivity, we carried out additional studies of ceramics at a constant current. As can be seen in Fig. 5, the conductivity values of curve 2, obtained as a result of measuring the dielectric properties of ceramics at a constant current (corresponding to the contribution of electronic conductivity), are more than two orders of magnitude lower than the total conductivity values at a frequency of 1 kHz. This indicates a clear predominance of ionic conductivity.

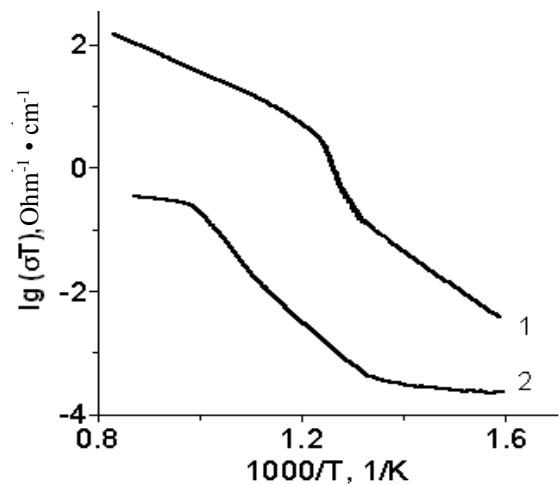


Fig. 5. Curves of electrical conductivity versus inverse temperature (1 – 1 kHz, 2 - direct current).

On the presented dependences of the dielectric constant and the tangent of the dielectric loss angle on temperature, pronounced anomalies are observed at a temperature of the order of 560°C (Fig. 6). These anomalies confirm the presence of a phase transition in $\text{La}_2\text{O}_3 \cdot 2\text{MoO}_3$.

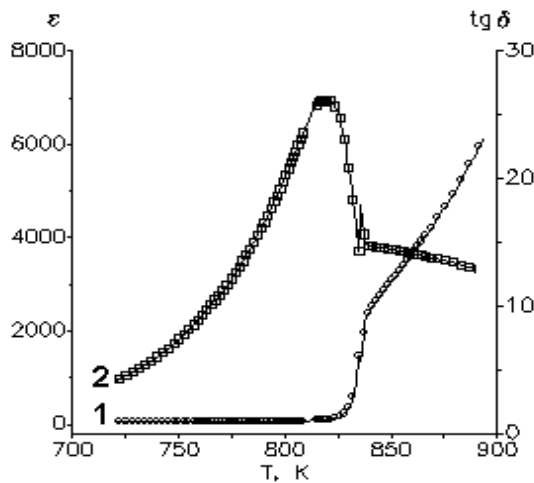


Fig. 6. Dielectric permeability (1) and dielectric loss tangent (2) $\text{La}_2\text{O}_3 \cdot 2\text{MoO}_3$ (1MHz).

Moreover, the curves of the dielectric constant, measured at different frequencies in the heating-cooling mode (Fig. 7), show temperature hysteresis. Such a pattern is characteristic of a phase transition of the I kind.

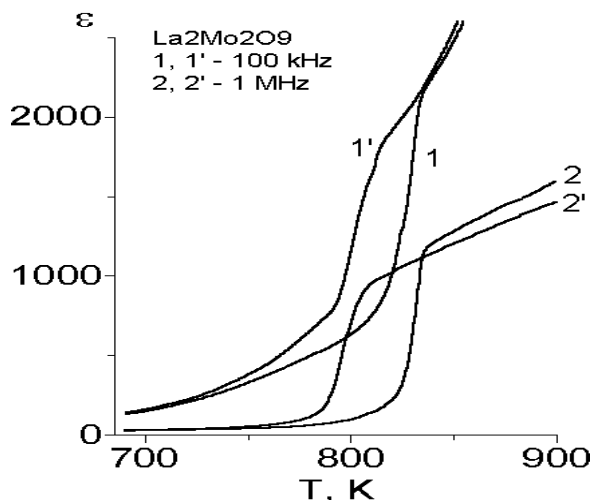


Fig. 7. The dielectric constant of $\text{La}_2\text{O}_3 \cdot 2\text{MoO}_3$.

In addition to the anomalies of the curves at temperatures of the order of 560°C , in our samples we found temperature maxima at lower temperatures. These anomalies can be attributed to relaxation maxima.

With an increase in the frequency from 200 Hz to 10 kHz, a shift of the relaxation maxima $\text{tg}\delta$ into the high-temperature region is observed (Fig. 8). This is due to the migration of ions in the crystal lattice over small distances at the nearest vacancies or at interstitial sites [9].

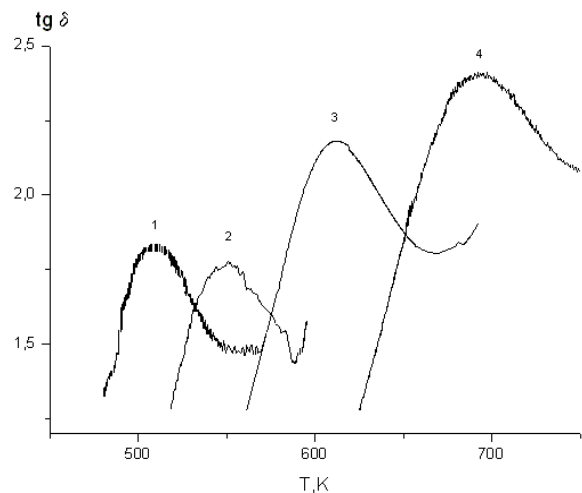


Fig. 8. Dependence of dielectric loss tangent on temperature at different frequencies: 200 Hz (1), 1 kHz (2), 10 kHz (3) and 100 kHz (4).

IV. CONCLUSION

Thus, we synthesized oxygen-conducting ceramics of lanthanum molybdate with a ratio of 1:2 $\text{La}_2\text{O}_3 \cdot 2\text{MoO}_3$. A first-order phase transition and high conductivity values of the high-temperature phase, reaching $7 \times 10^{-2} \text{ Ohm}^{-1} \text{ cm}^{-1}$ at a temperature on the order of 800°C , are detected. It is proved that conductivity has a predominantly ionic character.

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