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Electrical Properties of (1−x)La$_2$Mo$_2$O$_9$–xLa$_2$Mo$_3$O$_{12}$ (x = 0.15) Composite System

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Abstract

Electrical properties of (1–x)La$_2$Mo$_2$O$_9$–xLa$_2$Mo$_3$O$_{12}$ (x = 0.15) composite system are investigated. Introduction of an inert additional phase La$_2$Mo$_3$O$_{12}$ (adjacent phase to La$_2$Mo$_2$O$_9$ in the phase diagram) results in an increase in conductivity of composite by approximately one order of magnitude. This increase is associated with the appearance of a composite effect. The dominant ionic conductivity is maintained in the wide range of oxygen partial pressures. The calculated ion transport numbers are close to 1.

Keywords: lanthanum molybdate, LAMOX, heterogeneous doping, composites, oxide–ion conductivity

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1. Introduction

A widely developing field of alternative energetics is the creation of solid oxide fuel cells (SOFCs) working at intermediate temperatures (500–700°C) [1]. Today, yttria sta-bilized zirconia (YSZ) demonstrates the highest efficiency as electrolytic membrane of SOFC. However, electrolytes based on YSZ undergo a severe degradation of properties during the operation and have a high operating temperature ∼900°C.

In 2000, a novel family of oxygen ionic conductors was reported by Lacorre et al. [2], namely LAMOX. The ionic conductivity of lanthanum molybdate La$_2$Mo$_2$O$_9$ is compa-rable with that of YSZ reaching 0.06 S/cm at 800°C. La$_2$Mo$_2$O$_9$ undergoes a reversible phase transition around 580°C [3] from a high-temperature β-La$_2$Mo$_2$O$_9$ (cubic syn-gony, space group $P2_13$) to a low-temperature α-La$_2$Mo$_2$O$_9$(monoclinic syngony, space group $P2_1$), resulting in a decrease in conductivity by 2–3 orders of magnitude at low temperatures. The crystallographic sites in β-La$_2$Mo$_2$O$_9$ for the occupation of oxygen

How to cite this article: G. S. Partin, N. A. Kochetova, and I. E. Animitsa, (2018), "Electrical Properties of (1–x)La$_2$Mo$_2$O$_9$–xLa$_2$Mo$_3$O$_{12}$ (x = 0.15) Composite System" in *Sino-Russian ASRTU Conference Alternative Energy: Materials, Technologies, and Devices*, KnE Materials Science, pages 8–13. DOI 10.18502/kms.v4i2.3031

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ions are partially available, resulting in a high concentration of structural oxygen vacancies, which provides enough paths for the migration of oxygen ions [2, 4]. A decrease in conductivity resulting from the α-β phase transition and low chemical stability in the reducing atmosphere limits practical applications of this material. Thereby, suppressing phase transition and maintaining high conductivity values at intermediate temperatures are of great importance.

In this article, heterogeneous doping technique was used to optimize the functional properties of lanthanum molybdate $La_2Mo_2O_9$ for the first time. It should be noted that conductivity of an inert additional phase $La_2Mo_3O_{12}$ is 2–3 orders of magnitude lower than conductivity of the matrix phase. Achievement of high values of conductivity in $(1–x)La_2Mo_2O_9–xLa_2Mo_3O_{12}$ (x = 0.15) composite system is associated with the so-called composite effect, which was first detected by Liang [5] in $\{(100\%–x)LiI–xAl_2O_3\}$ composites. This phenomenon is manifested in increase of ionic conductivity of salt or oxide upon heterogeneous doping with an inert dispersed oxide.

2. Methods

The polycrystalline samples of $La_2Mo_2O_9$ and $La_2Mo_3O_{12}$, as well as $(1–x)La_2Mo_2O_9–xLa_2Mo_3O_{12}$ (x = 0.15) composite system were obtained by means of conventional solid-state reaction method from La_2O_3 and MoO_3 powders of the highly pure grade. The powders with ethanol were thoroughly mixed in an agate mortar. Then, three stages of annealing in air were carried out with a stepwise increase in the temperature from 450 to 950°C for $La_2Mo_2O_9$ and to 900°C for $La_2Mo_3O_{12}$. Composites were sintered for 24 h at 900°C. The phase composition of obtained powder samples was established by means of X-ray phase analysis (XRD) at room temperature using a Bruker D8 Advance powder diffractometer (CuK_α radiation, angle range of 2θ = 10–80° with a scan step of 0.02°).

Pellets for conductivity measurements represented disks with thickness of ∼2–3 mm and diameter of ∼15 mm obtained by uniaxial compaction at 8 MPa in a textolite mold and sintered for 24 h at 900–950°C in air. Powder of the platinum with an alcohol solution of colophony (1 wt %) was used to apply electrodes on polished face surfaces of sintered pellets. Electrodes were sintered with slow heating at 1–2°C/min and conditioning for 6 h at 900°C.

Conductivity was measured using a two-electrode ac scheme with an Elins Impedancemeter Z-1000P in the frequency range of 500 Hz to 3 MHz on the basis of the complex impedance technique. Measurements were carried out in the cooling

mode at the rate of 1°C/min, the impedance spectra were recorded on a PC every 25 min. The bulk and grain boundary conductivities were estimated using the equivalent circuit method in the ZView program.

The oxygen partial pressure Po_2 was controlled and maintained using an oxygen electrochemical pump governed by a Zirconia-M automatic adjuster [6].

3. Results

According to the XRD data, all the XRD reflexes of $La_2Mo_2O_9$ were indexed by monoclinic symmetry with space group $P2_1$, which agreed with that described in [2]. $La_2Mo_3O_{12}$ crystallized in monoclinic symmetry (space group $C2/c$), which agrees with the data of [7].

Samples of $La_2Mo_2O_9$ and $La_2Mo_3O_{12}$ can be described as single-phase, the impurity content does not exceed 1%. The XRD pattern of $(1-x)La_2Mo_2O_9-xLa_2Mo_3O_{12}$ ($x = 0.15$) composite contains only reflexes of two initial compounds; no chemical interaction is observed between the components.

The temperature dependences of bulk conductivity of $La_2Mo_2O_9$ and $La_2Mo_3O_{12}$ phases, as well as composite based on it are given in Figure 1. The bulk component of conductivity was calculated from the impedance spectra. An increase in conductivity observed in Figure 1 for composite with $x = 0.15$ by approximately one order of magnitude is associated with appearance of a composite effect in the studied system. The influence of $La_2Mo_3O_{12}$ heterogeneous dopant on ionic transport is more pronounced at temperatures lower than temperature of the α-β phase transition (~580°C). It should also be noted that addition of inert phase does not suppress the phase transition and does not stabilize high-conductivity β-$La_2Mo_2O_9$ at room temperature, as occurs in some cases of homogeneous doping, for example, when Mo is replaced by W [8].

It was reported in the early papers [2, 4] that oxygen ions O^{2-} in $La_2Mo_2O_9$ acted as the main charge carriers. In this study, the nature of carriers was determined by conductivity measurements with a variation of the oxygen partial pressure Po_2 in gas phase. Experimental isotherms of conductivity (Figure 2) are close to linear form and correspond to the electrolytic region of Po_2. According to the theoretical notions concerning the relationship between Po_2 and the concentration of defects in the crystal lattice [9], σ_{ion} is independent of Po_2 in the medium electrolytic region, $\sigma_{,h} \sim Po_2^{\pm 1/m}$, where σ_{ion}, σ_h, σ – ionic, hole, and electronic conductivity, respectively; the sign and the value of $1/m$ depend on the nature of carriers and the disordering type of crystal lattice. As follows from Figures 2(a) and (b), the conductivity values are almost unchanged
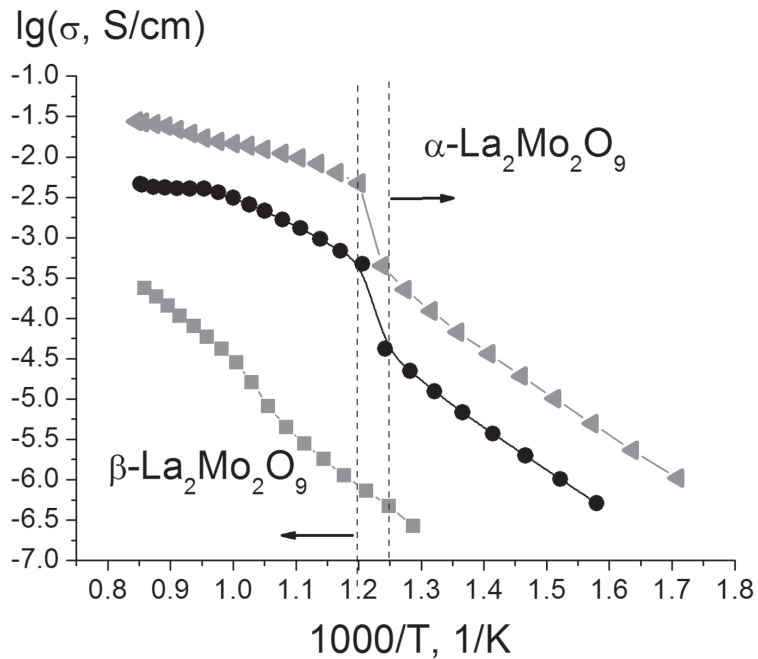
Figure 1: Temperature dependences of the bulk conductivity for $(1-x)La_2Mo_2O_9-xLa_2Mo_3O_{12}$ composites in air: $\bullet - x = 0$; $\blacktriangleleft - x = 0.15$; $\blacksquare - x = 1$. The dotted lines indicate the temperature range corresponding to the α-β phase transition.

with a variation of P_{O_2}. The value of $1/m$ is close to zero; therefore, it can be concluded that dominant ionic conductivity is maintained both for $La_2Mo_2O_9$ matrix phase and for composites in the wide range of oxygen partial pressures $0.21–3.2 \times 10^{-5}$ atm. The ion transport numbers t_{ion} calculated according to Equation (1) from the conductivity-P_{O_2} dependences are 0.93–0.98.
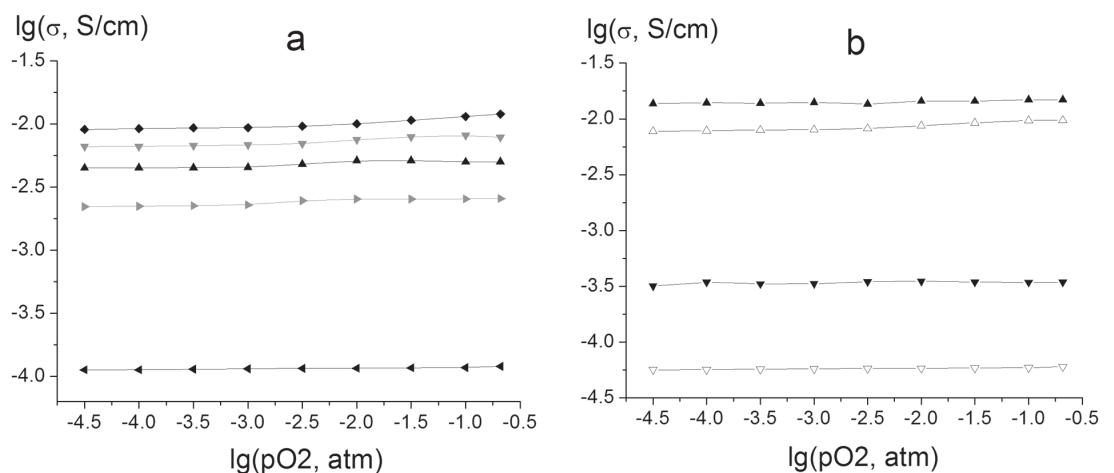
$$t_{ion} = \sigma_{ion}/\sigma_{ion} + \sigma_h \qquad (1)$$

Figure 2: Oxygen partial pressure dependences of the conductivity for (a) $La_2Mo_2O_9$ at temperatures: $\blacklozenge -$ 830°C; $\blacktriangledown - 780$°C; $\blacktriangle - 730$°C; $\blacktriangleright - 630$°C; $\blacktriangleleft - 530$°C; and (b) $(1-x)La_2Mo_2O_9-xLa_2Mo_3O_{12}$ (open signs $- x = 0$; closed signs $- x = 0.15$) at temperatures: $\blacktriangle - 800$°C; $\blacktriangledown - 500$°C.

4. Conclusion

The phases of $La_2Mo_2O_9$ and $La_2Mo_3O_{12}$, as well as $(1-x)La_2Mo_2O_9-xLa_2Mo_3O_{12}$ (x = 0.15) composite system were obtained by means of conventional solid-state reaction method. No chemical interaction is observed between the components; the impurity content does not exceed 1%.

It was established that introduction of 15 molar % $La_2Mo_3O_{12}$ resulted in an increase in conductivity of composite by approximately one order of magnitude. An increase in conductivity is manifestation of composite effect in the composite system. The influence of $La_2Mo_3O_{12}$ on electrical properties of composite is more pronounced at temperatures lower than temperature of the α-β phase transition ($\sim$580°C). However, addition of inert phase does not suppress the phase transition.

The dominant ionic conductivity is maintained both for $La_2Mo_2O_9$ matrix phase and for composites in the range of oxygen partial pressures $0.21-3.2\times10^{-5}$ atm.

Funding

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