New oxide-ion conductors with La$_2$Mo$_3$O$_9$ structure

Elena Kharitonova, Valentina Voronkova, Ekaterina Orlova, Daria Kolesnikova, Faculty of Physics, M.V. Lomonosov Moscow State university (Russia). E-mail: harit@polyt.phys.msu.ru

The lanthanum molybdate La$_2$Mo$_3$O$_9$ (LM) attracts attention as perspective oxide ion conductor with the conductivity 0.06 S/cm at 800°C [1]. The molybdates of such composition with other rare earths, with the exception of praseodymium Pr [2], don’t exist under usual synthesis conditions; however there are tungstates with La, Pr, Nd, Sm, Eu, Gd [3]. LM has a phase transition of the order-disorder type at the temperature close to 580°C and two phases: low-temperature monoclinic α-phase and high-temperature cubic β-phase. La$_2$W$_2$O$_9$ (IW) has similar phase transition, but at the temperature of 1070°C [4, 5]. X-ray investigations showed that cubic LW β-phase corresponds to cubic LM β-phase [5]. The monoclinic Nd$_2$W$_2$O$_9$ (NW) and Pr$_2$W$_2$O$_9$ (PW) also have high-temperature transitions at 1255°C and 1200°C, respectively [6 - 9]. We can assume that the structure of high temperature NW and PW phases may be similar to that of LM and they may have oxide-ion conductivity.

With the aim of search of novel oxide-ion conductors with the LM structure compositions in the La$_2$Mo$_3$O$_9$ - Nd$_2$W$_2$O$_9$ - “Nd$_4$Mo$_6$O$_{19}$” (LM - NW - “NM”) and La$_2$Mo$_3$O$_9$ - Pr$_2$W$_2$O$_9$ - Pr$_2$Mo$_3$O$_9$ (LM - PW - PM) systems were examined.

All specimens were prepared by solid state synthesis. The expansive field of the compounds with the LM-structure was discovered in the above systems. It should be noted, that in both systems the compounds with LM structure and full substitution of La for other lanthanide (Pr, Nd) are formed. Pure PM decomposes at 700 - 900°C with arising of Pr$_2$Mo$_3$O$_9$ and recombines into itself at higher temperatures (above 1000°C). An addition of 10% W or La in PM-based solid solutions leads to disappearance of this instability. Pure “NM” is a mix of Nd$_2$Mo$_6$O$_{19}$ and Nd$_4$Mo$_6$O$_{19}$-type compounds with LM-type structure are formed in pseudo binary “NM” - NW system even at small amount of W (3 - 7%).

In the case of LM - NW - “NM” system the α → β phase transition, which was observed in pure LM, is suppressed with addition of Nd or W and cubic phase was stabilized at room temperature in all synthesized compounds. The pure PM is monoclinic at room temperature and undergoes the α → β phase transition at 520 - 540°C. However, mutual substitution La and Pr leads to disappearance of this transition and stabilization of cubic phase at 50 - 60% Pr. The cubic phase is also stabilized at room temperature on addition of W similar to Nd contained system.

All synthesized compounds with LM structure show high anionic conductivity like LM (10$^{-2}$ - 10$^{-2}$ S/cm at 800°C). An addition of Nd and W leads to little decreasing of conductivity value. The conductivity of NW compound was no better than 10$^{-4}$ S/cm at 800°C.

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