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A Study of Phase Formation in the Subsolidus Region of the System Na_2MoO_4–$MnMoO_4$–$Cr_2(MoO_4)_3$

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Abstract—Phase relationships in the subsolidus region of the system Na_2MoO_4–$MnMoO_4$–$Cr_2(MoO_4)_3$ were studied by means of X-ray diffraction and differential-thermal analyses. The possibility of obtaining a variable-composition phase $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ ($0 \le x \le 0.5$) and ternary molybdate $NaMn_3Cr(MoO_4)_5$ was examined. The temperature dependence of the conductivity of the phase Na_{1-x} $Mn_{1-x}Cr_{1+x}(MoO_4)_3$ was analyzed.

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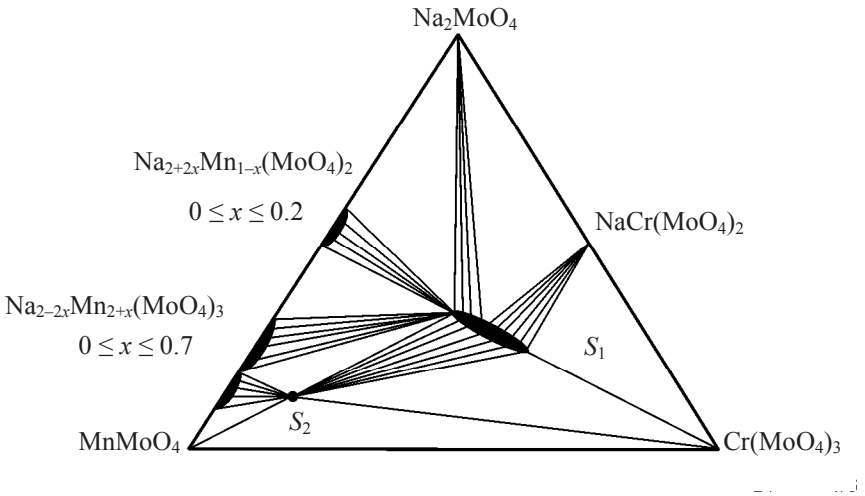
In recent years, considerable attention has been given to synthesis of phases with high ionic conductivity by lithium and sodium ions, which belong to the Nasicon type widely occurring in phosphate, arsenate, vanadate, silicate, sulfate, and molybdate systems [1–4]. The large crystallization field of the rhombohedral skeleton $\{[R_2(EO_4)_3]^{p-}\}_{3\infty}$ constituted by RO_6 octahedra and EO_4 tetrahedra is due to the wide isomorphism of cations of varied nature and size, which occupy crystallographic positions of the skeleton of the structure and its voids [5–8].

The aim of this study was to examine the phase formation in the system Na_2MoO_4–$MnMoO_4$–$Cr_2(MoO_4)_3$ in the temperature range 400–800°C; to find conditions in which $NaMnCr(MoO_4)_3$, variable-composition phases $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$, and ternary molybdate $NaMn_3Cr(MoO_4)_5$ are formed; and to determine the homogeneity region, thermal stability, and the temperature dependences of the conductivity, dielectric constant, and the dielectric loss tangent.

EXPERIMENTAL

As starting components for studies of the system served molybdate Na_2MoO_4, $MnMoO_4$, and $Cr_2(MoO_4)_3$ preliminarily synthesized by the solid-phase technique from Na_2CO_3, MnO, $Cr(NO_3)_3 \cdot 9H_2O$, and MoO_3. The interaction in the system Na_2MoO_4–$MnMoO_4$–$Cr_2(MoO_4)_3$ was studied in two stages. In the first stage, the phase composition of the intersection points of sections emerging from medium and double molybdates formed in the binary systems Na_2MoO_4–$MnMoO_4$, Na_2MoO_4–$Cr_2(MoO_4)_3$, and $MnMoO_4$–$Cr_2(MoO_4)_3$ was analyzed. In the second stage, the revealed quasibinary sections were examined, which enabled triangulation of the system (see figure).

The formation of the ternary molybdate $NaMn_3Cr(MoO_4)_5$ (1 : 3 ratio) was observed along the $NaCr(MoO_4)_2$–$MnMoO_4$ section at 600–650°C. The formation of $NaMnCr(MoO_4)_3$ was found in the sections $NaCr(MoO_4)_2$–$MnMoO_4$ and $Na_{2+2x}Mn_{1-x}(MoO_4)_2$–$Cr_2(MoO_4)_3$ ($0 \le x \le 0.2$) in the temperature range 570–650°C. The variable-composition phase $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ ($0 \le x \le 0.5$), which is an omission solid solution based on $NaMnCr(MoO_4)_3$, occurs within the plane of the Na_2MoO_4–$MnMoO_4$–$Cr_2(MoO_4)_3$ triangle and along the section $NaMnCr(MoO_4)_3$–$Cr_2(MoO_4)_3$. Samples with compositions belonging to quasibinary sections were prepared with a step of 2.5–5 mol %, and for ascertaining the composition of the forming ternary molybdate $NaMnCr(MoO_4)$ and the limits of the homogeneity region of the variable-composition phase $Na_{1-x}MN_{1-x}Cr_{1+x}(MoO_4)_3$, with a



Phase relationships in the system Na_2MoO_4–$MnMoO_4$–$Cr_2(MoO_4)_3$ at 700°C. (S_1) $Na_{1-x}Mn_{1-x}Cr_{1+x}(MnO_4)_3$ and (S_2) $NaMn_3 \cdot Cr(MoO_4)_5$.

step of 1 mol %. The samples were annealed at 400, 500, 550, 600, 650, and 700°C with multiple intermittent grindings every 20–30 h. The time of calcination at each temperature was 70–90 h. After the annealing, the samples were slowly cooled with the furnace. Nonequilibrium samples were subjected to additional annealing. The equilibrium in a system was considered to be attained if the phase composition of the corresponding samples remained unchanged after two successive annealings. The synthesis products were identified by means of X-ray phase analysis (XPA). X-ray diffraction patterns of the samples were obtained in an FR-552 chamber-monochromator (CuK_α radiation, Ge as internal standard). The resulting X-ray powder patterns were measured with an IZA-2 comparator. The X-ray diffraction patterns were processed using the Rentgen standard software package (see Table 1).

The differential-thermal analysis was performed with a MOM OF-103 derivatograph (Hungary) at a heating rate of 10 deg min^{-1} (0.3–0.4-g samples).

The temperature dependence of the conductivity σ, dielectric constant ε, and dielectric loss tangent tan δ were studied using the Vest and Tallan polarization method [6] and densely compacted ceramic samples in the form of pellets 10 mm in diameter and 1–1.5 mm thick, with platinum electrodes. The electrodes were deposited by firing-in a platinum paste. The electrical properties were studied with an E8-4 ac bridge at a frequency of 103 Hz, using an R-5025 capacitance box, which made it possible to extend the range in which the dielectric loss tangent could be measured (determination accuracy ±5%). The dc current was measured with an E6-13A teraohmmeter at a fixed voltage of 30–50 mV.

The reproducibility of the measurement results was verified in the heating-and-cooling mode in the temperature range 20–600°C. The sample temperatures in the course of electrical measurements were measured with a Chromel–Alumel thermocouple connected to a V7-21A voltmeter with an accuracy of ±2°C.

According to the XPA data, the interaction of $NaCr \cdot (MoO_4)$ with $MnMoO_4$ begins in the temperature range 550–600°C at a calcination duration of 80–100 h.

Table 1. Crystallographic parameters of the ternary molybdate and variable-composition phase $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$

Composition	*a*	*c*	*V/Z*
	Å		
$NaMnCr(MoO_4)_3$	9.319(5)	22.825(3)	286.10
$Na_{0.9}Mn_{0.9}Cr_{1.1}(MoO_4)_3$	9.321(4)	22.829(2)	286.27
$Na_{0.8}Mn_{0.8}Cr_{1.2}(MoO_4)_3$	9.323(8)	22.837(3)	286.55
$Na_{0.7}Mn_{0.7}Cr_{1.3}(MoO_4)_3$	9.327(5)	22.845(5)	286.88
$Na_{0.6}Mn_{0.6}Cr_{1.4}(MoO_4)_3$	9.337(4)	22.878(2)	287.91
$Na_{0.5}Mn_{0.5}Cr_{1.5}(MoO_4)_3$	9.342(2)	22.881(3)	288.22

The single-phase ternary molybdate $NaMnCr(MoO_4)_3$ and the omission solid solution on its basis, $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$, were obtained at 680°C and a calcination time of 120 h; the ternary molybdate $NaMnCr(MoO_4)_5$ was synthesized as a single-phase preparation at 700°C and annealing for 150 h.

$Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ and $NaMnCr(MoO_4)_5$ incongruently melt at 825 and 840°C, respectively, without undergoing polymorphic transformations.

According to the XPA data, $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ crystallizes in the trigonal crystal system (space group $R\bar{3}c$) and is isostructural with the ternary molybdate $Na_{0.625}Zn_{0.625}Sc_{1.375}(MoO_4)_3$ [2]. The wide extent of the crystallization field ($0 \le x \le 0.5$) with the Nasicon structure is determined by the possibility of isomorphic substitutions in the octahedra. The octahedral positions (M) statistically filled by Mn and Cr atoms contain an excess amount of chromium (at $x > 0$) and are deficient in manganese. Sodium occupying the skeleton voids does not distort the lattice symmetry and is also deficient.

These specific structural features of $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ and the nature of the cation distribution lead to an increased contribution from Cr–O bonds to the overall electrostatic balance of the structure. For the balance of the structure to be retained, it is necessary that Na–O bonds should be weakened; this is provided by a deficiency of sodium in the voids of the skeleton and by an increase in its size, which results in that the unit cell of $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ becomes larger, and the homogeneity region, wider (Table 1). The compound $NaMn_3Cr(MoO_4)_5$ crystallizes in the triclinic crystal system (space group $P\bar{1}$, $Z = 2$), is isostructural with $NaMg3In(MoO_4)$ [4], and has the following lattice parameters: $a = 6.965(2)$ Å, $b = 17.585(4)$ Å, and $c = 6.884(2)$ Å; $\alpha = 88.00(2)°$, $\beta = 101.35(1)°$, and $\gamma = 92.14(2)°$. The crystal structure of $NaMg_3In(MoO_4)_5$ is based on a 3D skeleton constituted by MoO_4 tetrahedra and $Mg(In)O_6$ octahedra. The closed voids in the skeleton are occupied by sodium atoms. A distinctive feature of this structure is the presence of fragments constituted by four octahedra forming a planar tetragon and twin octahedra connected by common edges.

As temperature increases from 20 to 600°C, the conductivity of $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ varies within the range 10^{-8}–10^{-2} Ω^{-1} cm^{-1}, with predominantly ionic conduction being characteristic ($t_i = 0.76$–0.88 (Table 2). The activation energies E_a are within the range 1.34–1.85 eV. As x increases in a series of solid solutions, the conductivity grows, which is due to the structural features of Nasicon-like phases. In the case of a heterovalent substitution $Na^+ + Mn^{2+} \rightarrow Cr^{3+}$ in a series of solid solutions, additional vacancies are formed in the sodium sublattice, which affect the mobility of sodium cations in the skeleton voids combined into a system of interconnected channels [2–4]. A correlation is observed between the variation of σ and that of the unit cell volume of the variable-composition phase.

In the temperature range 20–600°C, the dielectric constant varies from 120 to 780, and the dielectric loss

Table 2. Electrical parameters of the variable-composition phase $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ ($0 \le x \le 0.5$)

x	20°C		300°C		500°C		600°C		E_a, eV
	σ, Ω cm^{-1}	t_i	σ, Ω cm^{-1}	t_i	σ, Ω cm^{-1}	t_i	σ, Ω cm^{-1}	t_i	
0	5.84×10^{-8}	0.88	7.23×10^{-6}	0.76	4.85×10^{-3}	0.75	5.36×10^{-2}	0.78	1.85
0.1	6.92×10^{-8}	0.88	7.64×10^{-6}	0.78	5.67×10^{-3}	0.77	5.71×10^{-2}	0.79	1.77
0.2	7.84×10^{-8}	0.87	8.68×10^{-6}	0.84	5.94×10^{-3}	0.78	6.08×10^{-2}	0.75	1.64
0.3	8.15×10^{-8}	0.88	9.87×10^{-6}	0.83	7.34×10^{-3}	0.81	6.81×10^{-2}	0.78	1.58
0.4	8.86×10^{-8}	0.88	2.86×10^{-5}	0.85	8.55×10^{-3}	0.84	7.93×10^{-2}	0.84	1.42
0.5	9.88×10^{-8}	0.87	5.16×10^{-5}	0.89	9.74×10^{-3}	0.88	8.72×10^{-2}	0.84	1.34

tangent, from 2.6 to 16.4. The temperature dependences of ε and tanδ are exponential, without peaks or dips in the curves, which indicates that $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ undergoes no phase transitions and shows no ferroelectric properties.

The high ionic conductivity of the variable-composition phase suggests that $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ can be used as a solid electrolyte with conduction by sodium ions.

CONCLUSIONS

(1) A variable-composition phase $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ ($0 \le x \le 0.5$) and a ternary molybdate $NaMn_3Cr(MoO_4)5$ were obtained in the system Na_2MoO_4–$MnMoO_4$–$Cr_2(MoO_4)_3$ by the method of solid-phase reactions.

(2) An X-ray phase analysis demonstrated that the variable-composition phase crystallizes in the trigonal crystal system (space group $R\bar{3}c$) (Nasicon structural type), and the ternary molybdate $NaMn_3Cr(MoO_4)_5$ belongs to the triclinic crystal system (space group $P\bar{1}$) [$NaMgIn(MoO_4)_5$ structural type].

(3) $Na_{1-x}Mn_{1-x}Cr_{1+x}(MoO_4)_3$ compounds exhibit a mixed ionic-electronic conduction, with predominance of the ionic component.

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