

PHYSICOCHEMICAL ANALYSIS
OF INORGANIC SYSTEMS

Phase Formation in the System Involving Silver,
Magnesium, and Indium Molybdates

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Abstract—The subsolidus region of the Ag_2MoO_4 – MgMoO_4 – $\text{In}_2(\text{MoO}_4)_3$ ternary salt system has been studied by X-ray powder diffraction. The formation of new compounds $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ ($0 \leq x \leq 0.6$) and $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$ has been established. The unit cell parameters of solid-solution samples have been determined. The $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ phase of variable composition has a NASICON-type structure (space group $R\bar{3}c$) $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$ is isostructural to sodium magnesium indium molybdate of the same formula unit and crystallizes in triclinic system (space group $P\bar{1}$, $Z = 2$) with the following unit cell parameters: $a = 7.0374(5)$ Å, $b = 17.932(1)$ Å, $c = 6.9822(4)$ Å, $\alpha = 87.309(6)^\circ$, $\beta = 100.832(6)^\circ$, $\gamma = 92.358(6)^\circ$. The compounds $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ and $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$ are thermally stable up to 960 and 1030°C, respectively.

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The interactions in systems containing molybdates of mono-, bi- and trivalent metals are of interest from the standpoint of both revealing phase formation regularities and synthesizing new materials with various important physicochemical properties. Compounds that demonstrate crystallochemical similarity to NASICON-type ones with a high ionic conductivity [1–5] are promising.

This work studies phase formation in the subsolidus region of the system involving silver, magnesium, and indium molybdates and determines the X-ray diffraction and thermal characteristics of ternary molybdates and the conditions for their synthesis.

EXPERIMENTAL

Silver, magnesium, and indium molybdates that were previously synthesized by the solid-phase method including the staged annealing of AgNO_3 (pure for analysis grade), MgO (chemically pure grade), In_2O_3 (pure grade), and molybdenum trioxide (chemically pure grade) in the stoichiometric ratio at 350–450 (Ag_2MoO_4), Ag_2MoO_4 , 400–750 (MgMoO_4), and 400–800°C ($\text{In}_2(\text{MoO}_4)_3$) served as initial components. The X-ray diffraction and thermal characteristics of the synthesized compounds agree satisfactorily with data [6–9]. The $\text{Ag}_2\text{Mg}_2(\text{MoO}_4)_3$ and $\text{AgIn}(\text{MoO}_4)_2$ double molybdates were synthesized by a solid-phase method from the relevant neutral molybdates as described in [10–12].

Phase formation in the Ag_2MoO_4 – MgMoO_4 – $\text{In}_2(\text{MoO}_4)_3$ system was studied by the intersecting sections method in the subsolidus region. The MgMoO_4 –

$\text{AgIn}(\text{MoO}_4)_2$ join, where intermediate phases were formed, was studied over the entire concentration region in steps of 5–10 mol % and in the neighborhood of new compounds, in steps of 2.0–2.5 mol %. While equilibrium was attained, the phase composition was monitored by X-ray diffraction.

To determine a possible homogeneity region in the Ag_2MoO_4 – MgMoO_4 – $\text{In}_2(\text{MoO}_4)_3$ system, $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ samples were prepared in $\Delta x = 0.1$ steps within the range $0 \leq x \leq 0.7$ and stepwise annealed in air in steps of 50°C starting at 350°C with intermediate grinding every 20–30 h. The annealing duration was 50–100 h at every temperature. Every rise in temperature was preceded by an X-ray diffraction study of a sample. The homogeneity region boundaries were determined by X-ray powder diffraction in air-quenched samples. The homogeneity extent was estimated by X-ray diffraction from both the absence of impurity lines and the changes in the unit cell parameters of air-quenched samples.

X-ray diffraction studies were performed on a Bruker D8 Advance automatic powder diffractometer ($\text{CuK}\alpha$ radiation, graphite monochromator, maximal angle $2\theta = 90^\circ$, 0.01° – 0.02° scan steps, 1 s per point) and on an FR-552 monochromator chamber ($\text{CuK}\alpha_1$ radiation, Ge internal standard).

Differential thermal analysis was performed on an MOM OD-103 derivatograph (heating rate was 10 K/min, sample size was 0.3–0.4 g).

Table 1. Indexing of X-ray diffraction pattern for $\text{Ag}_{0.7}\text{Mg}_{0.7}\text{In}_{1.3}(\text{MoO}_4)_3$

$2\theta_{\text{exp}}$, deg	I/I_0	d_{exp} , Å	hkl	$\Delta(2\theta_{\text{exp}} - 2\theta_{\text{theor}})$, deg
13.108	4	6.75	012	-0.008
18.523	3	4.7901	104	-0.004
18.613	12	4.7671	110	+0.001
21.826	100	4.0721	113	-0.009
22.667	5	3.9229	006	+0.006
22.841	7	3.8934	202	-0.012
26.356	21	3.3916	024	+0.018
28.865	23	3.0931	211	-0.005
29.495	15	3.0284	116	-0.002
29.621	36	3.0158	122	-0.006
32.297	5	2.7718	018	+0.012
32.474	4	2.7571	214	+0.003
32.543	46	2.7514	300	-0.010
34.477	1	2.6014	125	+0.007
37.547	2	2.3954	208	-0.002
39.326	17	2.2911	119	-0.024
39.523	5	2.2801	223, 131	-0.007, +0.016
40.017	3	2.2531	036	+0.005
42.229	10	2.1401	128	-0.009
43.972	2	2.0592	315	+0.001
44.476	11	2.0370	226	+0.004
44.566	6	2.0331	042	+0.000
46.258	1	1.9626	0012	+0.042
46.647	2	1.9472	404	-0.015
48.066	3	1.8929	137	+0.010
48.204	2	1.8878	321	-0.007
48.436	1	1.8793	2110	+0.013
48.686	2	1.8703	232	+0.004
50.329	1	1.8130	1112	-0.015
50.518	12	1.8067	318	-0.009
50.646	14	1.8024	324, 410	-0.019, +0.019
51.907	3	1.7615	229	+0.003
52.047	11	1.7571	235, 143	-0.003, +0.035
54.296	17	1.6895	048	-0.003
55.693	5	1.6504	327	+0.006
55.809	1L	1.6473	0114	+0.009
56.021	4	1.6415	1310	+0.015
56.178	8	1.6373	146	+0.003
57.749	3	1.5965	0312	-0.023
58.022	6	1.5896	054, 330	-0.011, +0.024
59.386	6	1.5563	241, 2014	-0.026, -0.018

RESULTS AND DISCUSSION

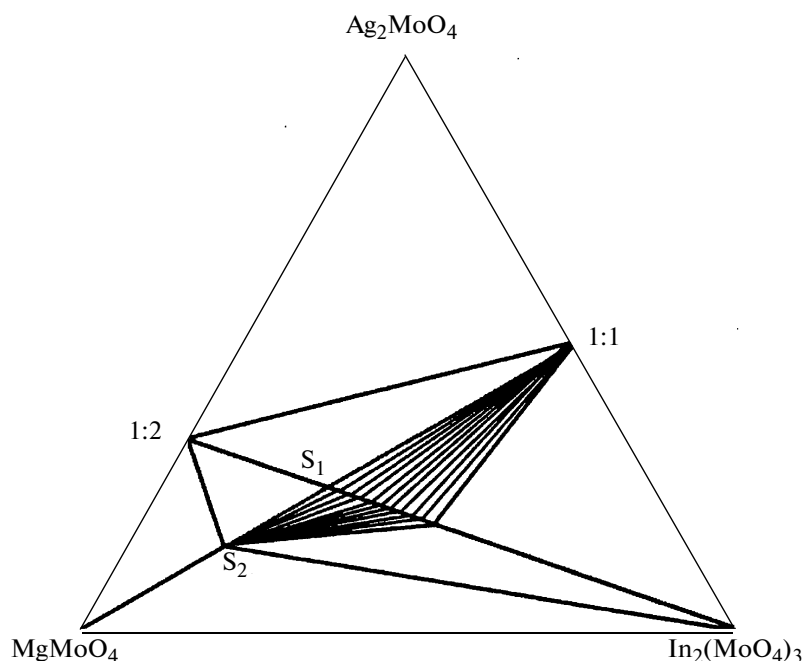
The Ag_2MoO_4 – MgMoO_4 and Ag_2MoO_4 – $\text{In}_2(\text{MoO}_4)_3$ systems were studied in [10–13], so we have not additionally considered them.

The Ag_2MoO_4 – $\text{In}_2(\text{MoO}_4)_3$ and Ag_2MoO_4 – MgMoO_4 edges of the Ag_2MoO_4 – MgMoO_4 – $\text{In}_2(\text{MoO}_4)_3$ concentration triangle are characterized by the formation of $\text{Ag}_2\text{Mg}_2(\text{MoO}_4)_3$ and $\text{AgIn}(\text{MoO}_4)_2$ double molybdates. Silver magnesium molybdate $\text{Ag}_2\text{Mg}_2(\text{MoO}_4)_3$ belongs to the $\text{Na}_2\text{Mg}_5(\text{MoO}_4)_6$ structural family, crystallizes in triclinic system (space group $P\bar{1}$, $Z = 2$), undergoes a reversible polymorphic transformation at 500–530°C, and melts incongruently at 740°C. The homogeneity region expands towards MgMoO_4 to reach 2.0–2.5 mol % at 500°C [10]. The $\text{AgIn}(\text{MoO}_4)_2$ double molybdate exists in two polymorphs: low-temperature α - $\text{AgIn}(\text{MoO}_4)_2$ ($\text{Na}_2\text{Zr}(\text{WO}_4)_3$ structure type) transforms to high-temperature triclinic β - $\text{AgIn}(\text{MoO}_4)_2$ ($\text{NaIn}(\text{MoO}_4)_2$ structure type) at 600°C. The heating of a metastable phase obtained by quenching results in the $\beta \rightarrow \alpha$ transition at ~450°C. The double molybdate melts incongruently at 650°C [11–13].

We have not detected any phase on the MgMoO_4 – $\text{In}_2(\text{MoO}_4)_3$ edge under our experimental conditions.

To investigate the interactions in the Ag_2MoO_4 – MgMoO_4 – $\text{In}_2(\text{MoO}_4)_3$ system, we prepared mixtures of neutral and double molybdates in a specified stoichiometric ratio, including the compositions of the intersection points for all sections existing in the system. The analysis of the phase composition of the system at intersection points and points located inside the Ag_2MoO_4 – MgMoO_4 – $\text{In}_2(\text{MoO}_4)_3$ triangle shows that at 620°C, phase relations are characterized by the quasi-binary joins: MgMoO_4 – $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$, $\text{Ag}_2\text{Mg}_2(\text{MoO}_4)_3$ – $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$, $\text{Ag}_2\text{Mg}_2(\text{MoO}_4)_3$ – $\text{AgIn}(\text{MoO}_4)_2$, $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$ – $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$, $0 \leq x \leq 0.5$, $\text{Ag}_2\text{Mg}_2(\text{MoO}_4)_3$ – $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$, $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ – $\text{AgIn}(\text{MoO}_4)_2$, $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ – $\text{In}_2(\text{MoO}_4)_3$, and $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$ – $\text{In}_2(\text{MoO}_4)_3$ (figure).

According to the X-ray powder diffraction data, the synthesized $\text{AgMgIn}(\text{MoO}_4)_3$ and $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$ triple molybdates do not have an appreciable homogeneity region along the $\text{AgIn}(\text{MoO}_4)_2$ – MgMoO_4 join. An $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ phase of variable composition is formed along the $\text{AgMgIn}(\text{MoO}_4)_3$ – $\text{In}_2(\text{MoO}_4)_3$ join and represents an $\text{AgMgIn}(\text{MoO}_4)_3$ based subtraction solid solution, whose single-phase region reaches $x = 0.5$. Weak $\text{In}_2(\text{MoO}_4)_3$ reflections appear in X-ray diffraction patterns at a higher concentration of indium cations. We did not manage to separate individual phases at $x = 0$ and 0.1 by varying the time and temperature of annealing. Along with the $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ phase, the β - $\text{AgIn}(\text{MoO}_4)_2$ double molybdate was revealed in samples.



Phase relation diagram for the $\text{MgMoO}_4\text{-Ag}_2\text{MoO}_4\text{-In}_2(\text{MoO}_4)_3$ system. $S_1\text{-Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$, $S_2\text{-AgMg}_3\text{In}(\text{MoO}_4)_5$.

It should be noted that the extent of $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ solid solution quenched from 700°C increases up to $x = 0.6$.

X-ray powder diffraction showed that the $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ compounds are isostructural to sodium zinc scandium molybdate [14], which has a rhombohedral unit cell (space group $R\bar{3}c$, $Z = 6$), as to reflection positions and intensity ratios. The indexing results for $\text{Ag}_{0.7}\text{Mg}_{0.7}\text{In}_{1.3}(\text{MoO}_4)_3$ are given in Tables 1 as an example.

Parameters of some compositions of $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ solid solution, namely, a , c , and unit cell volume, increase in the region with lower silver concentrations (Table 2).

The individual $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$ was obtained upon annealing for 100–120 h and $650\text{--}700^\circ\text{C}$. It is isostructural to $\text{NaMg}_3\text{In}(\text{MoO}_4)_5$, which has been synthesized by us earlier [15] and indexed in triclinic system (space group $P\bar{1}$, $Z = 2$) with the following unit cell parameters: $a = 7.0374(5) \text{ \AA}$, $b = 17.932(1) \text{ \AA}$, $c = 6.9822(4) \text{ \AA}$, $\alpha = 87.309(6)^\circ$, $\beta = 100.832(6)^\circ$, $\gamma = 92.358(6)^\circ$, $V = 863.99 \text{ \AA}^3$, $\rho_{\text{calc}} = 4.21 \text{ g/cm}^3$ (Table 3).

$\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ is thermally stable up to 960°C ; $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$ melts incongruently at 1030°C . There is no polymorphic transformations.

In summary, phase formation in the $\text{Ag}_2\text{MoO}_4\text{-MgMoO}_4\text{-In}_2(\text{MoO}_4)_3$ system was studied for the first time. New triple molybdates $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$ and $\text{AgMgIn}(\text{MoO}_4)_3$ have been synthesized, and the region of $\text{AgMgIn}(\text{MoO}_4)_3$ -based solid solutions has been discovered. Crystallographic and thermal characteristics were determined for the compounds synthesized. It has been established that $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$, where $0 \leq x \leq 0.6$, are related to the NASICON

Table 2. X-ray diffraction characteristics of a variable-composition $\text{Ag}_{1-x}\text{Mg}_{1-x}\text{In}_{1+x}(\text{MoO}_4)_3$ phase

Compound	a , Å	c , Å	V , Å^3
$\text{Ag}_{0.8}\text{Mg}_{0.8}\text{In}_{1.2}(\text{MoO}_4)_3$	9.5284(11)	23.523(4)	1849.5
$\text{Ag}_{0.7}\text{Mg}_{0.7}\text{In}_{1.3}(\text{MoO}_4)_3$	9.5339(6)	23.531(2)	1852.3
$\text{Ag}_{0.5}\text{Mg}_{0.5}\text{In}_{1.5}(\text{MoO}_4)_3$	9.5439(11)	23.730(4)	1871.9

Table 3. Indexing of X-ray diffraction pattern for $\text{AgMg}_3\text{In}(\text{MoO}_4)_5$

$2\theta_{\text{exp}}$, deg	I/I_0	d_{exp} , Å	hkl	$\Delta(2\theta_{\text{exp}} - 2\theta_{\text{theor}})$, deg	$2\theta_{\text{exp}}$, deg	I/I_0	d_{exp} , Å	hkl	$\Delta(2\theta_{\text{exp}} - 2\theta_{\text{theor}})$, deg
9.901	4	8.926	020	-0.028	28.936	2	3.083	-2-21	+0.012
12.915	6	6.849	001	-0.006	29.128	10	3.063	-1-22	-0.003
13.925	<1	6.355	110	-0.045	29.422	4	3.033	-230	+0.003
15.936	1	5.557	-120, 021	-0.004, +0.022	29.511	1	3.024	032	+0.005
16.450	2	5.384	120	+0.002	29.936	1	2.982	060	-0.014
16.553	<1	5.351	0-21	+0.038	30.014	9	2.975	-132	-0.004
18.725	<1	4.735	-121	-0.024	30.300	<1	2.947	230	-0.003
19.312	1	4.592	031, -130	+0.002, +0.004	30.589	<1	2.920	0-32	-0.011
19.681	7	4.507	-1-21	+0.000	30.732	<1	2.907	-1-51	-0.005
19.816	1	4.477	040	+0.005	31.072	1	2.876	201	-0.006
19.974	<1	4.442	130	-0.011	31.189	<1	2.865	102	+0.013
20.104	1	4.413	0-31	-0.002	31.313	3	2.854	-2-31	-0.019
20.503	1	4.328	1-11	-0.003	31.420	11	2.845	2-11	+0.001
21.546	10	4.121	-131	+0.004	31.498	4	2.838	-1-32, 112	-0.023, +0.011
22.188	17	4.003	121	-0.006	31.566	2	2.832	211	-0.037
22.828	<1	3.892	-1-31	+0.001	31.938	2	2.799	151	-0.004
23.297	4	3.815	041, -140	-0.016, +0.007	32.158	2	2.781	-240	+0.025
24.029	2	3.701	140	-0.003	32.241	6	2.774	042, -160	-0.004, +0.019
24.162	2	3.681	0-41	+0.000	32.554	9	2.748	-241	+0.003
24.848	100	3.580	050	-0.001	32.777	5	2.730	221	+0.000
24.941	20	3.567	1-31	-0.004	33.215	5	2.695	-202	-0.020
25.096	5	3.546	-141	+0.002	33.269	13	2.691	240, -212	-0.014, +0.019
25.767	2	3.455	200	+0.005	33.544	1	2.669	0-42	-0.002
25.997	70	3.425	002	-0.011	33.865	7	2.645	-2-12	+0.005
26.089	41	3.413	-210	+0.002	34.140	6	2.624	-222	+0.004
26.281	11	3.388	012	-0.015	34.255	2	2.616	-2-41	-0.002
26.417	14	3.371	210	+0.002	34.444	2	2.602	132, 2-31	-0.009, -0.004
26.575	7	3.352	-1-41	+0.001	34.728	1	2.581	231	+0.009
26.667	7	3.340	-201, 0-12	-0.041, -0.003	35.508	8	2.526	-250, 052	-0.025, -0.004
26.835	18	3.320	-211	+0.003	35.730	2	2.511	-232, -251	-0.014, +0.020
26.966	3	3.304	-112	+0.009	36.713	2	2.446	250	-0.001
27.348	23	3.259	-220, -2-11	-0.002, +0.003	37.002	13	2.428	071, 0-52	-0.009, +0.001
27.526	3	3.238	-1-12	-0.005	37.322	2	2.407	241, -2-32	-0.012, +0.017
27.660	7	3.222	-150	-0.001	37.902	4	2.372	-1-52, -242, 170	-0.019, +0.023, -0.020
27.973	9	3.187	-221, 220	-0.005, -0.003	39.213	13	2.296	062, -260	-0.008, -0.002
28.118	6	3.171	-122, 141	-0.036, +0.017	39.419	6	2.284	-261, 003, -162	-0.032, -0.001, +0.002
28.248	4	3.157	0-22, 1-41	-0.011, +0.024					
28.430	12	3.137	150	-0.001					

structural type (space group $R\bar{3}c$), which suggests a high ionic conductivity.

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