Synthesis, crystal structure and electrophysical properties of triple molybdates containing silver, gallium and divalent metals

A possibility of the triple molybdates formation with both NASICON-like and NaMg$_3$In(MoO$_4$)$_5$ structures in the Ag$_2$MoO$_4$–AMoO$_4$–Ga$_2$(MoO$_4$)$_3$ (A = Mn, Co, Zn, Ni) systems was studied by powder X-ray diffraction analysis. It was established that NASICON-like phases Ag$_{2-x}$A$_{1-x}$Ga$_{1+x}$(MoO$_4$)$_3$ are not formed. The triple molybdates Ag$_x$Ga(MoO$_4$)$_5$ (A = Mn, Co, Zn) isosstructural to triclinic NaMg$_3$In(MoO$_4$)$_5$ (sp. gr. P$ar{1}$, Z = 2) were synthesized and characterized. The structure of the obtained compounds was refined for AgZn$_3$Ga(MoO$_4$)$_5$ according to the powder data by the Rietveld method. The structure consists of MoO$_4$ tetrahedra, couples of edge-shared M(1)O$_6$ octahedra, and trimers of edge-shared M(2)O$_6$, M(3)O$_6$ and M(4)O$_6$ octahedra, which are linked by the common vertices to form a 3D framework. High-temperature conductivity measurements revealed that the conductivity of AgMn$_3$Ga(MoO$_4$)$_5$ at 500°C reaches 10$^{-2}$ S/cm, which is close to one of the known NASICON-type ionic conductors.

Keywords: triple molybdates; silver; gallium; solid-state synthesis; powder X-ray diffraction; Rietveld refinement; ionic conductivity.

Introduction

A synthesis and studying of complex oxide compounds, the development of new materials with functionally significant properties based on those are among the main areas of the materials science. An important place in the study and obtaining of new phases with valuable physicochemical properties belongs to molybdates, in particular triple ones, which are among the fastest-growing groups of complex oxide compounds containing a tetrahedral anion and three different cations. One of the largest families of these compounds is molybdates containing 1-, 2- and 3-charged cations. In particular, silver-containing NASICON-like phases

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Ag_{1-x}A_{1-x}R_{1+x}(MoO_4)_3 (A = Mg, Co, R = Al; A = Mg, R = In) with different homogeneity range and triclinic AgA_xR(MoO_4)_5 (A = Mg, R = Cr, Fe, Ga; A = Mn, R = Al, Cr, Fe, Sc, In) having high ionic conductivity (10^{-3}–10^{-2} S/cm) are of interest. For a number of phases: AgMg_{3}R(MoO_4)_5 (R = Cr, Fe), AgMn^{II}_{3}(Mn^{III}_{0.26}Al_{0.74})(MoO_4)_5, Ag_{0.90}Al_{1.06}Co_{2.94}(MoO_4)_5, and AgFe^{II}_{3}Fe^{III}(MoO_4)_5 single crystals were obtained and their crystal structures were determined [1–9].

The purpose of this work is to study the possibility of forming triple molybdates Ag_{1-x}A_{1-x}Ga_{1+x}(MoO_4)_3 and AgA_xGa(MoO_4)_5 (A = Mn, Co, Zn, Ni) and investigate crystal structure and electro-physical properties of the obtained compounds.

**Experimental**

The initial materials were simple molybdates of silver, manganese, cobalt, zinc, nickel, MoO_3, and Ga_2O_3 (reagent grade).

Ag_2MoO_4 and molybdates of divalent metals were obtained by the step annealing of stoichiometric mixtures of AgNO_3 (analytical grade), MnO, Co(NO_3)_2·6H_2O, ZnO, MoO_3 (all chemically pure), NiO (reagent grade) at 350–450 °C (Ag_2MoO_4), 400–750 °C (MnMoO_4), 300–700 °C (CoMoO_4), 500–700 °C (ZnMoO_4), 450–750 °C (NiMoO_4) in the air with intermittent grindings every 15 hours for better sample homogenization. Power X-ray diffraction (PXRD) patterns of the prepared compounds do not contain reflections of starting or impurity phases. PXRD and thermal characteristics of all prepared compounds agree well with corresponding data reported in [10–15].

Sample compositions Ag_{1-x}A_{1-x}Ga_{1+x}(MoO_4)_3 (0 ≤ x ≤ 0.7, Δx = 0.1) and AgA_xGa(MoO_4)_5 were prepared by the annealing of appropriate stoichiometric mixtures of Ag_2MoO_4, AMoO_4, MoO_3 and Ga_2O_3. The initial mixtures were annealed starting at 300 °C followed by raising the temperature by 20–50 °C (in some cases, 5–10 °C) with intermittent grindings every 20–30 hours for sample homogenization. The calcination time at each temperature was 30–70 h. The phase composition of the obtained products was controlled by the PXRD analysis before each increasing of the annealing temperature.

PXRD patterns were collected at room temperature on a Bruker D8 ADVANCE diffractometer using Cu Kα radiation in the 2θ range from 5° to 100° with a step of 0.02076°. Possible impurity phases were checked by comparing their PXRD patterns with those in the Powder Diffraction File. The crystal structure refinement was carried out with the GSAS [16] program suite using PXRD data. Lattice parameters and individual scale factors were established, and five common peak-shape parameters of the pseudo-Voigt function (No. 2), one asymmetry parameter and one parameter for the zero-point correction were used to describe the powder patterns. The background level was described by a combination of 15-order Chebyshev polynomials. Isotropic displacement parameters (Uiso) were refined, and grouped by chemical similarity by used constrains.

Thermoanalytic studies were carried out on a STA 449 F1 Jupiter NETZSCH thermoanalyser (Pt crucible, heating rate of 10 °C/min in Ar stream).

Ceramic disks for dielectric investigations were prepared by the calcination of pressed powder at 600 °C for 2 h. The disks were of 9–10 mm in diameter and...
1–2 mm thick, the electrodes were deposited by painting the disk bases with colloidal platinum followed by subsequent one hour annealing at about 580 °C. The direct current (DC) electric conductivity was measured with a V7–38 microammeter. To study the ion transfer, electrical conductivity was measured on an alternating current (AC) by the two-contact method in the frequency range 1 Hz–1 MHz in the temperature range 25–560 °C at the rate of 4 °C/min at both heating and cooling using a Novocontrol Beta-N impedance analyzer. The activation energy of electrical conductivity was calculated from the slope of the straight lines corresponding to the Arrhenius dependence in \( \lg(\sigma T) - (10^3 / T) \) coordinates.

Results and discussion

**PXRD characteristics**

The presence of NASICON-like phases in the \( \text{Ag}_2\text{MoO}_4-\text{AMoO}_4-\text{Ga}_2(\text{MoO}_4)_3 \) systems was determined according to PXRD analysis of samples \( \text{Ag}_{1-x}\text{A}_x\text{Ga}_{1+x}(\text{MoO}_4)_3 \) (\( 0 \leq x \leq 0.7, \Delta x = 0.1 \)) which were annealed in the temperature range from 300 °C to melting point. The final annealed temperature was 550–700 °C and depended on both the composition of the reaction mixtures and the nature of the divalent metal. It was established that, despite the close values of the Al\(^{3+}\) (0.53) and Ga\(^{3+}\) (0.62 Å [17]) radii, gallium containing triple molybdates with NASICON-like structure, apparently, do not exist. All our attempts to obtain rhombohedral phases \( \text{Ag}_{1-x}\text{A}_x\text{Ga}_{1+x}(\text{MoO}_4)_3 \), by solid state synthesis did not lead to a positive result, probably this is due to the low reactivity of gallium in the molybdate systems. Thus, the simple gallium molybdate \( \text{Ga}_2(\text{MoO}_4)_3 \) has not yet been obtained by ceramic technology, and only recently it was synthesized by the sol-gel method [18]. Besides, silver-gallium double molybdate is not synthesized either by ceramic technology or by co-precipitation. In [19] this compound was obtained by the calcining of mixtures of \( \text{AgNO}_3, \text{Ga}_2\text{O}_3, \text{MoO}_3 \) (in ratio 2:1:4) at 350–400 °C for 8–10 h, followed by cooling, homogenization, and the repeated 12–20 hours annealing at 500–550 °C, but the PXRD data of the product are not given by the authors. It should be noted that in none of the later publications (including those of the same authors) additional information about this compound was found.

At the same time, in the \( \text{Ag}_2\text{MoO}_4-\text{AMoO}_4-\text{Ga}_2(\text{MoO}_4)_3 \), systems triple molybdates of composition \( \text{Ag}_3\text{A}_\text{Ga}(\text{MoO}_4)_5 \) were found. These compounds were synthesized by the solid-state reactions at 550–600 °C (\( \text{A} = \text{Mn} \)), 540–550 °C (\( \text{A} = \text{Zn} \)), 500–530 °C (\( \text{A} = \text{Co} \)) for 80–100 h. However, nickel-containing compound was not obtained in the single-phase state, even after sintering at temperatures as high as 600–650 °C for 250–300 hours. This may be due to the smallest radius of Ni\(^{2+}\) cation (0.69 Å for \( \text{CN} = 6 \) [17]) in the studied series of simple molybdates of divalent metals.

The triple molybdates \( \text{Ag}_3\text{A}_\text{Ga}(\text{MoO}_4)_5 \) (\( \text{A} = \text{Zn}, \text{Mn}, \text{Co} \)) were found to melt incongruently at temperatures of 644, 727, and 739 °C, respectively.

The powder XRD patterns of as-prepared single-phase compounds \( \text{Ag}_3\text{A}_\text{Ga}(\text{MoO}_4)_5 \) are similar and show that these oxides are isostructural to triclinic \( \text{NaMg}_3\text{In}(\text{MoO}_4)_5 \) (sp. gr. \( P\overline{1}, Z = 2 \)) [20]. The diffractograms of the \( \text{Ag}_3\text{A}_\text{Ga}(\text{MoO}_4)_5 \) (\( \text{A} = \text{Mn}, \text{Co}, \text{Zn} \)) were indexed with taking into account our data obtained earlier in the course of single-crystal structure de-
termination of AgMg₃R(MoO₄)₅, R = Fe, Cr [7]. The result of indexing the PXRD patterns for AgA₃Ga(MoO₄)₅ (A = Mn, Co, Zn) are given in Table 1. Unit-cell parameters are listed in Table 2.

Crystal structure of AgZn₃Ga(MoO₄)₅

The crystal structure of AgZn₃Ga(MoO₄)₅ was refined according to the Rietveld method [21], starting with the atomic coordinates of AgMg₃Fe(MoO₄)₅ structure [7]. Crystal data, data collection and structure refinement details are summarized in Table 3. Experimental, theoretical, and difference PXRD patterns for the AgZn₃Ga(MoO₄)₅ are shown in Figure 1. The fractional

Table 1

| h k l | AgMg₃Ga(MoO₄)₅ | AgZn₃Ga(MoO₄)₅ | AgCo₃Ga(MoO₄)₅ |
|-------|----------------|----------------|-----------------|
|       | I/I₀ 2θobs.,°  | 2θcal.,°       | I/I₀ 2θobs.,°   | 2θcal.,°       | I/I₀ 2θobs.,° | 2θcal.,° |
| 0 0 2 | 3 9.861 9.850  | 2 9.981 9.991  | 2 10.006 10.019 |
| 0 1 0 | 1 12.782 12.767| 1 12.954 12.945| 1L 12.956 12.943|
| 1 0 0 | 9 12.903 12.894| 9 13.058 13.064| 9 13.112 13.108|
| 0 1 1 |               |               | 1L 13.769 13.750|
| 1 0 1 | 1L 13.654 13.637| 1 13.778 13.808| 1L 13.853 13.849|
| 0 –1 1 |               | 1L 14.021 13.998| 1L 14.005 14.017|
| –1 0 1 | 1L 13.974 13.977| 2 14.170 14.175| 1 14.231 14.226|
| 0 0 3 | 1L 14.805 14.798| 1 15.010 15.011| 1L 15.061 15.052|
| 1 0 2 | 1 15.924 15.959| 1L 16.154 16.157| 1 16.177 16.200|
| 0 –1 2 | 1L 16.388 16.393| 1L 16.577 16.576| 1 16.625 16.619|
| –1 0 2 | 1L 16.529 16.538| 1L 16.799 16.783| 1L 16.819 16.844|
| 1 1 1 |               | 1L 17.079 17.075|               |
| –1 –1 1 |               | 1L 17.541 17.562| 1L 17.596 17.610|
| 1 1 2 | 1L 18.728 18.728|               |               |
| 1 0 3 | 1L 19.304 19.310|               |               |
| –1 –1 2 | 2 19.638 19.630| 3 19.826 19.822| 3 19.892 19.891|
| 0 0 4 | 1 19.780 19.774|               | 1L 20.127 20.115|
| –1 1 0 | 1L 19.792 19.792| 1L 20.115 20.122| 20.154|
| –1 0 3 | 1L 20.025 20.033| 1L 20.340 20.336|               |
| –1 1 1 | 1L 20.406 20.425| 1L 20.774 20.790| 1L 20.819 20.817|
| 1 1 3 | 3 21.572 21.577| 4 21.846 21.856| 5 21.861 21.864|
| 1 –1 2 | 6 22.117 22.117| 10 22.419 22.427| 10 22.483 22.482|
| –1 –1 3 | 1 22.959 22.996| 1L 23.048 23.085|               |
| 1 0 4 | 3 23.267 23.270| 3 23.569 23.573| 3 23.646 23.631|
| 0 1 4 | 23.265 2 23.662 23.668| 1 23.695 23.675|
| 0 –1 4 | 1 23.959 23.944| 10 24.193 24.222| 3 24.313 24.306|
| –1 0 4 | 1 24.086 24.078| 2 24.441 24.445| 1 24.511 24.529|
| 0 0 5 | 16 24.793 24.787| 100 25.145 25.148| 86 25.221 25.218|
| –1 1 3 | 6 24.869 24.848| 16 25.307 25.312| 16 25.344 25.346|
| h  | k  | l  | AgMn₃Ga(MoO₄)₅ | AgZn₃Ga(MoO₄)₅ | AgCo₃Ga(MoO₄)₅ |
|----|----|----|----------------|----------------|----------------|
|    |    |    | I/I₀ 2θ_{obs.} ° | 2θ_{cal.} ° | I/I₀ 2θ_{obs.} ° | 2θ_{cal.} ° | I/I₀ 2θ_{obs.} ° | 2θ_{cal.} ° |
| 1  | 1  | 4  | 3 | 25.122 | 25.119 | 5 | 25.459 | 25.465 | 6 | 25.480 | 25.478 |
| 0  | 2  | 0  | 3 | 25.701 | 25.697 | 2 | 26.072 | 26.058 | 2 | 26.055 | 26.054 |
| 2  | 0  | 0  | 73 | 25.959 | 29.954 | 83 | 26.307 | 26.302 | 100 | 26.396 | 26.392 |
| 0  | 2  | 1  | 23 | 26.036 | 26.025 | 38 | 26.417 | 26.422 | 26.403 |
| 2  | 0  | 1  | 10 | 26.255 | 26.250 | 20 | 26.596 | 26.590 | 26.679 | 26.676 |
| 0  | -2 | 1  | 6  | 26.337 | 26.333 | 22 | 26.664 | 26.674 | 26.697 | 26.690 |
| -1 | -1 | 4  | 4  | 26.483 | 26.488 | 7 | 26.780 | 26.782 | 7 | 26.888 | 26.890 |
| 1  | 2  | 0  | 8  | 26.613 | 26.601 | 3 | 26.883 | 26.881 | 26.892 |
| -2 | 0  | 1  | 6  | 26.614 | 26.614 | 7 | 26.984 | 26.984 | 27.079 | 27.081 |
| 1  | 2  | 1  | 11 | 26.835 | 26.829 | 25 | 27.132 | 27.137 | 18 | 27.133 | 27.131 |
| 2  | 1  | 1  | 2  | 27.007 | 27.001 | 5 | 27.283 | 27.278 | 3 | 27.350 | 27.345 |
| -1 | -1 | 2  | 11 | 27.307 | 27.306 | 26 | 27.575 | 27.575 | 19 | 27.613 | 27.609 |
| 0  | 2  | 2  | 3  | 27.285 | 27.285 | 4 | 27.712 | 27.731 | 3 | 27.705 | 27.703 |
| -2 | -1 | 1  | 3  | 27.507 | 27.503 | 4 | 27.790 | 27.784 | 3 | 27.880 | 27.879 |
| 0  | 1  | 5  | 6  | 27.622 | 27.611 | 10 | 28.081 | 28.084 | 8 | 28.109 | 28.105 |
| 0  | -2 | 2  | 3  | 27.874 | 27.873 | 6 | 28.208 | 28.210 | 5 | 28.255 | 28.250 |
| 1  | 2  | 2  | 2  | 27.961 | 27.970 | 4 | 28.320 | 28.322 | 4 | 28.308 | 28.304 |
| 1  | -1 | 4  | 2  | 28.066 | 28.064 | 6 | 28.423 | 28.425 | 5 | 28.512 | 28.510 |
| 2  | 1  | 2  | 2  | 28.114 | 28.121 | 28.423 | 3 | 28.454 | 28.481 |
| -2 | 0  | 2  | 2  | 28.164 | 28.167 | 1 | 28.567 | 28.573 | 2 | 28.672 | 28.678 |
| 0  | -1 | 5  | 6  | 28.342 | 28.336 | 16 | 28.678 | 28.676 | 13 | 28.782 | 28.778 |
| -1 | 0  | 5  | 1  | 28.893 | 28.900 | 1 | 29.000 | 28.997 | 28.997 |
| -1 | -2 | 2  | 1  | 28.877 | 28.882 | 2 | 29.163 | 29.159 | 1 | 29.223 | 29.217 |
| -2 | -1 | 2  | 4  | 29.081 | 29.082 | 10 | 29.391 | 29.390 | 9 | 29.499 | 29.501 |
| 0  | 2  | 3  | 3  | 29.376 | 29.367 | 4 | 29.859 | 29.869 | 3 | 29.837 | 29.839 |
| 2  | 0  | 3  | 1L | 29.525 | 29.516 | 2 | 29.898 | 29.888 | 1 | 29.985 | 29.973 |
| 0  | 0  | 6  | 1  | 29.860 | 29.850 | 1 | 30.300 | 30.287 | 1 | 30.383 | 30.372 |
| 1  | 2  | 3  | 1L | 29.929 | 29.927 | 1 | 30.365 | 30.334 | 1 | 30.324 | 30.310 |
| 2  | 1  | 3  | 4  | 30.055 | 30.056 | 9 | 30.397 | 30.397 | 9 | 30.453 | 30.450 |
| 0  | -2 | 3  | 1L | 30.175 | 30.189 | 1 | 30.527 | 30.539 | 1 | 30.590 | 30.603 |
| -2 | 0  | 3  | 1L | 30.513 | 30.488 | 1 | 30.983 | 30.940 | 1L | 31.055 | 31.055 |
| -1 | -5 | 1L | 30.622 | 30.621 | 1L | 30.981 | 31.088 | 1L | 31.106 |
| -1 | 2  | 0  | 1  | 30.953 | 30.949 | 2 | 31.460 | 31.462 | 1 | 31.483 | 31.484 |
| -1 | -2 | 3  | 2  | 31.213 | 31.207 | 4 | 31.501 | 31.509 | 4 | 31.594 | 31.592 |
| -2 | 1  | 0  | 1  | 31.618 | 31.616 | 1L | 31.691 | 31.698 | 18 | 31.865 | 31.883 |
| -2 | -1 | 3  | 2  | 31.748 | 31.755 | 18 | 31.865 | 31.883 | 31.865 |
| -1 | 2  | 1  | 8  | 31.303 | 31.304 | 22 | 31.849 | 31.854 | 31.865 | 31.865 |

Continuation of table 1
atomic coordinates, isotropic atomic displacement parameters, cation occupancies and main selected interatomic distances are presented in Tables 4 and 5. The populations of four independent positions \( M = (Zn, Ga) \) and three incompletely occupied Ag sites were refined with keeping the electrical neutrality of the chemical formula. The final compositions of the crystals are close to stoichiometric \( AgZn_3Ga(MoO_4)_5 \) with a negligible silver deficiency.

In the structure \( AgZn_3Ga(MoO_4)_5 \) all atoms are located in general positions. Coordination polyhedra of Mo atoms are tetrahedra with Mo–O distances of 1.714–1.824 Å, which are similar to the values found in other molybdates containing a tetrahedral anion. Cations \( Zn^{2+} \) and \( Ga^{3+} \) are statistically distributed on octahedral positions \( M_1–M_4 \) with the \( (Zn, Ga)–O \) bond lengths of 1.940–2.129 Å. Both Ag1 and Ag3 cations are coordinated by four O atoms (Ag1–O 2.358 Å, Ag3–O 2.415 Å), while Ag2 cation has \( CN = 5 \) (Ag2–O 2.495 Å). The structure of \( AgZn_3Ga(MoO_4)_5 \) consists of \( MoO_4 \) tetrahedra, couples of edge-shared \( M(1)O_6 \) octahedra, and trimers of edge-shared \( M(2)O_6, M(3)O_6 \) and

| h k l | \( AgMn_3Ga(MoO_4)_5 \) | \( AgZn_3Ga(MoO_4)_5 \) | \( AgCo_3Ga(MoO_4)_5 \) |
|-------|---------------------|---------------------|---------------------|
|       | \( I/I_0 \) | \( 2\theta_{obs.} \),° | \( 2\theta_{cal.} \),° | \( I/I_0 \) | \( 2\theta_{obs.} \),° | \( 2\theta_{cal.} \),° | \( I/I_0 \) | \( 2\theta_{obs.} \),° | \( 2\theta_{cal.} \),° |
| 1 –2 1 | 2 | 31.408 | 31.410 | 2 | 31.912 | 31.899 | 3 | 31.945 | 31.935 |
| 2 –1 1 | 1 | 31.440 | 31.428 | 31.914 | 31.914 | 1 | 31.996 | 31.999 |
| 1 –1 5 | 1 | 31.853 | 31.857 | 3 | 32.264 | 32.264 | 2 | 32.362 | 32.364 |
| –1 1 5 | 1L | 31.974 | 31.980 | 31.957 | 31.958 | 1 | 32.590 | 32.619 |
| 0 2 4 | 2 | 32.137 | 32.125 | 32.653 | 32.689 | 2 | 32.654 | 32.663 |
| 2 0 4 | 4 | 32.239 | 32.238 | 32.647 | 32.741 | 6 | 32.736 |
| 2 –1 2 | 1 | 32.512 | 32.535 | 33.015 | 33.127 | 1 | 33.106 |
| 1 2 4 | 3 | 32.569 | 32.567 | 33.038 | 33.020 | 7 | 33.014 |
| 1 –2 2 | 3 | 32.655 | 32.656 | 33.131 | 33.133 | 4 | 33.188 | 33.186 |
| 0 –1 6 | 2 | 33.363 | 33.368 |
| 0 –2 4 | 7 | 33.135 | 33.134 | 33.511 | 33.603 | 11 | 33.601 |
| 2 2 0 | 1 | 33.214 | 33.200 | 33.510 | 33.551 | 1 | 33.568 |
| 2 2 1 | 2 | 33.311 | 33.313 | 33.634 | 33.683 | 5 | 33.681 |
| –2 0 4 | 1 | 33.426 | 33.434 | 33.941 | 34.059 | 1 | 34.066 |
| 1 1 6 | 1L | 33.460 | 33.454 | 33.948 |
| –2 –2 1 | 3 | 33.847 | 33.852 | 34.158 | 34.160 | 8 | 34.239 | 34.239 |

Cu Kα1 radiation (\( l = 1.54056 \) Å)

| Unit-cell parameters for \( AgA_3Ga(MoO_4)_5 \) (\( A = Mn, Zn, Co \)) |
|---------------------|---------------------|---------------------|
| \( A \) | \( a, Å \) | \( b, Å \) | \( c, Å \) | \( \alpha° \) | \( \beta° \) | \( \gamma° \) | \( V, Å^3 \) |
| Mn | 6.9844 (3) | 7.0519 (4) | 17.9700 (8) | 87.796 (4) | 87.529 (5) | 79.386 (4) | 868.71 |
| Zn | 6.9037 (3) | 6.9639 (4) | 17.7147 (8) | 88.107 (4) | 87.440 (4) | 78.982 (4) | 834.87 |
| Co | 6.8810 (4) | 6.9657 (4) | 17.669 (1) | 87.895 (5) | 87.344 (5) | 78.976 (5) | 830.04 |
Table 3
Crystal data and structure refinement for AgZn3Ga(MoO4)5

| Structural formula | AgZn3Ga(MoO4)5 |
|--------------------|----------------|
| Formula weight, $M_r$ (g mol$^{-1}$) | 1172.58 |
| Temperature (K) | 298(2) |
| Crystal system, space group (#) | Triclinic, $P\overline{1}$ (2) |

| Unit-cell parameters: | |
|----------------------|--------|
| $a$ (Å) | 6.9035 (5) |
| $b$ (Å) | 6.9643 (5) |
| $c$ (Å) | 17.7160 (14) |
| $\alpha$ (°) | 88.1039 (11) |
| $\beta$ (°) | 87.4338 (12) |
| $\gamma$ (°) | 78.9880 (9) |

| Unit-cell volume, $V$ (Å$^3$) | 835.0 (2) |
| Formula unit, $Z$ | 2 |
| Calculated density, $\rho_{cal}$ (g cm$^{-3}$) | 4.66 |

Refinement $R$ factors and goodness of fit:

- $wR_p$: 0.0511
- $R_p$: 0.0382
- $R_{exp}$: 0.0152
- $R(F^2)$: 0.05815
- $\chi^2$: 3.40

Table 4
Structural parameters for AgZn3Ga(MoO4)5

| Atom | Occupancy | $x$ | $y$ | $z$ | $U_{iso}$ |
|------|-----------|-----|-----|-----|-----------|
| Mo1  | 1         | 0.2722(8) | 0.3095(8) | 0.5282(3) | 0.030(2) |
| Mo2  | 1         | 0.2129(8) | 0.8293(9) | 0.2856(3) | 0.028(2) |
| Mo3  | 1         | 0.6843(8) | 0.2187(8) | 0.3109(3) | 0.023(2) |
| Mo4  | 1         | 0.2811(9) | 0.0522(9) | 0.9044(3) | 0.029(2) |
| Mo5  | 1         | 0.2520(8) | 0.5491(8) | 0.0863(3) | 0.021(2) |
| M1   | 0.788(1)Zn+0.212(1)Ga | 0.1834(12) | 0.8241(11) | 0.4938(5) | 0.0126(3) |
| M2   | 0.901(1)Zn+0.099(1)Ga | 0.1704(14) | 0.0855(16) | 0.1145(5) | 0.045(4) |
| M3   | 0.798(1)Zn+0.202(1)Ga | 0.7829(12) | 0.4310(13) | 0.1239(4) | 0.014(3) |
| M4   | 0.505(1)Zn+0.495(1)Ga | 0.2546(12) | 0.3014(13) | 0.7370(4) | 0.023(3) |
| Ag1  | 0.323(3)Ag | 0.149(3) | 0.339(3) | 0.2857(12) | 0.062(5) |
| Ag2  | 0.328(3)Ag | 0.122(4) | 0.308(4) | 0.3155(13) | 0.062(5) |
| Ag3  | 0.342(3)Ag | 0.097(3) | 0.370(3) | 0.3445(11) | 0.062(5) |
| O1   | 1         | 0.511(5)  | 0.194(5)  | 0.5163(18) | 0.015(1) |
| O2   | 1         | 0.289(4)  | 0.366(4)  | 0.6238(17) | 0.015(1) |
| O3   | 1         | 0.171(4)  | 0.545(5)  | 0.4601(18) | 0.015(1) |
| O4   | 1         | 0.130(5)  | 0.126(5)  | 0.4978(18) | 0.015(1) |
M(4)O₆ octahedra, which are linked by the common vertices to form a 3D framework (Fig. 2). In the large framework cavities, the silver cations are disordered on three close positions with the distances Ag–Ag 0.595(4) Å and 1.101(2) Å. Such a disordering is also typical of other compounds of this isostructural series [7, 9], suggesting a possible mobility of the Ag⁺ cations in the compounds. This is favored not only by defects in Ag positions along with their irregular coordina-

| Atom | Occupancy | x    | y    | z    | Uiso |
|------|-----------|------|------|------|------|
| O5   | 1         | 0.189(4) | 0.872(4) | 0.3866(18) | 0.015(1) |
| O6   | 1         | 0.477(5) | 0.719(4) | 0.2580(17) | 0.015(1) |
| O7   | 1         | 0.140(5) | 0.053(5) | 0.2220(19) | 0.015(1) |
| O8   | 1         | 0.098(5) | 0.641(5) | 0.2687(18) | 0.015(1) |
| O9   | 1         | 0.419(5) | 0.280(4) | 0.3590(17) | 0.015(1) |
| O10  | 1         | 0.804(5) | 0.191(4) | 0.3830(18) | 0.015(1) |
| O11  | 1         | 0.681(5) | 0.995(5) | 0.2696(17) | 0.015(1) |
| O12  | 1         | 0.774(4) | 0.370(5) | 0.237(2)   | 0.015(1) |
| O13  | 1         | 0.198(4) | 0.121(4) | 0.997(2)   | 0.015(1) |
| O14  | 1         | 0.468(5) | 0.040(4) | 0.0841(15) | 0.015(1) |
| O15  | 1         | 0.831(5) | 0.202(5) | 0.1174(16) | 0.015(1) |
| O16  | 1         | 0.238(4) | 0.305(5) | 0.8544(17) | 0.015(1) |
| O17  | 1         | 0.249(4) | 0.546(4) | 0.987(2)   | 0.015(1) |
| O18  | 1         | 0.485(5) | 0.488(5) | 0.1153(17) | 0.015(1) |
| O19  | 1         | 0.171(4) | 0.778(5) | 0.1292(18) | 0.015(1) |
| O20  | 1         | 0.097(4) | 0.410(5) | 0.1173(18) | 0.015(1) |

Fig. 1. Observed (black line) and calculated (red line) XRD patterns of AgZn₃Ga(MoO₄)₅. Vertical bars indicate the positions of the Bragg peaks. The lower trace depicts the difference between the experimental and calculated intensity values.

Fig. 2. Projection views of the structure of AgZn₃Ga(MoO₄)₅ along the a axis. The blue spheres and small red spheres indicate Ag and oxygen atoms, respectively.
| Mo1-tetrahedron | Mo2-tetrahedron | Mo3-tetrahedron | Mo4-tetrahedron |
|-----------------|-----------------|-----------------|-----------------|
| Mo1–O1          | 1.696(3)        | Mo2–O5          | 1.819(3)        |
| –O2             | 1.764(3)        | –O6             | 1.889(3)        |
| –O3             | 1.726(3)        | –O7             | 1.891(3)        |
| –O4             | 1.858(3)        | –O8             | 1.698(3)        |
| <Mo1–O>         | 1.761           | <Mo2–O>         | 1.824           |

| Mo5-tetrahedron | M1-octahedron | M2-octahedron | M3-octahedron |
|-----------------|---------------|---------------|---------------|
| Mo5–O17         | 1.758(4)      | M1–O1         | 2.092(3)      |
| –O18            | 1.683(3)      | –O3           | 2.068(3)      |
| –O19            | 1.773(3)      | –O10          | 2.186(3)      |
| –O20            | 1.640(3)      | –O4           | 2.070(2)      |
| <Mo5–O>         | 1.714         | –O5           | 1.918(3)      |
|                 |               | –O4           | 2.124(3)      |
|                 |               | <M1–O>        | 2.076         |

| M4-octahedron | Ag1-polyhedron | Ag2-polyhedron | Ag3-polyhedron |
|---------------|----------------|---------------|---------------|
| M4–O8         | 2.398(4)       | Ag1–O9        | 2.29(4)       |
| –O11          | 2.033(4)       | –O8           | 2.08(3)       |
| –O2           | 2.053(3)       | –O7           | 2.33(4)       |
| –O6           | 1.837(3)       | –O12          | 2.73(4)       |
| –O16          | 2.079(3)       | <Ag1–O>       | 2.358         |
| –O12          | 2.320(3)       |               |               |
| <M4–O>        | 2.120          |               |               |

| Ag2-polyhedron | Ag3-polyhedron |
|---------------|---------------|
| Ag2–O9        | 2.19(4)       | Ag3–O9        | 2.22(4)       |
| –O10          | 2.70(4)       | –O8           | 2.28(4)       |
| –O8           | 2.41(4)       | –O10          | 2.62(4)       |
| –O7           | 2.45(4)       | –O3           | 2.54(3)       |
| –O12          | 2.725(3)      | <Ag3–O>       | 2.415         |
| <Ag2–O>       | 2.495         |               |               |

| Ag1–Ag2       | 0.595(4)      |
| Ag1–Ag3       | 1.101(2)      |
tion, but also a rather flexible polyhedral framework of the NaMg₃In(MoO₄)₅ structure type, which involves interconnected cavities.

**Electrophysical properties**

As was noted in the previous section, the structural features of the obtained molybdates allow us to expect these compounds to have the increased ionic conductivity. This was already confirmed by us in the case of AgMg₃Al(MoO₄)₅ (σ = 2.5 × 10⁻² S/cm) and AgMn₃Al(MoO₄)₅ (σ = 7.1 × 10⁻³ S/cm) at 500°C [7]. In this work as an example, the results of studying electrophysical properties for AgMn₃Ga(MoO₄)₅ are presented.

It was found that the DC conductivity of ceramic sample AgMn₃Ga(MoO₄)₅, measured with the V7–38 device, is negligible as compared to the ac conductivity (Fig. 3) in temperature region of 100–560°C. As the platinum electrodes are blocking in the DC conductivity measurement mode, the DC conductivity of AgMn₃Ga(MoO₄)₅ corresponds to the electronic one. Therefore, it can be concluded that the AC conductivity is almost equal to the ionic one.

It is seen that near room temperature the conductivity is as small as 10⁻⁷ S/cm but quickly rises with temperature to values of about 10⁻² S/cm. It is noteworthy that the conductivity in AgMn₃Ga(MoO₄)₅ increases with temperature in non-monotonic way showing distinct breaks on lgσ = f(1/T) curves at 310°C. Above these temperature the lgσ = f(1/T) dependences are almost linear with the small activation energy value Eₐ = 0.26 eV. Above 310°C, the ionic conductivity of AgMn₃Ga(MoO₄)₅ increases up to 2.03·10⁻² S/cm at 500°C, which is close to the corresponding characteristics of the known ionic conductors.

**Conclusions**

The possibility of the formation of silver-containing gallium triple molybdates with Mn, Co, Zn, Ni, analogous to the phases Ag₁₋ₓAₓ₁₋ₓRₓ(MoO₄)₃ and Ag₃R₃(Al₂MoO₁₂) obtained by us in the Ag₂MoO₄−AMoO₄−R₂(MoO₄)₃ (A = Mg, Co; R = Al; A = Mg, R = In) systems, was studied. It was shown that in the Ag₂MoO₄−AMoO₄−Ga₃(MoO₄)₃ (A = Mn, Co, Zn, Ni) systems the NASICON-like phases of the composition Ag₁₋ₓAₓ₁₋ₓ(R₁₋ₓ)(MoO₄)₃ are not formed. The triple molybdates of the composition Ag₃Ga(MoO₄)₅ (A = Mn, Co, Zn) were synthesized and characterized. AgNi₃Ga(MoO₄)₅ was not obtained in the single-phase state. It was established that the obtained compounds incongruently melt and belong to the structural type of triclinic NaMg₃In(MoO₄)₅ (sp. gr. P1, Z = 2). The structure of the obtained compounds was refined by the Rietveld method using the powder diffraction data for AgZn₃Ga(MoO₄)₅. The structural features of the obtained molybdates allow us to expect these compounds to have the increased ionic conductivity. This was
confirmed by studying electrophysical properties of \( \text{AgMn}_3\text{Ga(MoO}_4\text{)}_5 \). It was shown that the high-temperature electrical conductivity of this compound reaches \( 10^{-2} \text{ S/cm at } E_a = 0.26 \text{ eV} \), which is close to the corresponding characteristics of the known ionic conductors.

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