Oxygen-Conducting Compounds with La$_2$Mo$_2$O$_9$ Structure in the Ternary System La$_2$Mo$_2$O$_9$–Sm$_2$W$_2$O$_9$–Sm$_2$Mo$_2$O$_9^+$: Synthesis and Properties

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Abstract—Polycrystalline samples in the ternary system La$_2$Mo$_2$O$_9$–Sm$_2$W$_2$O$_9$–Sm$_2$Mo$_2$O$_9^+$ were synthesized in air. The region of the existence of compounds with the lanthanum molybdate (La$_2$Mo$_2$O$_9$) structure in this system was determined. The polymorphism of the synthesized compounds was studied. Doping with samarium or with samarium and tungsten was shown to lead to the suppression of the transition between the monoclinic and cubic phases $\alpha \rightarrow \beta$ and the appearance of the transition $\beta_{ms} \rightarrow \beta$ between two cubic phases. In samples with a high samarium content, the phase transition $\beta_{ms} \rightarrow \beta$ manifests itself as significant anomalies in the temperature dependences of the dielectric permeability and electric conductivity. An increase in the concentration of samarium in the samples leads to a substantial decrease in the conductivity compared with the nondoped compound La$_2$Mo$_2$O$_9$.

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INTRODUCTION

The high ionic conductivity of the compound La$_2$Mo$_2$O$_9$ was found in 2000 by Lacorre et al. [1]. At present, this compound is extensively studied as a promising material for solid-state electrolytes.

At room temperature, lanthanum molybdate La$_2$Mo$_2$O$_9$ containing oxides La$_2$O$_3$ and MoO$_3$ in a ratio of 1 : 2 has a pseudo-cubic monoclinic structure with the unit cell parameter $a = 7.155$ Å [2]. This compound undergoes a first-order order–disorder phase transition (PT) $\alpha \rightarrow \beta$ at 580°C accompanied by an increase in the oxygen conductivity by two orders of magnitude [1]. The low-temperature monoclinic $\alpha$ phase is transformed into the cubic $\beta$ phase with dynamic disorder of oxygen atoms. A study of the characteristic features of PT in La$_2$Mo$_2$O$_9$ showed that, upon the rapid cooling of the compound existing in the $\beta$ phase, the latter remains in the metastable state $\beta_{ms}$ down to room temperature and it is transformed into the monoclinic $\alpha$ phase only upon heating to 450°C [3, 4]. The doping of La$_2$Mo$_2$O$_9$ with various ions replacing lanthanum or molybdenum, as a rule, leads to the suppression of the main phase transition $\alpha \rightarrow \beta$, but the transition $\beta \rightarrow \beta_{ms}$ persists; the temperature of the latter increases from 450 to 600°C with the increasing content of the dopant [4–6].

Rare earth molybdates containing oxides in a ratio of 1 : 2 are not formed with other rare earth elements, except for Pr$_2$Mo$_2$O$_9$ [7, 8]. The partial replacement of lanthanum in La$_2$Mo$_2$O$_9$ was studied by doping with Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, and Y [9–18]. A continuous series of solid solutions with La$_2$Mo$_2$O$_9$ was observed only for Pr [8]. In all other cases, limited solid solutions were obtained.

As for rare earth tungstates, Ln$_2$W$_2$O$_9$ exists for Ln = La, Pr, Nd, Sm, Eu, and Gd [19, 20]. At 1070°C, La$_2$W$_2$O$_9$ undergoes a phase transition from the triclinic to the cubic $\beta$ phase isostructural with $\beta$-La$_2$Mo$_2$O$_9$ [21–25]. At room temperature, tungstates with neodymium [20–23] and praseodymium [26, 27] containing oxides in a ratio of 1 : 2 have a monoclinic structure, which is transformed into an unknown phase at 320 and 420°C, respectively. The high-temperature phase of these compounds is cubic and appears at 1200 and 1255°C, respectively [26, 28, 29]. This phase is apparently isostructural with the cubic phase of La$_2$Mo$_2$O$_9$.

With the aim of extending the range of compounds with the La$_2$Mo$_2$O$_9$ structure, the ternary systems La$_2$Mo$_2$O$_9$–Pr$_2$W$_2$O$_9$–Pr$_2$Mo$_2$O$_9$ and La$_2$Mo$_2$O$_9$–Nd$_2$W$_2$O$_9$–Nd$_2$Mo$_2$O$_9$ were studied in [30]. The compound with the composition Nd$_2$Mo$_2$O$_9^+$ was marked with a symbol + because it is a mixture of the phases Nd$_4$Mo$_4$O$_{16}$ and Nd$_2$Mo$_2$O$_9$. Large regions of existence of compounds with the La$_2$Mo$_2$O$_9$ structure were found in these systems. In the system with Nd, the region of the existence of compounds with the La$_2$Mo$_2$O$_9$ structure is somewhat smaller than the Pr-containing system. It should be noted that, upon the
replacement of molybdenum in these systems with 10% of tungsten, lanthanum can be completely replaced with neodymium. The conductivity of the compounds found in the ternary systems appeared to be slightly lower than that of nondoped La$_2$Mo$_2$O$_9$.

The ternary system La$_3$Mo$_2$O$_9$–Sm$_2$W$_2$O$_9$–Sm$_2$Mo$_2$O$_9^+$ with the rare earth element Sm, the ionic radius of which is smaller than those of La, Pr, and Nd, is practically unknown. In [15], polycrystalline samples with different compositions were synthesized in the system La$_{2-x}$Sm$_x$Mo$_2$O$_9$ and solid solutions with the La$_2$Mo$_2$O$_9$ structure were obtained in the range 0 ≤ x ≤ 0.4. Only the melting point (1245°C) is known for the compound Sm$_2$W$_2$O$_9$ [31]. The X-ray powder diffraction pattern of this compound collected at room temperature provides evidence that this compound belongs to the monoclinic system [20]. In the present work we studied the phase formation, thermal and conducting properties, and the polymorphism of samarium-containing compounds with the La$_2$Mo$_2$O$_9$ structure in the abovementioned ternary system.

**EXPERIMENTAL**

Polycrystalline samples in the ternary system La$_3$Mo$_2$O$_9$–Sm$_2$W$_2$O$_9$–Sm$_2$Mo$_2$O$_9^+$ were prepared by solid-phase synthesis starting from La$_2$O$_3$, Sm$_2$O$_3$, MoO$_3$, and WO$_3$ of special purity grade. Rare earth