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New entropy-stabilized lanthanum–samarium molybdates with a fluorite-like structure

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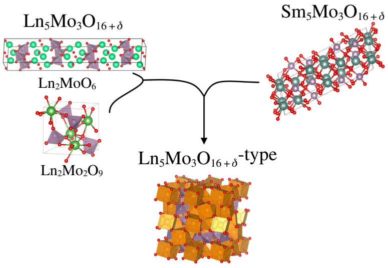
Novel lanthanum–samarium molybdates with a fluorite-like structure were synthesized from metal oxides using solid-state synthesis. The total conductivity of these phases reached 10^{-2} S cm^{-1} at 700 °C.



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The rare-earth element (REE) molybdates $Ln_5Mo_3O_{16+\delta}$, where Ln = La to Tb, exhibit exceptionally high oxide-ionic conductivity.[1,2] These molybdates (cubic symmetry with the space group[3]) can be synthesized for rare-earth elements ranging from La to Tb under reducing conditions. The oxidation of these compounds leads to the formation of oxidized phases, which are metastable for most rare-earth elements in the series from La to Tb except for praseodymium and neodymium.[4,5] Among the oxidized phases, the lanthanum molybdate exhibited the highest ionic conductivity, but it decomposed into a mixture of La_2MoO_6 and $La_2Mo_2O_9$ phases when exposed to air.[1] Furthermore, substituting lanthanum for neodymium in the isostructural neodymium molybdate significantly enhanced the overall conductivity.[2]

The cubic structure of lanthanum molybdates can be stabilized through aliovalent isomorphous substitutions in the lanthanum and molybdenum sublattices with ions of lowers charge.[6,7] However, this approach often leads to an undesirable reduction in the number of charge carriers and lower conductivity values. Therefore, the stabilization of the cubic structure of lanthanum molybdate without diminishing the oxygen content is of interest in the context of developing new oxygen-ion conductors.

There is no consensus in the literature regarding the stoichiometry of these compounds. Cubic fluorite-like molybdates of neodymium and praseodymium have been attributed to wide ranges of homogeneity from 3 : 4 to 7 : 8 for neodymium molybdate and from 8 : 11 to 7 : 8 for a praseodymium analogue.[5,8] The existence of the solid solutions was supported by the mutual substitutions of rare-earth metals and molybdenum.[9] It can be assumed that in some cases, for fluorite-like REE molybdates, compositions with reduced molybdenum content in the system may be more stable compared to $Ln_5Mo_3O_{16+\delta}$. Therefore, the investigation of the $La_{5-x}Sm_xMo_{3-y}O_{16+\delta-3y}$ system is of interest.

Samples of the $La_{2.5}Sm_{2.5}Mo_{3-y}O_{16.5-3y}$ system ($y = 0$, 0.125, 0.25, 0.375, or 0.5) were synthesized from stoichiometric mixtures of precalcined metal oxides (purity of at least 99.9%) by a solid-state method. The synthesis was carried out with the assumption that the interaction proceeded through the following reaction:

$$2.5La_2O_3 + 2.5Sm_2O_2 + (3-y)MoO_2 \rightarrow La_{2.5}Sm_{2.5}\,Mo_{3-y}O_{16.5-3y}.$$

Isovalent replacement of lanthanum with samarium, which has a smaller ionic radius [$r_i(La^{+3}) = 1.16$ Å and $r_i(Sm^{+3}) = 1.079$ Å for coordination number 8 (Shannon)], in the $La_{5-x}Sm_xMo_3O_{16+\delta}$ system led to the formation of a cubic fluorite-like phase within the equimolar composition range (Figure 1, curve *1*). However, single-phase samples were not obtained. The impurity phase was identified as the molybdate $La_2Mo_2O_9$ based on energy-dispersive X-ray spectroscopy (EDX) and XRD analysis. The concentration of the impurity phase $La_2Mo_2O_9$ diminished with decreasing molybdenum oxide content of the $La_{2.5}Sm_{2.5}Mo_{3-y}O_{16.5-3y}$ system, and a sample of $La_{2.5}Sm_{2.5}Mo_{2.75}O_{15.75}$ ($y = 0.25$) was single-phase (Figure 1, curve *3*). Further reduction in the molybdenum oxide content was accompanied by the appearance of diffraction peaks corresponding to a tetragonal phase with a La_2MoO_6-type structure and space group $I4_1/acd$ (Figure 1, curve *4*). The compound with $y = 0.5$ corresponded to the equimolar composition in the $La_{2-x}Sm_xMoO_6$ system (Figure 1, curve *5*), where La_2MoO_6 and monoclinic Sm_2MoO_6 (space group $C2/c$) phases coexisted.

The formation of a fluorite-like phase with a cubic structure, which is not characteristic of lanthanum and samarium molybdates of this composition, can be explained by an increase in mixing entropy due to the presence of two cations occupying the same positions in the crystal structure. Moreover, the enthalpy of mixing for the cubic phase is minimal, as the average ionic radius of lanthanum and samarium is close to the radius of neodymium, for which this structure is stable. Despite the fact that the mixing entropy of a two-component solid solution takes on small values compared to high-entropy solid

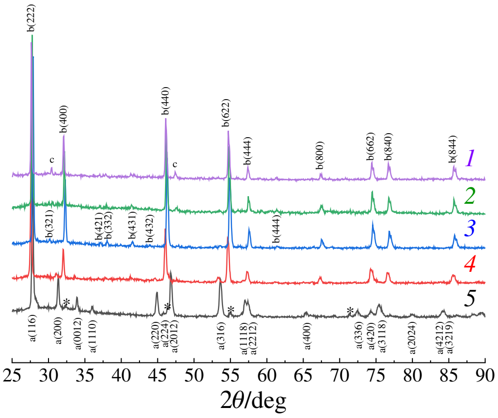

Figure 1 XRD patterns of $La_{2.5}Sm_{2.5}Mo_{3-y}O_{16.5-3y}$ samples: y = (*1*) 0, (*2*) 0.125, (*3*) 0.25, (*4*) 0.375, and (*5*) 0.5. (a) La_2MoO_6, (b) $Ln_5Mo_3O_{16+\delta}$, (c) $La_2Mo_2O_9$, and (*) Sm_2MoO_6.

solutions, apparently, it is sufficient for stabilizing the cubic fluorite-like structure.

The EDX results confirmed that the impurity phase in the sample with $y = 0.125$ was a solid solution based on $La_2Mo_2O_9$, while it corresponds to La_2MoO_6 (Online Supplementary Materials, Table S1) for the sample with $y = 0.375$. The even distribution of elements on the sample surface with $y = 0.25$ confirmed its homogeneity, and the experimentally determined elemental composition was consistent with that calculated by the formula.

Low-intensity reflections in the diffraction patterns of compositions with $y = 0$ and 0.125 were successfully described using the Rietveld method with the cubic $La_2Mo_2O_9$ structure (Figures S1, S2). For the sample with $y = 0.375$, the tetragonal La_2MoO_6 structure was applied to describe impurity reflections (Figure S2). The smaller unit cell parameters of the impurity phases [$a = 7.155$ Å for $La_2Mo_2O_9$,[10] and $a = 5.79701(3)$ Å and $b = 32.0353(3)$ Å for La_2MoO_6[11]] were due to the partial substitution of lanthanum with smaller samarium, which is consistent with the results of elemental analysis (Table S2).

A decrease in the molybdenum oxide content of the system led to an increase in the unit cell parameter of the fluorite-like phase. This dependence can be explained by a redistribution of larger lanthanum and smaller samarium ions between the phases present in the system. As the value of y increased, the concentration of the higher lanthanum impurity phase $Ln_2Mo_2O_9$ decreased. This led to increasing the lanthanum content in the structure of the fluorite-like lanthanum–samarium molybdate. An increase in the lanthanum content of the $Ln_5Mo_3O_{16+\delta}$ phase led to an increase in the unit cell parameter. The occupancy of the molybdenum position (12*d*) was also refined for the single-phase composition with $y = 0.25$, and the refined value was 0.93(3), which corresponds to the calculated formula $La_{2.5}Sm_{2.5}Mo_{2.75}O_{15.75}$.

Interatomic distances calculated from the refined atomic coordinates are provided in Table S3. Compared to the known fluorite-like molybdates of neodymium and praseodymium, which can be obtained by the calcination of starting oxides in air, lanthanum–samarium molybdates exhibited high Ln1–O1 and Ln2–O2 interatomic distances due to the larger lanthanum ions occupying rare-earth element positions in the structure.

The relationship between conductivity and temperature follows the Arrhenius equation, and it can be described as a straight line in the $\log\sigma - 1000/T$ coordinates for all samples in the test temperature range (Figure 2).

A decrease in the concentration of the highly charged Mo^{6+} ions in the $La_{2.5}Sm_{2.5}Mo_{3-y}O_{16.5-3y}$ system resulted in the elimination of stronger electrostatic interactions between the charge carriers (O^{2-}) and the cationic sublattice. The activation energy decreased with decreasing molybdenum content (1.01, 0.97, and 0.88 eV for y = 0, 0.125, and 0.25, respectively). However, a decrease in the molybdenum oxide content also led to a decrease in the pre-exponential factor due to the elimination of charge carrier particles.

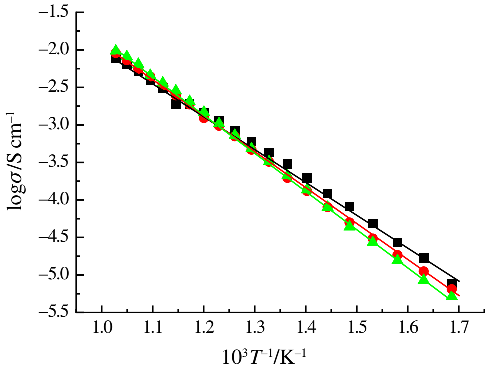

Figure 2 Plots of $\log\sigma = f(1000/T)$ for $La_{2.5}Sm_{2.5}Mo_{3-y}O_{16.5-3y}$ samples: y = (▲) 0, (●) 0.125, and (■) 0.25.

For compositions close to $La_{2.5}Sm_{2.5}Mo_{2.75}O_{15.75}$ but containing impurity phases (y = 0 and 0.125), the conductivity was apparently determined by the main phase, as the nature of the dependence of conductivity was similar to that of the single-phase sample. Thus, we can conclude that the presence of impurity phases in small quantities did not significantly affect the conductivity.

For the first time, we successfully synthesized single-phase mixed lanthanum–samarium molybdates with a fluorite-like structure. The experimental results not only broadened the range of similar compounds but also served as a useful tool for predicting new functional materials with different structures.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.02.044.

References

1 M. Tsai, M. Greenblatt and W. McCarroll, *Chem. Mater.*, 1989, **1**, 253.
2 E. I. Get'man, K. A. Chebyshev, L. V. Pasechnik, L. I. Ardanova, N. I. Selikova and S. V. Radio, *J. Alloys Compd.*, 2016, **686**, 90.
3 P. H. Hubert, *Bull. Soc. Chim. Fr.*, 1975, 475.
4 M. J. Martínez-Lope, J. A. Alonso, D. Sheptyakov and V. Pomjakushin, *J. Solid State Chem.*, 2010, **183**, 2974.
5 M. Mokhosoev and E. Get'man, *Izv. Akad Nauk SSSR, Ser. Neorg. Mater.*, 1969, **5**, 908 (in Russian).
6 J. P. Faurie and R. Kohlmuller, *Rev. Chim. Miner.,* 1971, **8**, 241.
7 T. D. Vu, F. Krichen, M. Barre, R. Busselez, K. Adil, A. Jouanneaux, E. Suard and F. Goutenoire, *J. Solid State Chem.*, 2016, **237**, 411.
8 V. I. Voronkova, I. A. Leonidov, E. P. Kharitonova, D. A. Belov, M. V. Patrakeev, O. N. Leonidova and V. L. Kozhevnikov, *J. Alloys Compd.*, 2014, **615**, 395.
9 A. M. Antipin, N. I. Sorokina, O. A. Alekseeva, A. N. Kuskova, E. P. Kharitonova, E. I. Orlova and V. I. Voronkova, *Acta Crystallogr.*, 2015, **B71**, 186.
10 P. Lacorre, F. Goutenoire, O. Bohnke, R. Retoux and Y. Laligant, *Nature,* 2000, **404**, 856.
11 J. S. Xue, M. R. Antonio and L. Soderholm, *Chem. Mater.*, 1995, **7**, 333.

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