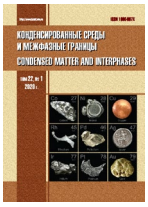

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Synthesis and characterisation of ternary molybdates $AgZn_3R(MoO_4)_5$ (R = In, Fe)

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Abstract

An important role in the study and the obtaining of new phases with valuable physical and chemical properties is taken by ternary compounds with a tetrahedral anion containing various combinations of mono- and multivalent cations, including ternary molybdates and tungstates. Silver ternary molybdates $AgA_3R(MoO_4)_5$ with the $NaMg_3In(MoO_4)_5$ structural type (triclinic crystal system, space group $P\bar{1}$, Z = 2) are of particular interest and have a high ion conductivity (10^{-3}–10^{-2} S/cm). In this regard, the aim of this work was to reveal the possibility to form similar compounds in silver, zinc, indium, and iron molybdate and tungstate systems and to determine the effect of the nature of tetrahedral anion and three-charged cations on their obtaining and properties.

Polycrystalline samples were synthesized using a ceramic technology and studied by differential thermal (DTA) and X-ray diffraction analysis (XRD).

The research resulted in obtaining a new ternary molybdates $AgZn_3R(MoO_4)_5$ (R = In, Fe) crystallising in the triclinic crystal system (space group $P\bar{1}$, Z = 2). The sequence of chemical transformations that occur during the formation of these compounds, their crystallographic and thermal characteristics were determined. Unit cell parameters for the indium compound are as follows: a = 6.9920(4), b = 7.0491(4), c = 17.9196(9) Å, α = 87.692(5), β = 87.381(5), γ = 79.173(5)°; and for the iron compound: a = 6.9229(3), b = 6.9828(4), c = 17.7574(8) Å, α = 87.943(4), β = 87.346(5), γ = 78.882(5)°. It was established that silver-containing ternary zinc tungstates with indium and iron with a similar structure are not formed.

Keywords: ternary molybdates, silver, tungsten, solid-state synthesis, X-ray diffraction analysis (XRD), thermal properties.

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1. Introduction

Currently, a lot of attention is paid to searching, synthesising, and extending the range of application of complex oxide compounds, and using them to develop new materials with functionally relevant properties.

An important role in the study and the obtaining of new phases with valuable physical and chemical properties is given to ternary compounds with a tetrahedral anion containing various combinations of mono- and multivalent cations, including ternary molybdates and tungstates. One of the largest families within this class of compounds are molybdates with one-, two-, and three- charged cations. Silver NASICON-like rhombohedral phases $Ag_{1-x}A_{1-x}R_{1+x}(MoO_4)_3$ (A = Mg, Co, R = Al, Sc; A = Mg, R = In) [1–4] and the triclinic $AgA_3R(MoO_4)_5$ (A = Mg, R = Cr, Fe, Ga; A = Zn, R = Ga; A = Fe^{II}, R = Fe^{III}; A = Mn, R = Al, Cr, Fe, Sc, In) [5–10] are of particular interest due to a high ionic conductivity (10^{-3}–10^{-2} S/cm) [4, 7, 10]. Both structural types occur in systems where two- and three-charged cations tend to have octahedral coordination and the radius of the three-charged cation does not exceed 1 Å.

The characteristic features of the phase formation in systems, where the considered phases are formed are shown in Fig. 1 (by the example of Ag_2MoO_4–$MgMoO_4$–$In_2(MoO_4)_3$ [3]). The subsolidus structure of this system is determined by the formation of the NASICON-type ternary molybdates $AgMgIn(MoO_4)_3$ (S_1) and $AgMg_3In(MoO_4)_5$ (S_2) without any visible homogeneity regions along the section $AgIn(MoO_4)_2$–$MgMoO_4$. The phase of variable composition $Ag_{1-x}Mg_{1-x}In_{1+x}(MoO_4)_3$ (S_1) is formed along the section $AgMgIn(MoO_4)_3$–$In_2(MoO_4)_3$ and is an omission solid solution based on the ternary molybdate $AgMgIn(MoO_4)_3$ where homogeneity region is up to x = 0.6.

According to X-ray diffraction analysis (XRD), triple molybdates $AgA_3R(MoO_4)_5$ are isotypical to $NaMg_3R(MoO_4)_5$, R = In, Al (triclinic crystal system, space group $P\bar{1}$, Z = 2 [11,12]).

Crystals were obtained and their structure was determined for $AgMg_3R(MoO_4)_5$ (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 $AgFe^{II}_3Fe^{III}(MoO_4)_5$ [5–8]. The data from the X-ray powder patterns obtained by a full-profile analysis (Rietveld method) [13] were used to refine the crystal structures of $AgM_3Ga(MoO_4)_5$ (M = Mg, Zn) [9, 10].

Research was conducted to reveal a possibility to form similar compounds in silver, zinc, indium, and iron molybdate and tungstate systems and to determine the effect of the nature of tetrahedral anion and three-charged cations on their obtaining and properties.

2. Experimental

The source components were molybdates and tungstates of silver, zinc, and indium iron molybdate obtained by annealing of the stoichiometric mixtures of $AgNO_3$ (analytical reagent grade), ZnO (chemically pure grade), In_2O_3 (extra-pure grade), $Fe(NO_3)_3·9H_2O$ (analytical reagent grade), MoO_3 (chemically pure grade), and WO_3 (chemically pure grade) at 350–450 °C (Ag_2MoO_4), 500–700 °C ($ZnMoO_4$), 400–800°C ($In_2(MoO_4)_3$, 300–700 °C ($Fe_2(MoO_4)_3$), 480–520 °C (Ag_2WO_4), 650–850 °C ($ZnWO_4$), 700–900 °C ($In_2(WO_4)_3$). The single-phase of synthesised products was monitored by X-ray analysis and in some cases by thermographic analysis. The synthesised compounds were identified by comparing with the results of previous studies and the ICDD PDF-2 database [14–17].

$AgZn_3R(ЭO_4)_5$ (R = In, Fe; $Э$ = Mo; R = In, $Э$ = W) samples were prepared from molybdates and tungstates, taken in stoichiometric proportions. Ag_2WO_4, $ZnWO_4$, WO_3 and $Fe(NO_3)_3·9H_2O$ were

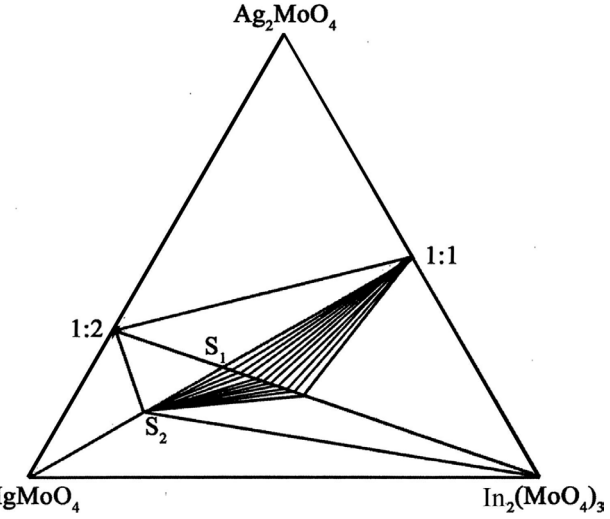

Fig. 1. Scheme of subsolidus phase relations in the Ag_2MoO_4–$MgMoO_4$–$In_2(MoO_4)_3$ system (S_1 – $Ag_{1-x}Mg_{1-x}In_{1+x}(MoO_4)_3$, S_2 – $AgMg_3In(MoO_4)_5$) [3]

used to synthesize $AgZn_3Fe(WO_4)_5$, in this case heat treatment started with 350°C.

The mixtures were gradually annealed in air with increments of 20–50 °C (in some cases 5–10°C) starting from 400–450 °C (for molybdates) and 550–600 °C (for tungstates), and finishing before they started to melt with intermediate homogenisation after 20–30 hours. The heat treatment time at each temperature was 30–70 hours. The phase composition of the sintered products was monitored by XRD before the annealing temperature was increased.

X-ray studies of polycrystalline products were carried out using a Bruker automated powder diffractometer D8 Advance (λCuK_α, scanning step 0.02076°) and Thermo ARL (λCuK_α, scanning step 0.02°).

Crystallographic characteristics of polycrystalline samples were determined based on isostructural compound data. Unit cell parameters were refined by the least-squares method using ICDD software package to prepare experimental standards. Smith-Snyder criterion F_{30} [18] was used as a validation criterion for XRD pattern indexing.

Thermoanalytical investigations were performed using a NETZSCH STA 449 F1 Jupiter device (Pt-crucible, heating rate 10 deg/min in a flow of argon).

3. Results and discussion

According to the XRD, the sequence of chemical transformations that occur during the formation of $AgZn_3R(MoO_4)_5$ (R = In, Fe) from a stoichiometric mixture of molybdates can be described in the following scheme:

$$\left.\begin{matrix} Ag_2MoO_4 \\ ZnMoO_4 \\ R_2(MoO_4)_3 \end{matrix}\right\} \rightarrow \left.\begin{matrix} AgR(MoO_4)_2 \\ ZnMoO_4 \\ AgZn_3R(MoO_4)_5 \end{matrix}\right\} \rightarrow$$
$$\rightarrow AgZn_3R(MoO_4)_5$$

The primary product of the solid-phase interaction between Ag_2MoO_4, $ZnMoO_4$ and $R_2(MoO_4)_3$ (R = In, Fe) is double molybdate $AgR(MoO_4)_2$. An increase in temperature to 470–500 °C (R = In) and 420–450°C (R = Fe) leads to the formation of $AgZn_3R(MoO_4)_5$ in the reaction mixture. In the single-phase state, these compounds were obtained at 650–700 °C (R = In) and 600–650°C (R = Fe). The heat treatment time was 100–120 h. Further annealing only resulted in a better formation of the ternary molybdate structure.

As an example, Fig. 2 shows the $AgZn_3Fe(MoO_4)_5$ X-ray diffraction pattern.

X-ray diffraction analysis revealed that $AgZn_3R(MoO_4)_5$ synthesised compounds

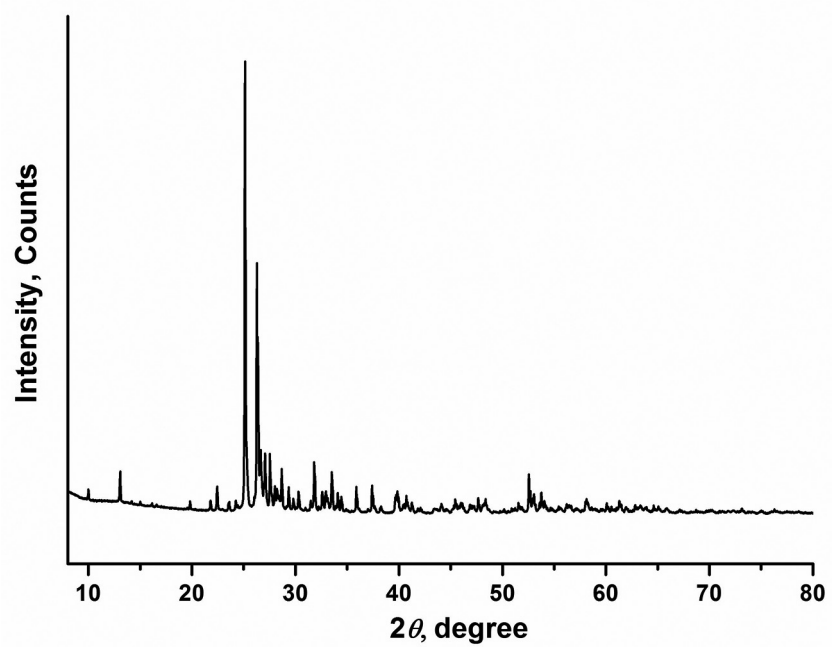

Fig. 2. X-ray diffraction pattern for ternary molybdate $AgZn_3Fe(MoO_4)_5$

are isostructural to each other and to the previously obtained $NaMg_5R(MoO_4)_5$ [11,12] and $AgA_3R(MoO_4)_5$ [5–10].

The structural features of the considered group of ternary molybdates are that MoO_4 tetrahedra and pairs and triplets of (*A*, *R*)O $_6$-octahedra connected along the edges share common vertices and form three-dimensional frameworks. Silver cations disordered over three closely-spaced positions are located in large frame voids.

Crystallochemical analysis of the inner space of the frame revealed the presence of channels located along the *a* axis, connected with channels along the *c* axis which contributes to increased ionic conductivity experimentally confirmed in the case of $AgA_3R(MoO_4)_5$ (*AR* = MgAl, MnAl, MnGa) [7,10].

The indexing results of $AgZn_3R(MoO_4)_5$ (*R* = In, Fe) powder patterns are shown in Table 1, and their crystallographic characteristics are shown in Table 2 (it also contains previously published data for an isostructural gallium analogue). It is evident that the parameters *a, b,* and *c* and the volume of $AgZn_3R(MoO_4)_5$ unit cells decrease with a decreasing radius of the triply-charged cation.

Thermal characteristics of $AgZn_3R(MoO_4)_5$ were defined. All phases melt incongruently. The indium compound has the highest thermal stability, with a decrease in the size of the three-charged cation in $In^{3+} – Fe^{3+} – Ga^{3+}$ (r_R^{3+}= 0.80, 0.65,

Table 1. Indexing results for $AgZn_3R(MoO_4)_5$ (*R* = In, Fe) X-ray diffraction patterns

hkl	$AgZn_3In(MoO_4)_5$*				$AgZn_3Fe(MoO_4)_5$**			
	$2\theta_{exp}$,°	I/I_0	d_{exp}, Å	$\Delta = 2\theta_{exp} - 2\theta_{calc}$, °	$2\theta_{exp}$,°	I/I_0	d_{exp}, Å	$\Delta = 2\theta_{exp} - 2\theta_{calc}$, °
1	2	3	4	5	6	7	8	9
0 0 2	9.878	3	8.95	+0.001	9.966	2	8.87	+0.002
0 1 0					12.929	1L	6.842	–0.014
1 0 0	12.900	9	6.857	–0.010	13.024	6	6.792	+0.009
1 0 1	13.633	1	6.490	+0.005	13.769	1L	6.426	+0.001
–1 0 1	13.989	1	6.326	+0.000	14.148	1L	6.255	–0.002
0 0 3	14.841	2	5.964	+0.001	14.990	1L	5.905	–0.014
0 1 2	15.957	1	5.550	–0.034	16.105	1	5.499	+0.015
1 0 2				–0.001				+0.005
0 –1 2	16.448	1L	5.385	–0.015	16.550	1L	5.352	+0.008
1 1 1	16.874	1	5.250	–0.010	17.027	1L	5.203	–0.022
–1 –1 1	17.370	1L	5.101	+0.027				
1 0 3	19.300	1L	4.595	+0.019	19.508	1L	4.547	–0.009
–1 –1 2	19.643	1L	4.516	+0.007	19.779	2	4.485	+0.007
–1 1 0	19.824	1	4.475	+0.005	20.095	1L	4.415	–0.007
0 0 4				+0.009				
–1 0 3	20.080	1L	4.418	+0.005	20.291	1L	4.373	+0.007
–1 1 1	20.459	1L	4.337	+0.009				
1 1 3	21.549	2	4.120	+0.004	21.751	2	4.083	+0.009
1 –1 2	22.161	5	4.008	–0.002	22.390	6	3.968	+0.005
–1 –1 3	22.789	1	3.899	+0.012				
1 0 4	23.306	3	3.814	–0.013	23.507	2	3.781	–0.002
0 1 4				+0.003	23.575	1	3.771	+0.010
0 –1 4	24.017	2	3.702	–0.001	24.190	3	3.676	+0.004
–1 0 4	24.147	4	3.683	+0.002	24.397	1	3.645	+0.003
0 0 5	24.857	100	3.579	+0.005	25.088	100	3.547	+0.002
–1 1 3					25.243	11	3.525	+0.009
1 1 4	25.120	3	3.542	–0.011	25.361	4	3.509	–0.004
0 2 0	25.734	3	3.459	–0.007	25.997	1	3.425	+0.000

Continuation of Table. 1

1	2	3	4	5	6	7	8	9
2 0 0	25.949	51	3.431	−0.003	26.235	52	3.394	+0.003
0 2 1	26.055	35	3.417	−0.004	26.346	28	3.380	+0.002
2 0 1	26.233	10	3.394	+0.001	26.516	10	3.359	+0.004
0 −2 1	26.366	10	3.378	+0.006	26.622	11	3.346	+0.002
−1 −1 4	26.532	5	3.357	+0.019	26.735	3	3.332	+0.010
1 2 0	26.606	7	3.348	−0.023	26.790	1	3.325	+0.007
−2 0 1				+0.016	26.917	4	3.310	+0.007
1 2 1	26.806	16	3.323	−0.006	27.036	12	3.295	+0.002
2 1 1	26.948	2	3.306	−0.006	27.169	2	3.280	+0.011
−1 −2 1	27.303	21	3.264	−0.002	27.503	12	3.240	+0.002
0 2 2				+0.009	27.640	2	3.225	+0.001
−2 −1 1	27.473	2	3.244	+0.001	27.700	2	3.218	+0.008
1 0 5	27.634	2	3.225	+0.006				
0 1 5	27.675	4	3.221	−0.005	27.983	6	3.186	+0.006
0 −2 2	27.931	6	3.192	−0.007	28.164	3	3.166	+0.004
1 2 2				+0.007	28.202	2	3.162	+0.005
2 1 2	28.070	2	3.176	−0.011	28.303	1	3.151	+0.010
1 −1 4	28.135	2	3.169	−0.010	28.378	2	3.142	+0.004
−2 0 2	28.188	1	3.163	+0.004	28.504	1	3.129	+0.010
−1 1 4	28.263	1	3.155	−0.010	28.637	9	3.115	−0.011
0 −1 5	28.430	11	3.137	−0.006				+0.002
−1 −2 2	28.887	1	3.088	+0.009	29.101	1L	3.066	−0.002
−2 −1 2	29.088	7	3.067	−0.012	29.314	5	3.044	+0.007
1 1 5	29.168	1L	3.059	−0.037				
0 2 3	29.400	3	3.036	−0.002	29.767	3	2.999	−0.002
2 0 3	29.502	1	3.025	−0.001				+0.035
2 1 3	30.002	7	2.976	−0.005	30.270	5	2.950	+0.004
0 −2 3	30.267	1L	2.951	−0.013	30.502	1L	2.928	−0.001
−1 −1 5	30.708	2	2.909	−0.003	30.950	1L	2.887	−0.011
−1 2 0	31.020	1	2.881	−0.007	31.416	1L	2.845	−0.011
−1 -2 3	31.244	2	2.860	−0.001	31.454	2	2.842	+0.002
−1 2 1	31.372	16	2.849	−0.003	31.785	14	2.813	+0.002
−2 −1 3					31.679	1L	2.822	+0.012
2 −1 1	31.474	6	2.840	−0.010	31.859	2	2.807	−0.010
1 −1 5	31.944	2	2.799	−0.013	32.223	1	2.776	−0.011
0 2 4	32.167	3	2.780	−0.002	32.556	6	2.748	+0.015
2 0 4	32.231	5	2.775	+0.001				−0.005
0 1 6					32.642	1	2.741	+0.000
1 2 4	32.552	10	2.788	−0.005	32.883	5	2.722	+0.009
2 −1 2				+0.018	32.926	2	2.718	+0.027
1 −2 2	32.722	5	2.735	+0.006	33.085	4	2.705	+0.002
−2 1 2					33.384	1	2.682	+0.007
2 2 0	33.127	1	2.702	+0.013				+0.012
0 −2 4	33.224	17	2.694	−0.008	33.473	9	2.675	+0.002
2 2 1				+0.018	33.506	4	2.672	+0.006
1 1 6	33.488	1	2.674	−0.010	33.822	1L	2.648	−0.006
−2 0 4				+0.012	33.863	1	2.645	+0.013
−2 −2 1	33.823	8	2.268	−0.013	34.060	4	2.6301	+0.000

The end of the Table. 1

1	2	3	4	5	6	7	8	9
2 2 2	34.120	5	2.626	−0.012	34.398	2	2.6050	+0.002
−1 −2 4	34.203	2	2.619	+0.002	34.434	1	2.6024	+0.003
−2 −1 4	34.398	1	2.605	−0.012				
−1 2 3				−0.002	34.873	1L	2.5706	+0.004
2 −1 3				+0.005	34.788	1L	2.5767	−0.002
1 −2 3	34.709	1L	2.582	−0.017	35.041	1L	2.5587	+0.006
−2 1 3	34.926	1L	2.567	+0.011	35.407	1L	2.5331	+0.004
0 0 7	35.064	1L	2.557	+0.016				−0.001
−1 −1 6								+0.018
2 0 5	35.519	10	2.525	−0.011	35.854	7	2.5025	−0.002
2 2 3	35.643	1	2.517	+0.046	36.002	1	2.4925	+0.009
1 2 5	35.711	1	2.512	+0.039	36.139	1	2.4834	+0.000
2 1 5	35.790	1L	2.507	+0.018				+0.011
−1 1 6	36.257	1L	2.4756	−0.009				
0 −2 5	36.679	1	2.4481	−0.001	36.968	1	2.4296	−0.011
2 −1 4	36.899	2	2.4340	−0.030	37.233	1L	2.4129	+0.025
−1 2 4				+0.001	37.438	1	2.4002	−0.022
−2 0 5	36.963	11	2.4299	+0.001	37.367	8	2.4046	+0.007
1 −2 4	37.269	4	2.4107	+0.001	37.638	1	2.3879	−0.009
−2 −2 3				+0.005	37.514	1	2.3955	+0.024
−2 1 4	37.545	1L	2.3936	−0.007				
−1 −2 5	37.672	1L	2.3858	−0.015				
−2 −1 5	37.831	1	2.3761	+0.005	38.165	1	2.3561	−0.003
2 2 4	37.912	3	2.3712	−0.002	38.269	1	2.3499	−0.003
−1 0 7	38.013	1	2.3652	−0.003				
1 1 7					38.455	1L	2.3390	+0.000
1 3 1	38.884	1	2.3142	−0.018				
0 3 0					39.464	1L	2.2815	−0.028
3 1 1	39.113	1	2.3012	+0.034				
0 2 6	39.212	6	2.2956	−0.004	39.702	3	2.2684	−0.002
2 0 6				+0.005	39.605	4	2.2737	−0.013
3 0 0	39.361	4	2.2872	−0.004	39.816	5	2.2621	−0.007
1 2 6				+0.034				+0.015
3 0 1	39.479	2	2.2807	+0.009	39.937	2	2.2556	−0.003
1 3 2	39.619	1L	2.2729	+0.018				
−3 −1 1					40.053	1L	2.2493	−0.007
2 −1 5					40.251	1L	2.2387	+0.020
−3 0 1	39.896	5	2.2578	−0.003	40.360	2	2.2329	−0.003
−2 −2 4				+0.013	40.185	1	2.2422	+0.009
−1 2 5					40.499	2	2.2255	−0.013
0 3 2	40.015	4	2.2513	+0.002				−0.004
0 0 8	40.289	5	2.2367	+0.004	40.680	5	2.2161	−0.008
0 −2 6	40.529	3	2.2240	+0.008	40.851	1	2.2072	−0.007

* F_{30} = 83.2 (0.0075, 48)
** F_{30} = 96.4 (0.0066, 47)

Table 2. Crystallographic characteristics of $AgZn_3R(MoO_4)_5$ (R = In, Fe, Ga)

R	a, Å	b, Å	c, Å	α°	β°	γ°	V, Å^3
In	6.9920(4)	7.0491(4)	17.9196(9)	87.692(5)	87.381(5)	79.173(5)	866.13
Fe	6.9229(3)	6.9828(4)	17.7574(8)	87.943(4)	87.346(5)	78.882(5)	841.08
Ga [10]	6.9037(3)	6.9639(4)	17.7147(8)	88.107(4)	87.440(4)	78.982(4)	834.87

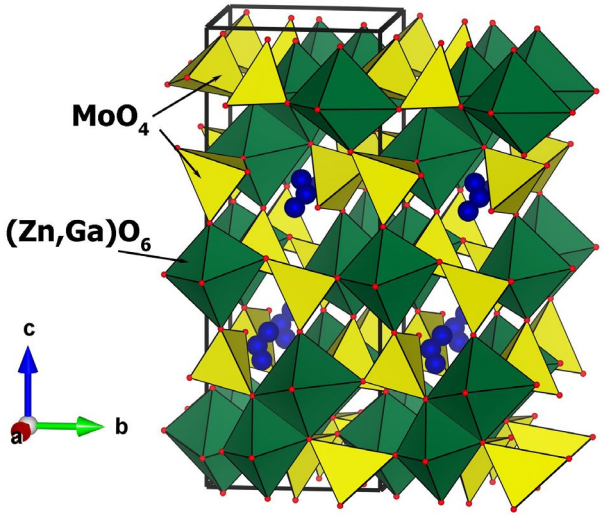

Fig. 3. A general view of $AgZn_3Ga(MoO_4)_5$ structure [10]

0.62 E for CN = 6 respectively [19]) the melting temperature decreases (832°C – 777°C – 644°C).

Despite similar values for Mo (VI) and W (VI) sizes (0.41 and 0.42 E for CN = 4, respectively [19]), ternary tungstates with a similar structure apparently do not exist. All our attempts to obtain $AgZn_3R(WO_4)_5$ triclinic phases (variation by thermal treatment and heat treatment modes) did not lead to any positive results, which is probably due to a significantly lower susceptibility of W (VI) (as compared to Mo (VI)) to tetrahedral coordination [20].

4. Conclusions

Thus, the possibility to form silver, zinc, and indium (iron) ternary molybdates and tungstates, of the $NaMg_3In(MoO_4)_5$ structural type (triclinic crystal system, space group $P\bar{1}$, Z = 2) were studied for the first time. New ternary molybdates $AgZn_3R(MoO_4)_5$ (R = In, Fe) were obtained. The sequence of chemical transformations that occur during their synthesis from a stoichiometric mixture of molybdates was determined. The crystallographic and thermal characteristics of synthesized compounds were identified. The frame structure of this group of phases containing connected cavities, the defective positions of silver cations, their low and open coordination can contribute to the increased Ag-ion conductivity of the received compounds. It was established that such phases do not form in tungsten systems.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Kotova I. Yu. Phase formation in the Ag_2MoO_4–$CoMoO_4$–$Al_2(MoO_4)_3$ system. *Russ. J. Inorg Chem.* 2014;59: 844–848. DOI: https://doi.org/10.7868/s0044457x14080133

2. Kotova I. Yu., Korsun V. P. Phase in the Ag_2MoO_4–$MgMoO_4$–$Al_2(MoO_4)_3$. *Russ. J. Inorg. Chem.* 2010;55(6): 955–958. DOI: https//doi.org/10.1134/S0036023610060203

3. Kotova I. Yu., Korsun V. P. Phase formation in the system involving silver, magnesium, and indium molybdates. *Russ. J. Inorg. Chem.* 2010;55(12): 1965–1969. DOI: https//doi.org/10.1134/S0036023610120247

4. Kotova I. Yu., Belov D. A., Stefanovich S. Yu. $Ag_{1-x}Mg_{1-x}R_{1+x}(MoO_4)_3$ Ag^+-conducting NASICON-like phases, where R = Al or Sc and $0 \leqslant x \leqslant 0.5$. *Russ. J. Inorg. Chem.* 2011;56(8): 1189–1 193. DOI: https//doi.org/10.1134/S0036023611080122

5. Bouzidi C., Frigui W., Zid M. F. Synthèse et structure crystalline d'un matériau noir $AgMn^{II}_3(Mn^{III}_{0.26}Al_{0.74})(MoO_4)_5$. *Acta Crystallographica Section E Crystallographic Communications.* 2015; 71(3): 299–304. DOI: https//doi.org/10.1107/S2056989015003345

6. Nasri R., Chérif S. F., Zid M. F. Structure cristalline de la triple molybdate $Ag_{0.90}Al_{1.06}Co_{2.94}(MoO_4)_5$. *Acta Crystallographica Section E Crystallographic Communications.* 2015; 71(4): 388–391. DOI: https//doi.org/10.1107/s2056989015005290

7. Kotova I. Yu., Solodovnikov S. F., Solodovnikova Z. A., Belov D. A., Stefanovich S. Yu., Savina A. A., Khaikina E. G. New series of triple molybdates $AgA_3R(MoO_4)_5$ (A = Mg, R = Cr, Fe; A = Mn, R = Al, Cr, Fe, Sc, In) with framework structures and mobile silver ion sublattices. *Journal of Solid State Chemistry.* 2016;238: 121–128. DOI: https//doi.org/10.1016/j.jssc.2016.03.003

8. Balsanova L. V. The synthesis of crystals of silver oxide phases based on molybdenum, investigation of their structure and properties. *ESSUTM Bulletin*. 2015;5: 63–69. (In Russ., abstract in Eng.)

9. Kotova I. Yu., Savina A. A., Khaikina E. G. Crystal structure of new triple molybdate $AgMg_3Ga(MoO_4)_5$ from Rietveld refinement. *Powder Diffraction*. 2017;32(4): 255–260. DOI: https//doi.org/10.1017/S0885715617000811

10. Kotova I. Yu., Savina A. A., Vandysheva A. I., Belov D. A., Stefanovich S. Yu. Synthesis, cristal structure and electrophysical properties of triple molybdates containing silver, gallium and divalent metals. *Chimica Techno Acta*. 2018;5(3): 132–143. DOI: https://doi.org/10.15826/chimtech.2018.5.3.02

11. Klevtsova R. F., Vasiliev A. D., Kozhevnikova N. M., Glinskaya L. A., Kruglik A. I., Kotova I. Yu. Synthesis and crystal structural study of ternary molybdate $NaMg_3In(MoO_4)_5$. *Journal of Structural Chemistry*. 1994;34(5): 784–788. DOI: https://doi.org/10.1007/BF00753580

12. Hermanowicz K., Maczka M., Wolcyrz M., Tomaszewski P. E., Paściak M., Hanuza J. Crystal structure, vibrational properties and luminescence of $NaMg_3Al(MoO_4)_5$ crystal doped with Cr^{3+} ions. *Journal of Solid State Chemistry*. 2006;179(3): 685–695. DOI: https://doi.org/10.1016/j.jssc.2005.11.032

13. Rietveld H. M. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*. 1969;2: 65–71. DOI: https://doi.org/10.1107/s0021889869006558

14. Kohlmuller R., Faurie J.-P. Etude des systemes MoO_3–Ag_2MoO_4 et MoO_3–MO (M – Cu, Zn, Cd). *Bull. Soc. Chim. France*. 1968;11: 4379–4382.

15. Trunov V. K., Kovba L. M. The reaction of In_2O_3 with WO_3 and MoO_3. *Vestnik Moskovskogo universiteta. Khimiya*. 1967;1: 114–115 (In Russ.).

16. Trunov V. K., Kovba L. M. On interaction of trioxides of molybdenum and tungsten with sesquioxides of iron and chromium. *Izvestiya Akademii Nauk SSSR. Neorganicheskie Materialy*. 1966;2: 151–154. (In Russ.).

17. ICDD PDF-2 Data Base, Cards ## 00-049-0337, 00-035-0765, 01-073-0554, 01-083-1701, 01-074-1791.

18. Smith G. S., Snyder R. L. FN: A criterion for rating powder diffraction patterns and evaluating the reliability of powder-pattern indexing. *Journal of Applied Crystallography*. 1979;12(1): 60–65. DOI: https//doi.org/10.1107/S002188987901178X

19. Shannon R. D. Revised effective ionic radii and systematic studies of interatomic distances in dalides and chalcogenides. *Acta Crystallographica Section A*. 1976;32(5): 751–767. DOI: https://doi.org 10.1107/S0567739476001551

20. Poraj-Koshic M.A., Atovmjan L.O. *Kristallohimija i stereohimija koordinacionnyh soedinenij molibdena* [Crystal chemistry and stereochemistry of coordination compounds of molybdenum]. Moscow: Nauka Publ.; 1974. 230 p. (In Russ.)

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