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## PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

# Phase Formation in the $Ag_2MoO_4$–$MgMoO_4$–$Al_2(MoO_4)_3$ System

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**Abstract**—The subsolidus region of the $Ag_2MoO_4$—$MgMoO_4$—$Al_2(MoO_4)_3$ ternary salt system has been studied by X-ray phase analysis. The formation of new compounds $Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$ ($0 \le x \le 0.4$) and $AgMg_3Al(MoO_4)_5$ has been determined. The $Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$ variable-composition phase is related to the NASICON type structure (space group $R\bar{3}c$). $AgMg_3Al(MoO_4)_5$ 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: $a = 9.295(7)$ Å, $b = 17.619(2)$ Å, $c = 6.8570(7)$ Å, $\alpha = 87.420(9)°$, $\beta = 101.109(9)°$, $\gamma = 91.847(9)°$. The compounds $Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$ and $AgMg_3Al(MoO_4)_5$ are thermally stable up to 790 and 820°C, respectively.

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The demands of new industries and the advances in a number of new scientific and engineering lines stimulate investigations in the field of multicomponent systems and the development and synthesis of new solid-phase materials with a designed set of properties. Now a highly important place in the search and creation of new complex oxide materials offering promise as ionic semiconductors is held by compounds that demonstrate crystallochemical similarity to NASICON-type compounds [1–5].

This work studies phase formation in the subsolidus region of the silver magnesium aluminum molybdate system and determines the X-ray diffraction and thermal characteristics of triple molybdates and the conditions for their synthesis.

## EXPERIMENTAL

Molybdates $Ag_2MoO_4$, $MgMoO_4$, and $Al_2(MoO_4)_3$ that were previously synthesized by the solid-phase method, including the staged annealing of $AgNO_3$ (pure for analysis grade), MgO (chemically pure grade), $Al(NO_3)_3 \cdot 9H_2O$ (pure for analysis grade) and molybdenum trioxide (chemically pure grade) in a stoichiometric ratio at 350–450°C ($Ag_2MoO_4$), 400–750°C ($MgMoO_4$), and 300–700°C ($Al_2(MoO_4)_3$) served as initial components. The X-ray diffraction and thermal characteristics of the compounds obtained agree satisfactorily with data in [6–8].

Phase formation in the $Ag_2MoO_4$–$MgMoO_4$–$Al_2(MoO_4)_3$ system was studied by the "intersecting sections" method in the subsolidus region. The $MgMoO_4$–$AgAl(MoO_4)_2$ section, where intermediate phases were formed, was studied over the entire concentration region in steps of 5–10 mol % and in the vicinity of new compounds, in steps of 2.0–2.5 mol %. While equilibrium was attained, the phase composition was studied by X-ray diffraction.

To ascertain a possible homogeneity region in the $Ag_2MoO_4$–$MgMoO_4$–$Al_2(MoO_4)_3$ system, $Ag_{1-x}A_{1-x}Al_{1+x}(MoO_4)_3$ samples were prepared in $\Delta x = 0.1$ steps within the range $0 \le x \le 0.7$ and stepwise annealed in air in steps of 50°C starting at 300°C with intermediate grinding every 20–30 h. The duration of annealing was 50–100 h at every temperature. The homogeneity region boundaries were determined by X-ray phase analysis of air-annealed samples.

X-ray diffraction investigations were performed on a Brukeraks D8 Advance automatic powder diffractometer ($CuK_\alpha$ irradiation, graphite monochromator, maximal angle $2\theta = 90°$, 0.01°–0.02° scan steps, 1 s per point) and an FR-552 monochromator chamber ($CuK_{\alpha 1}$ irradiation, Ge internal standard). Unit cell parameters were determined on a Guinier G670 HUBER automated diffractometer.

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.** X-ray diffraction characteristics of an $Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$ variable-composition phase

| Compound | $a$, Å | $c$, Å | $V$, Å$^3$ |
|---|---|---|---|
| $AgMgAl(MoO_4)_3$ | 9.2320(16) | 22.800(4) | 1682.9 |
| $Ag_{0.8}Mg_{0.8}Al_{1.2}(MoO_4)_3$ | 9.1870(13) | 22.8046(19) | 1666.9 |
| $Ag_{0.6}Mg_{0.6}Al_{1.4}(MoO_4)_3$ | 9.1430(16) | 22.817(3) | 1651.8 |

**Table 2.** Indexing of X-ray diffraction pattern for $AgMg_3Al(MoO_4)_5$

| $2\theta_{exp}$, deg | $I/I_0$ | $d_{exp}$, Å | $h\,k\,l$ | $\Delta(2\theta_{exp} - 2\theta_{theor})$, deg | $2\theta_{exp}$, deg | $I/I_0$ | $d_{exp}$, Å | $h\,k\,l$ | $\Delta(2\theta_{exp} - 2\theta_{theor})$, deg |
|---|---|---|---|---|---|---|---|---|---|
| 10.052 | 5 | 8.793 | 020 | −0.006 | 28.817 | 15 | 3.096 | 022, $\bar{1}50$ | −0.037, +0.006 |
| 13.164 | 8 | 6.720 | 001 | −0.006 | 28.889 | 4 | 3.088 | 141 | +0.004 |
| 15.084 | 1 | 5.869 | 030 | +0.009 | 29.296 | 2 | 3.046 | $\bar{2}21$ | +0.002 |
| 16.263 | 2 | 5.446 | $0\bar{2}1$, 120 | −0.003, +0.009 | 29.570 | 13 | 3.019 | $\bar{1}22$ | +0.002 |
| 16.655 | 8 | 5.319 | $\bar{1}20$, $\bar{1}01$ | +0.003, +0.007 | 30.052 | 5 | 2.971 | 230, $0\bar{3}2$ | −0.008, +0.036 |
| 17.162 | 2 | 5.163 | $\bar{1}\bar{1}1$ | +0.005 | 30.464 | 11 | 2.932 | 060, $\bar{2}\bar{3}1$ | −0.008, +0.033 |
| 19.052 | 1 | 4.655 | $\bar{1}\bar{2}1$ | +0.000 | 30.588 | 12 | 2.920 | $\bar{1}\bar{3}2$ | −0.005 |
| 19.690 | 4 | 4.505 | $0\bar{3}1$,130 | −0.018, +0.047 | 30.694 | 2 | 2.910 | $\bar{2}30$ | −0.001 |
| 19.922 | 28 | 4.453 | $\bar{1}21$ | +0.003 | 31.164 | 1 | 2.868 | 032 | −0.004 |
| 20.244 | 2 | 4.383 | $\bar{1}30$, 101 | −0.027, +0.018 | 31.668 | 8 | 2.823 | $\bar{2}31$, 201 | −0.007, −0.003 |
| 20.461 | <1 | 4.337 | 031 | +0.007 | 31.954 | 1 | 2.799 | $\bar{1}32$ | −0.004 |
| 20.943 | 4 | 4.238 | 111 | −0.005 | 32.081 | 16 | 2.788 | 211, $2\bar{1}1$ | −0.017, +0.018 |
| 21.975 | 17 | 4.042 | $\bar{1}\bar{3}1$ | +0.003 | 32.438 | 2 | 2.758 | $1\bar{5}1$ | +0.010 |
| 22.566 | 60 | 3.937 | $1\bar{2}1$ | +0.003 | 32.778 | 1 | 2.730 | 151 | +0.007 |
| 23.161 | <1 | 3.837 | $\bar{1}31$ | −0.044 | 32.859 | 9 | 2.723 | $0\bar{4}2$, 240 | +0.000, +0.026 |
| 23.711 | 10 | 3.749 | $0\bar{4}1$ | −0.002 | 32.955 | 2 | 2.716 | 160 | −0.010 |
| 23.820 | 3 | 3.733 | 140 | −0.012 | 33.227 | 9 | 2.694 | $\bar{2}\bar{4}1$ | −0.007 |
| 24.348 | 3 | 3.653 | $\bar{1}40$ | −0.004 | 33.341 | 9 | 2.685 | $2\bar{2}1$ | −0.007 |
| 24.599 | 3 | 3.616 | 041 | +0.000 | 33.687 | 19 | 2.658 | $\bar{2}40$, $\bar{2}02$ | −0.005, +0.004 |
| 25.295 | 100 | 3.518 | 050 | −0.008 | 33.812 | 5 | 2.649 | $\bar{2}\bar{1}2$ | +0.012 |
| 25.491 | 33 | 3.492 | 131 | −0.003 | 34.170 | 3 | 2.622 | $\bar{1}\bar{6}1$, 042 | −0.028, +0.007 |
| 25.611 | 12 | 3.475 | $\bar{1}\bar{4}1$ | −0.002 | 34.341 | 7 | 2.609 | $\bar{2}12$ | +0.003 |
| 26.197 | 2 | 3.399 | 200 | +0.001 | 34.734 | 9 | 2.581 | $\bar{2}\bar{2}2$ | +0.001 |
| 26.497 | 63 | 3.361 | 002 | −0.004 | 35.100 | 3 | 2.555 | $1\bar{3}2$ | −0.010 |
| 26.582 | 42 | 3.351 | 210 | −0.013 | 35.299 | 2 | 2.541 | $2\bar{3}1$ | +0.000 |
| 26.800 | 24 | 3.324 | $0\bar{1}2$, $\bar{2}10$ | −0.020, +0.013 | 35.671 | 1 | 2.515 | 070 | +0.019 |
| 26.924 | 8 | 3.309 | $\bar{1}41$ | +0.001 | 35.761 | 1 | 2.509 | $\bar{2}22$, 132 | −0.016, −0.012 |
| 27.002 | 2 | 3.299 | $\bar{2}01$ | +0.010 | 36.191 | 9 | 2.480 | $0\bar{5}2$ | −0.005 |
| 27.187 | 6 | 3.277 | 012, $\bar{1}02$ | −0.006, +0.041 | 36.378 | 2 | 2.468 | $\bar{2}\bar{3}2$ | −0.005 |
| 27.280 | 20 | 3.266 | $\bar{2}\bar{1}1$ | −0.006 | 36.520 | 2 | 2.458 | $\bar{2}\bar{5}1$ | −0.017 |
| 27.432 | 3 | 3.249 | $\bar{1}\bar{1}2$ | +0.016 | 36.693 | <1 | 2.447 | $1\bar{6}1$ | −0.018 |
| 27.711 | 27 | 3.217 | $\bar{2}11$ | −0.003 | 37.013 | <1 | 2.427 | 161 | +0.025 |
| 27.898 | 3 | 3.195 | 220 | −0.008 | 37.187 | 2 | 2.416 | $\bar{2}50$ | −0.001 |
| 27.958 | 3 | 3.189 | $\bar{1}12$ | −0.001 | 37.700 | 11 | 2.384 | $0\bar{7}1$, 052 | −0.025, +0.000 |
| 28.256 | 8 | 3.156 | 150 | −0.005 | 37.847 | 1 | 2.375 | $\bar{2}32$, 170 | −0.025, +0.018 |
| 28.351 | 8 | 3.145 | $\bar{2}20$ | +0.003 | 37.847 | 1 | 2.375 | 170, $2\bar{4}1$ | −0.018, +0.046 |
| 28.475 | 5 | 3.132 | $\bar{2}\bar{2}1$ | −0.006 | 38.458 | 4 | 2.339 | $\bar{1}70$, $\bar{1}52$ | −0.010, +0.001 |
| 28.599 | 9 | 3.119 | $1\bar{4}1$, $\bar{1}\bar{2}2$ | −0.008, +0.000 | | | | | |

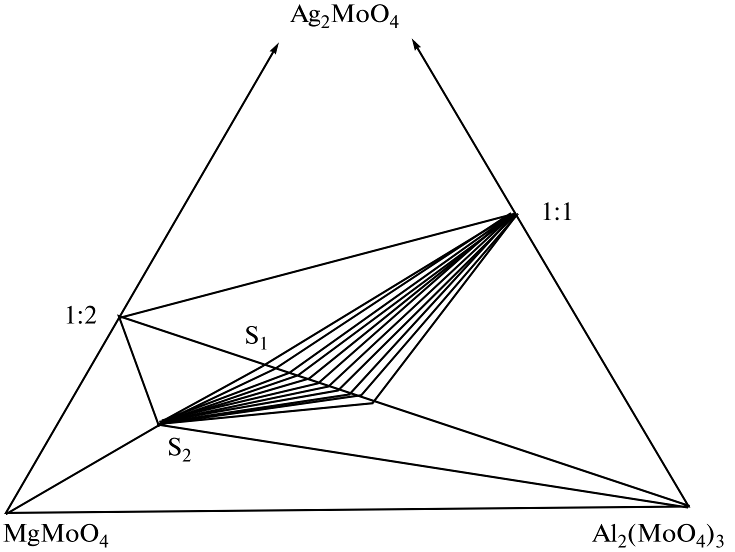

Diagram of subsolidus phase relations in the $MgMoO_4$–$Ag_2Mg_2(MoO_4)_3$–$AgAl(MoO_4)_2$–$Al_2(MoO_4)_3$ region for the $MgMoO_4$–$Ag_2MoO_4$–$Al_2(MoO_4)_3$ system. $S_1$ stands for $Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$; $S_2$ stands for $AgMg_3Al(MoO_4)_5$.

## RESULTS AND DISCUSSION

The $Ag_2MoO_4$–$MgMoO_4$ and $Ag_2MoO_4$–$Al_2(MoO_4)_3$ systems were studied in [9–12], so we did not additionally consider them.

The $Ag_2MoO_4$–$MgMoO_4$ and $Ag_2MoO_4$–$Al_2(MoO_4)_3$ sides of the $Ag_2MoO_4$–$MgMoO_4$–$Al_2(MoO_4)_3$ concentration triangle are characterized by the formation of $Ag_2Mg_2(MoO_4)_3$ and $AgAl(MoO_4)_2$ double molybdates. Silver magnesium molybdate $Ag_2Mg_2(MoO_4)_3$ belongs to the $Na_2Mg_5(MoO_4)_6$ structural family, at 500–530°C undergoes a reversible polymorphic transformation, and melts incongruently at 740°C. The homogeneity region expands towards $MgMoO_4$ to reach 2.0–2.5 mol % at 500°C [9]. Double molybdate $AgAl(MoO_4)_2$ crystallizes in monoclinic system ($NaFe(MoO_4)_2$ structural type), does not have an appreciable homogeneity region and melts incongruently [10–12]. In view of the nonexistence of congruent compounds in the $Ag_2MoO_4$–$Al_2(MoO_4)_3$ system [11], we confine the ternary salt system investigation to the $MgMoO_4$–$Ag_2Mg_2(MoO_4)_3$–$AgAl(MoO_4)_2$–$Al_2(MoO_4)_3$ region.

We have not detected any phases on the $MgMoO_4$–$Al_2(MoO_4)_3$ edge under our experimental conditions.

The $Ag_2Mg_2(MoO_4)_3$ and $AgAl(MoO_4)_2$ double molybdates necessary for studying phase formation in the $Ag_2MoO_4$–$MgMoO_4$–$Al_2(MoO_4)_3$ system, have been synthesized by the solid-phase method from the relevant neutral molybdates as described in [9–11].

To investigate interactions in the $Ag_2MoO_4$–$MgMoO_4$–$Al_2(MoO_4)$ system, we prepared a mixture of neutral and double molybdates in the stoichiometric ratio, including the compositions of the intersection points for all sections existing in the system. The results for the phase composition of the intersection points and points located inside the $Ag_2MoO_4$–$MgMoO_4$–$Al_2(MoO_4)$ triangle showed that, in the solid phase at 500°C, two-phase sections are $MgMoO_4$–$AgMg_3Al(MoO_4)_5$, $Ag_2Mg_2(MoO_4)_3$–$AgMg_3Al(MoO_4)_5$, $Ag_2Mg_2(MoO_4)_3$–$AgAl(MoO_4)_2$, $AgMg_3Al(MoO_4)_5$–$Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$, $0 \leq x \leq 0.4$), $Ag_2Mg_2(MoO_4)_3$–$Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$, $Ag_1Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$–$AgAl(MoO_4)_2$, $Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$–$Al_2(MoO_4)_3$, and $AgMg_3Al(MoO_4)_5$–$Al_2(MoO_4)_3$ (figure).

According to the X-ray powder diffraction data, the $AgMgAl(MoO_4)_3$ and $AgMg_3Al(MoO_4)_5$ triple molybdates synthesized do not have an appreciable homogeneity region along the $AgAl(MoO_4)_2$–$MgMoO_4$ section. An $Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$ variable-composition phase is formed along the $AgMgAl(MoO_4)_3$–$Al_2(MoO_4)_3$ section and represents an $AgMgAl(MoO_4)_3$-based solid solution, whose single-phase extent reaches $x = 0.4$. $Al_2(MoO_4)_3$ weak reflections appear in X-ray diffraction patterns at a higher concentration of aluminum cations.

X-ray powder diffraction showed that the $Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$ compounds are isostructural to sodium zinc scandium molybdate [13] with a rhombohedral lattice (space group $R\bar{3}c$, $Z = 6$) as to reflection positions and intensity ratios. The homogeneity extent was estimated from the change of lattice parameters for the samples annealed at 500°C and higher temperatures (Tables 1).

$AgMg_3Al(MoO_4)_5$ is isostructural to $NaMg_3In(MoO_4)_5$, which has been synthesized by us earlier [14] and indexed in triclinic system (space group $P\bar{1}$, $Z = 2$) with the following unit cell parameters: $a = 9.295(7)$ Å, $b = 17.619(2)$ Å, $c = 6.8570(7)$ Å,

$\alpha = 87.420(9)°$, $\beta = 101.109(9)°$, $\gamma = 91.847(9)°$, $V = 820.42$ Å$^3$, $\rho_{calc} = 4.078$ g/cm$^3$ (Table 2).

$AgMgAl(MoO_4)_3$ was found to melt incongruently at 790°C, and $AgMg_3Al(MoO_4)_5$ is thermally stable up to 820°C; polymorphous transformations do not occur.

In summary, the phase formation was studied in the $Ag_2MoO_4$–$MgMoO_4$–$Al_2(MoO_4)_3$ system for the first time. New triple molybdates $AgMg_3Al(MoO_4)_5$ and $AgMgAl(MoO_4)_3$ were synthesized, and the region of $AgMgAl(MoO_4)_3$-based solid solutions was discovered. Crystallographic and thermal characteristics were determined for the compounds obtained. It has been established that the compounds $Ag_{1-x}Mg_{1-x}Al_{1+x}(MoO_4)_3$ are of the NASICON structural type (space group $R\bar{3}c$), which suggests a high ionic conductivity.

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