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Silver Magnesium Molybdate and Silver Cobalt Molybdate: Synthesis and Ionic Conductivity

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Abstract—Impedance spectroscopy, X-ray powder diffraction, and electron microscopy are used to study silver magnesium and silver cobalt molybdates of composition $Ag_2A_2^{II}(MoO_4)_3$ (A = Mg, Co) and the products of their aliovalent doping by scandium(III) and vanadium(V). The double molybdates have high ionic conductivities at temperatures above 600 K. A partial aliovalent substitution of scandium for magnesium or vanadium for molybdenum increases the ionic conductivity of the molybdates below 473 K. The defect mobility and the enthalpy of defect formation in the $Ag_2Mg_2(MoO_4)_3$ structure are estimated proceeding from the experimental data.

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The demand for alternative energy sources gives an impetus to the search for new functional materials with high ionic conductivities. NASICON compounds (e.g., $LiZr_2(PO_4)_3$) are important in this respect [1, 2]. The NASICON structure is distinguished by large interstices, which are partially populated by low-charge cations and form two types of channels [3].

$M_2^IA_2^{II}(MoO_4)_3$ molybdates of uni- and divalent metals may be classified with the NASICON family [4]. The low charge, high polarizability of the electron shell, and cation radius approaching 1 Å allow us to classify silver as a "magic ion," whose compounds typically have high ionic conductivities [2].

Silver zinc molybdate $Ag_2Zn_2(MoO_4)_3$, prepared in [5], was found to have the $Na_2Mg_5(MoO_4)_6$ type structure [6]. $Na_2Mg_5(MoO_4)_6$ crystallizes in triclinic space group $P\bar{1}$. The $Ag_2A_2(MoO_4)_3$ (A = Mg, Mn, Co) double molybdates are isostructural to zinc silver molybdate [7]. Their structure is a three-dimensional framework, formed by MoO_4 tetrahedra and distorted AO_6 octahedra with average A–O distances of 2.081–2.085 Å for the magnesium compound and 1.986–2.136 Å for the cobalt compound [7]. The silver cations reside in interstices which form channels in the framework (Fig. 1). The channel size increases with the radius of the divalent element. Site splitting is observed for $Ag(I) \longrightarrow Ag(1A) + Ag(1B)$ [7], which is intrinsic to NASICON compounds [3]. It was also reported in [7] that $Ag_2Mg_2(MoO_4)_3$ experiences a reversible polymorphic transition at 773–803 K and that it melts incongruently at 1013 K; $Ag_2Co_2(MoO_4)_3$ melts incongruently at 900 K.

The goal of this work was to synthesize and investigate the ionic conductivity of $Ag_2A_2(MoO_4)_3$ double molybdates with A = Mg or Co and the products of their aliovalent doping by scandium and vanadium ions.

EXPERIMENTAL

Two routes were used to synthesize the double molybdates. The first route was as follows. Neutral silver and divalent metal molybdates were synthesized from molybdenum(VI) oxide (Acros, 99%), reagent grade silver nitrate, high-purity grade magnesium carbonate, and pure grade basic cobalt carbonate. Blends of the reagents were stirred in an agate mortar and annealed at 523–723 K for Ag_2MoO_4 and 523–973 K for $MgMoO_4$ and $CoMoO_4$, with the temperature elevated in 50-K steps. Annealing at each intermediate temperature lasted 10–15 h and was followed by stirring. In addition, Ag_2MoO_4 was prepared from solution by the exchange reaction

$$2AgNO_3 + Na_2MoO_4 \longrightarrow Ag_2MoO_4\downarrow + 2NaNO_3. \quad (1)$$

Both compounds were dissolved in hot water and combined under thorough stirring. The resulting precipitate was repeatedly washed with water by decantation until sodium cations were fully removed and then centrifuged.

The $Ag_2A_2(MoO_4)_3$ (A = Mg, Co) molybdates were prepared according to [7] from silver molybdate and divalent metal molybdate. A stoichiometric blend of the components was stirred in an agate mortar and annealed at 623–773 K with temperature elevation in 50-K steps, exposures at each temperature for 10–15 h,

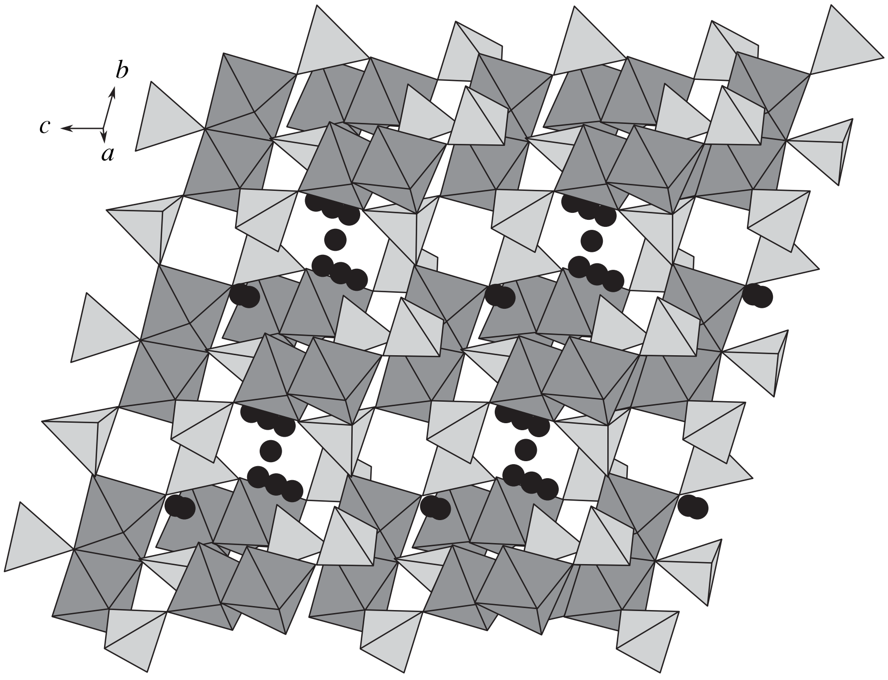

Fig. 1. Structure of $Ag_2A_2(MoO_4)_3$ (A = Mg, Mn, Co) double molybdates.

and intermittent stirring. The individual double molybdates were obtained as a result.

The above-described synthesis route requires a long time. Therefore, we used an alternative route to prepare the double molybdates, directly from molybdenum(VI) oxide, divalent metal carbonates, and silver(I) nitrate. A thoroughly stirred stoichiometric blend of the reagents was annealed using a similar scheme at 473–773 K with intermittent stirring, with the intermediate exposures shortened to 2–3 h.

The same scheme was used to synthesize silver magnesium molybdate samples in which magnesium ions were partially replaced by scandium or molybdenum ions were partially replaced by vanadium: $(Ag_{2-x}Mg_{2-x}Sc_x(MoO_4)_3$ and $Ag_{2+3x}Mg_2(Mo_{1-x}V_xO_4)_3$ ($x = 0.01$). The dopants used were reagent grade scandium oxide and high-purity grade vanadium oxide.

X-ray powder diffraction analysis was carried out using a Guinier FR-552 camera ($CuK_{\alpha 1}$ radiation, a germanium standard). X-ray diffraction patterns were scanned and digitized using specially designed software.

Microstructures were observed with a LEO Supra 50 VP scanning electron microscope. The distribution of the chemical elements was studied on a Jeol JSM-840A scanning electron microscope equipped with a PGT IMIX attachment for electron probe microanalysis.

Thermal analysis was performed on a Paulik-Paulik-Erdey Q-1500 D derivatograph and a Netzsch TG 209 F1 thermobalance using platinum crucibles. The heating rate was 10 K/min. The sample sizes were 0.3–0.5 g for the derivatograph and 10–20 mg for the thermobalance.

The conductivity was measured on cylindrical compacted pellets ($R = 2.5$ mm, $h = 3$ mm) with platinum leads from 298 to 773 K in 10-K steps using an IPU-p.62 ac bridge. The conductivity was found by extrapolating a semicircle to the ohmic resistance axis.

Figures 2a and 2b are micrographs of samples prepared using the second route. These samples are homogeneous crystalline masses with grain sizes of 1–2 mm for $Ag_2Mg_2(MoO_4)_3$ and 2–6 mm for $Ag_2Co_2(MoO_4)_3$. The electron probe shows the uniform distributions of molybdenum and the divalent metals; the cation ratio is as in the batch.

X-ray powder diffraction shows that Ag_2MoO_4 crystallizes in the cubic system ($a = 9.305(3)$ Å). However, the compound prepared by the solid-phase reaction contained some impurities. Therefore, we used the Ag_2MoO_4 sample deposited from solution in the synthesis of the double molybdates. Magnesium and cobalt molybdates are monoclinic; their refined unit cell parameters are $a = 10.27(1)$ Å, $b = 9.280(5)$ Å, $c = 7.019(5)$ Å, $\beta = 106.88(8)°$ and $a = 4.655(8)$ Å, $b = 5.680(6)$ Å, $c = 4.911(4)$ Å, $\beta = 89.511(9)°$, respectively.

Silver magnesium molybdate and silver cobalt molybdate are triclinic. Their X-ray diffraction patterns were indexed using the unit cell parameters from [7] (space group $P\bar{1}$). The products of aliovalent doping of $Ag_2Mg_2(MoO_4)_3$ by scandium and vanadium ions have

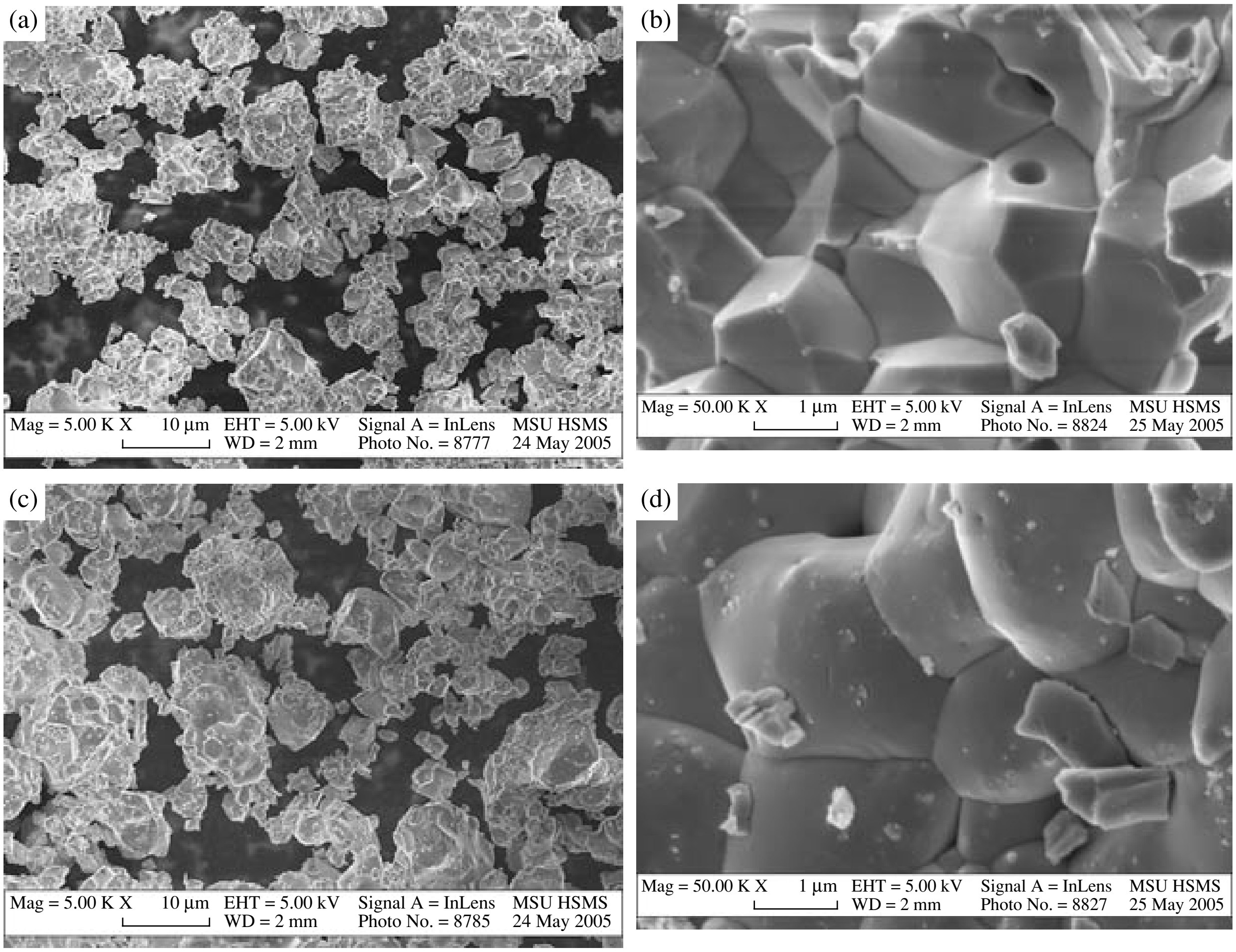

Fig. 2. Micrographs of (a, b) $Ag_2Mg_2(MoO_4)_3$ and (c, d) $Ag_2Co_2(MoO_4)_3$: (a, c) intact samples and (b, d) discs annealed at 773 K.

similar sets of reflections with slightly different unit cell parameters; therefore, we may say that solid solutions are formed.

Compacted materials noticeably change their conductivity upon sintering. The conductivities of the samples in the range 350–550 K during the second heating are 1.5–2 orders of magnitude higher than the values measured during the first heating. Subsequent heating/cooling cycles almost do not change the conductivity. The micrographs of the fracture of pellets obtained after preheating to 773 K show that the microstructure has noticeably changed during the annealing: single crystals are aggregated, and their edges are smoothed (Figs. 2b, 2d). Most likely, incipient (surface) melting occurs, although melting per se occurs at higher temperatures as shown by DTA: for $Ag_2Mg_2(MoO_4)_3$ at ~950 K (the half-width of the DTA peak is 80 K). The enhanced growth in conductivity of $Ag_2Mg_2(MoO_4)_3$ crystals at high temperatures (Fig. 4, curve *a*) also provides an argument in favor of the possibility of incipient, surface melting. The density of the substance during the annealing changes only insignificantly, increasing from 92 ± 1 by 0.5–0.7%. The change in the conductivity is most likely due to improved grain contacts.

Thus, pellets of the double molybdates are sintered at high temperatures. Accordingly, the ionic conductivity was then measured on samples presintered at 773 K.

Figure 4 displays the ionic conductivity σ versus reciprocal temperature for preannealed $Ag_2Mg_2(MoO_4)_3$ and $Ag_2Co_2(MoO_4)_3$ samples in the coordinates of the Frenkel equation:

$$\sigma T = A\exp(-E_a/RT). \qquad (2)$$

Here A is the frequency factor, E_a is the activation energy of conductivity, T is temperature in Kelvin degrees, and R is the universal gas constant. The calculated values of the activation energy and frequency factor for these samples are listed in the table. The magnesium compound has a high activation energy of conductivity, likely because of the smaller sizes of the interstices in which silver ions reside and the bordering faces of coordination polyhedra that silver(I) ions have to overcome when migrating.

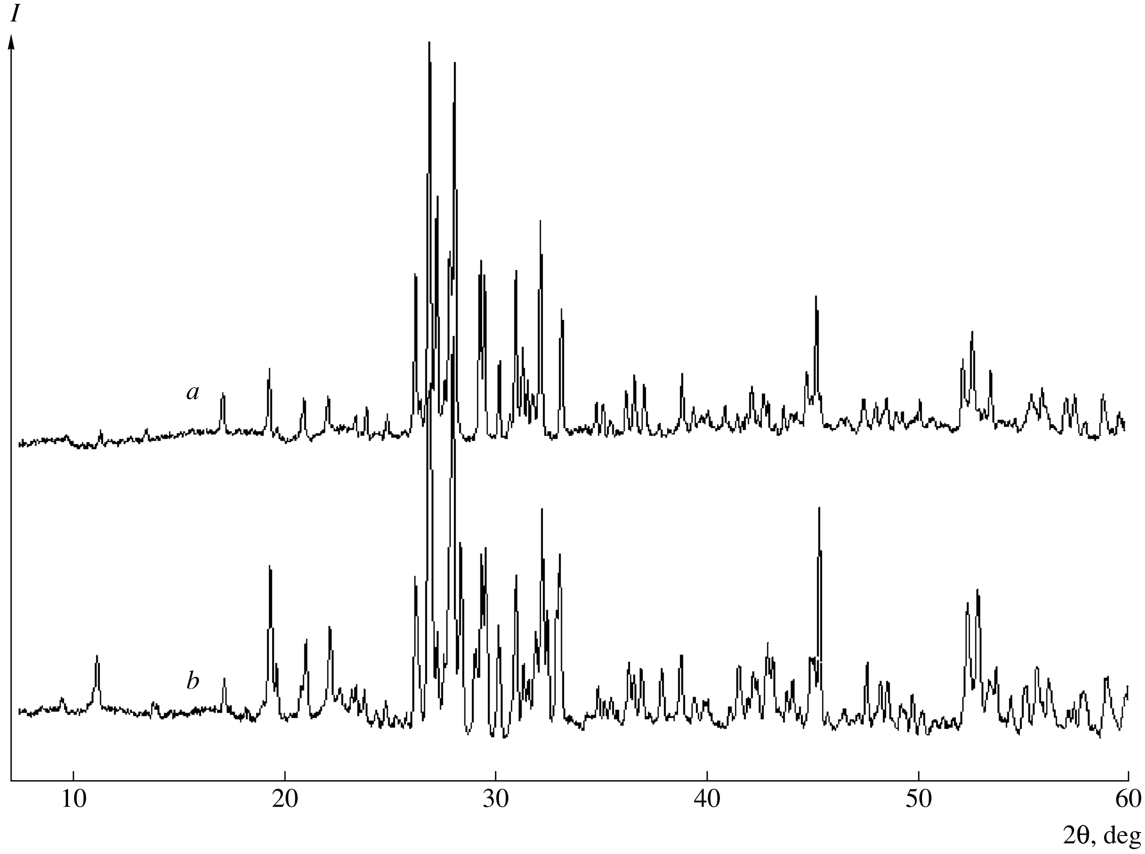

Fig. 3. X-ray diffraction patterns for (*a*) $Ag_2Mg_2(MoO_4)_3$ and (*b*) $Ag_2Co_2(MoO_4)_3$.

Aliovalent doping appreciably increases the ionic conductivity at low temperatures (below 473 K). At higher temperatures, the conductivities of doped materials nearly coincide with the conductivity of undoped $Ag_2Mg_2(MoO_4)_3$ (Fig. 5). This is because of doping-induced defect generation. Dopant scandium ions enter magnesium positions (Sc^{*}_{Mg}), with silver vacancies (V'_{Ag}) generated in order for the electroneutrality to hold. Here, in accordance with the Kröger and Wink symbolism [8], subscripts indicate the structural position in which the particle is situated and superscripts "*" and " ' ", respectively, denote the positive or negative charge of the particle relative to its position in the lattice. Accordingly, dopant vanadium ions enter molybdenum positions (V'_{Mo}), and extra silver ions enter interstices (Ag^{*}_{i}). At low dopant levels, the defect concentration may roughly be equated to the dopant ion concentration and the activation energy of conductivity equals the activation energy of mobility for defects (E_m). From the table, it follows that the activation energy of migration through vacancies for silver ions is slightly higher than the activation energy of migration through interstices. The frequency factor is dramatically reduced since the transport is controlled by the

Activation energies of conductivity for the $Ag_2A_2(MoO_4)_3$ (A = Mg, Co) double molybdates

Compound	Temperature range, K	E_a, kJ/mol	A, S K/cm
$Ag_2Mg_2(MoO_4)_3$	773–300	79 ± 1	$(1.2 \pm 0.3) \times 10^5$
$Ag_2Co_2(MoO_4)_3$	773–300	62.4 ± 0.6	$(1.1 \pm 0.1) \times 10^4$
$Ag_{1.99}Mg_{1.99}Sc_{0.01}(MoO_4)_3$	773–473	77 ± 1	$(4.7 \pm 0.9) \times 10^4$
	473–297	18.5 ± 0.9	$(1.3 \pm 0.3) \times 10^{-2}$
$Ag_{2.03}Mg_2(Mo_{0.99}V_{0.01}O_4)_3$	773–473	74 ± 1	$(3.6 \pm 0.8) \times 10^4$
	473–295	13 ± 2	$(2.1 \pm 0.8) \times 10^{-3}$

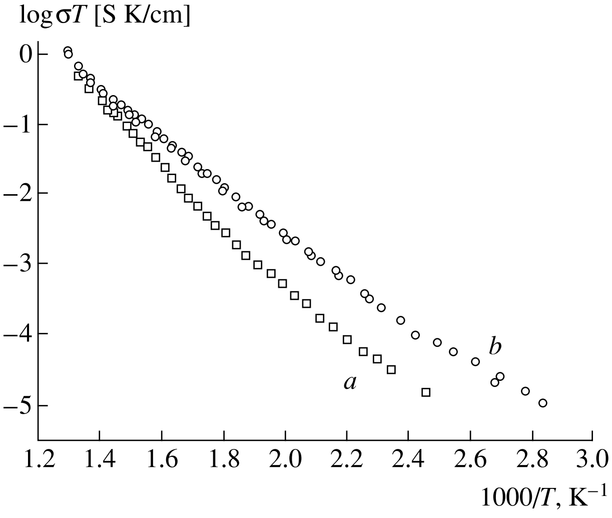

Fig. 4. Ionic conductivity vs. reciprocal temperature plots in the rectifying coordinates of the Frenkel equation for (*a*) $Ag_2Mg_2(MoO_4)_3$ and (*b*) $Ag_2Co_2(MoO_4)_3$.

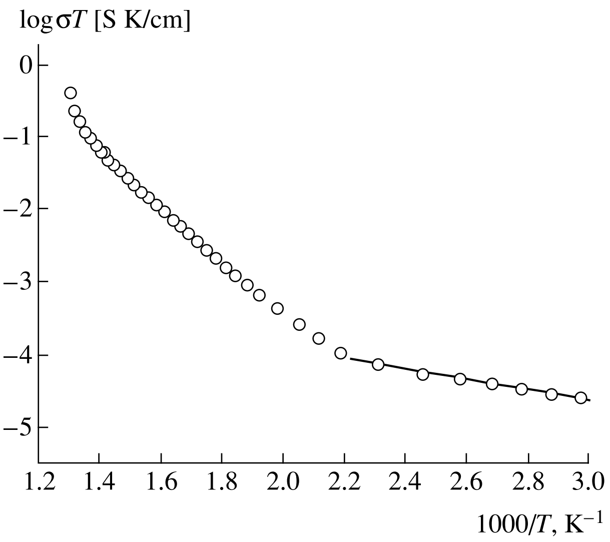

Fig. 5. Ionic conductivity vs. reciprocal temperature plot in the rectifying coordinates of the Frenkel equation for $Ag_{2.03}Mg_2(Mo_{0.99}V_{0.01}O_4)_3$.

concentration of inserted defects [2], which is far lower than the overall silver ion concentration. The calculated conductivity values for silver interstitials and vacancies at 300 K are 3.5×10^{-4} and 6×10^{-4} cm^2/(V s), respectively.

At high temperatures, intrinsic disorder dominates:

$$0(\text{ideal } Ag_2Mg_2(MoO_4)_3 \text{ crystal}) \Leftrightarrow V'_{Ag} + Ag_i^{*}. \tag{3}$$

The activation energy of conductivity equals $E_m + 1/2\Delta H$, where ΔH is the enthalpy of defect formation by reaction (2); for $Ag_2Mg_2(MoO_4)_3$, ΔH is calculated to be 120 ± 8 kJ/mol.

In summary, the $Ag_2A_2^{II}(MoO_4)_3$ (A = Mg, Co) compounds have relatively high ionic conductivities above 600 K; they are distinguished by high silver ion mobilities in migration through both vacancies and interstices. The high enthalpy of defect formation (120 ± 8 kJ/mol) is the major factor inhibiting a high ionic conductivity at low temperatures. We have shown that the directed defect generation in the structure through aliovalent doping is a way to solve the problem.

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