PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Chemical Interactions in Na⁺,Sr²⁺||Cl⁻,EO₄²⁻ (E = Mo,W) and Na⁺,Sr²⁺||Cl⁻,MoO₄²⁻,WO₄²⁻ Reciprocal Systems: Description and Study

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Abstract—Chemical interactions of salts in the four-component reciprocal system comprised of chlorides, molybdates, and tungstates of sodium and strontium are studied by the ion-balance method. DTA heating curves feature exotherms due to the interaction of $Na_2EO_4 + SrCl_2$ (E = Mo,W) and $Na_2MOO_4 + Na_2WO_4 + SrCl_2$ homogenized powdery batches. Cooling curves feature exotherms indicating the formation of exchange

reaction products upon crystallization of batches from NaCl + SrEO₄ melts in the Na⁺,Sr²⁺||Cl⁻,EO₄²⁻ and NaCl + SrMo_xW_{1-x}O₄ ternary reciprocal systems and in the Na⁺,Sr²⁺||Cl⁻,MoO₄²⁻,WO₄²⁻ four-component reciprocal system. Reaction products are identified by X-ray powder diffraction. The presence of double compounds Na₃ClMoO₄ and Na₃ClWO₄ in reaction products in the Na⁺,Sr²⁺||Cl⁻,EO₄²⁻ systems and the presence of Na₃ClMo_xW_{1-x}O₄ solid solutions (ss) in the Na⁺,Sr²⁺||Cl⁻,MoO₄²⁻,WO₄²⁻ system is considered in terms of divergence phenomena.

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INTRODUCTION

Alkaline-earth-metal molybdates, tungstates, and their isomorphic mixtures are widely used as phosphors for producing single crystals with the aim of using the stimulated Raman scattering (SRS) effect in lasers [1–6]. Strontium molybdate and strontium tungstate crystals and their solid solutions (ss) have most technologically convenient and close-to-record SRS characteristics. Therefore, studies of phase diagrams of multicomponent systems and chemical interactions involving molybdates and tungstates of alkaline-earth metals are not only of theoretical, but also of practical interest [7, 8].

EXPERIMENTAL

The Na⁺,Sr²⁺ $\|Cl^-,MoO_4^{2^-},WO_4^{2^-}$ four-component reciprocal system was previously studied by the conversion method [9]. In the study reported here, we used the following salts: specialty grade NaCl, pure grade Na₂MoO₄ and Na₂WO₄, and analytical reagent grade SrCl₂, SrMoO₄, and SrWO₄. The investigation tool was an STA 449 F3 Phoenix (Netzsch) simultaneous thermal analyzer [10, 11]. The thermo-e.m.f. source used was a Pt–Rh/Pt thermocouple. The accuracy of temperature determination after calibration with reference substances was $\pm 1.5^{\circ}$ C. X-ray powder diffraction experiments were carried out on a DRON-2.0 diffractometer (Ni_β-filtered Cu K_{α} radiation) [12–14]. The precursors were weighed on a Shimadzu AUX 220 analytical balance. The weighed precursors were pounded with an agate mortar and a pestle and then triturated with acetone; after acetone was evaporated, a 0.1-g aliquot of the powder was placed into a platinum microcrucible. A second crucible contained an Al₂O₃ (analytical reagent grade) reference. The heating rate was 10 K/min.

THEORY

The exchange reaction

Na₂EO₄ + SrCl₂ = 2NaCl + SrEO₄ (E = Mo,W),(1) is exothermic ($\Delta_r H_{298}^{\circ} < 0$) when $r_{Na^+} < r_{Sr^{2+}}$ and $r_{Cl^-} < r_{EO_4^{2-}}$: $r_{Na^+} = 0.098$ nm, $r_{Sr^{2+}} = 0.294$ nm, $r_{Cl^-} = 0.181$ nm,

 $r_{MOQ_{2}^{2-}} = 0.254 \text{ nm}, \text{ and } r_{WQ_{2}^{2-}} = 0.257 \text{ nm} [15, 16].$



Fig. 1. Phase tree for the Na⁺, $Sr^{2+} \|Cl^-$, MoO_4^{2-} , WO_4^{2-} four-component reciprocal system; D_1 and D_2 stand for Na₃ClMoO₄ and Na₃ClWO₄, respectively.

This prediction coincides with the direction of the reaction predicted in terms of Pearson's theory of hard and soft acids and bases, according to which a hard acid (Na⁺ cation) and a hard base (Cl⁻ anion) form a stable pair NaCl. A soft acid (Sr²⁺ cation) and a soft

base (EO_4^{2-}) form another stable pair.

Similar reasoning is valid for the reaction

$$Na_2MoO_4 + Na_2WO_4 + 2SrCl_2 = 4NaCl + SrMoO_4 + SrWO_4.$$
(2)

The interaction of homogenized powder mixtures in contact melting yields a labile yellow liquid phase, which is detected by DTA and electrical conductivity measurements [9, 17]. The formation of a liquid phase in the entire volume of the initial reaction mixture during programmed heating accelerates the chemical interaction of the components, which appears as exotherms on the DTA curves.

Here we studied chemical interactions between the

components of the Na^+ , $Sr^{2+} \| Cl^-$, MoO_4^{2-} , WO_4^{2-} system by the ion-balance based on the phase tree (Fig. 1) [18]; we also studied the behavior of powder reagents in reactions (1) and (2) under programmed heating.

Description of Chemical Reactions

in the Na⁺, Sr²⁺||Cl⁻, MoO₄²⁻, WO₄²⁻ Reciprocal System in Terms of Ion Balance

The precursors used were salts and double compounds. The number of precursors was three to six. Let us consider the following examples.

Let three salts be mixed: $Na_2MoO_4 + Na_2WO_4 +$ SrCl₂.

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Let us consider the equation

$$Na_2MoO_4 + Na_2WO_4 + 2SrCl_2$$

= xSrMoO_4 + ySrWO_4 + zNaCl, (3)

where x, y, and z are the factors to be determined.

Equate the factors at the ions in the left-hand and right-hand parts of the equation:

$$\begin{cases} 4Na^{+} = z \\ WO_{4}^{2-} = y \\ MoO_{4}^{2-} = x \\ 2Sr^{2+} = x = y \\ 4Cl^{-} = z \end{cases}$$

Solve the set of linear equations to obtain x = 1, y = 1, and z = 4. Since the factors are greater than zero, the following equation is implemented:

$$Na_2MoO_4 + Na_2WO_4 + 2SrCl_2$$

= SrMoO_4 + SrWO_4 + 4NaCl. (4)

The overall reaction can be decomposed to two simpler reactions:

$$Na_2MoO_4 + SrCl_2 = SrMoO_4 + NaCl and$$
 (5)

$$Na_2WO_4 + SrCl_2 = SrWO_4 + NaCl,$$
(6)

which are exchange reactions.

The salts in the right-hand part of the overall reactions are those of the SrMoO₄-SrWO₄-NaCl stable triangle. The melt-crystallizing salts are NaCl and $SrMo_{0.5}W_{0.5}O_4$ ss due to the ratio MoO_4^{2-} : $WO_4^{2-} = 1:1$.

Let the initial batch contains three salts: Na_2MoO_4 + $3Na_2WO_4 + 2SrCl_2$.

(1) Consider the $Na_2MoO_4-Na_2WO_4-NaCl-SrMoO_4-SrWO_4$ simplex.

Write the reaction equation as

$$3Na_2MoO_4 + 3Na_2WO_4 + 2SrCl_2 = xNa_2MoO_4 + yNa_2WO_4 + zNaCl + pSrMoO_4 + tSrWO_4.$$
 (7)

Equate the factors at ions in the left-hand and right-hand parts of the equation:

$$\begin{cases} MoO_4^{2-} = 3 = x + p \\ WO_4^{2-} = 3 = y + t \\ Na^+ = 12 = x + y + z, \\ Sr^{2+} = 2 = p + t \\ Cl^- = 4 = x + z \end{cases}$$

 $x + z = 4 \Rightarrow y = 12 - 4 = 8; t = 3 - y = 3 - 8 = -5.$

Since t = -5, the reaction products do not enter the Na₂MoO₄-Na₂WO₄-NaCl-SrMoO₄-SrWO₄ simplex.

(2) Consider the $Na_3CIMoO_4-Na_3CIWO_4-SrMoO_4-SrWO_4$ simplex.

Write the reaction equation as

$$3Na_2MoO_4 + 3Na_2WO_4 + 2SrCl_2 = xNa_3ClMoO_4 + yNa_3ClWO_4 + zSrMoO_4 + tSrWO_4.$$
(8)

Equate the factors at ions in the left-hand and right-hand parts of the equation:

$$Na^{+} = 12 = 3(x + y)$$

$$MoO_{4}^{2-} = 3 = y + z$$

$$WO_{4}^{2-} = 3 = x + t$$

$$Sr^{2+} = 2 = z + t$$

$$Cl^{-} = 4 = x + y$$

Since the ion ratio in the left-hand part of the equa-

tion is $\frac{\text{MoO}_4^{2^-}}{\text{WO}_4^{2^-}} = \frac{3}{3} = 1, \frac{z}{t} = 1$, too; that is, z = 1 and t =

1. Then, the number of MoO_4^{2-} ions is equal to the number of WO_4^{2-} ions, and x = 3 - z = 2; y = 3 - t = 2.

Check the correct determination Na⁺: 12 = 3(x + y) = 3(2 + 2). Since all factors are positive, the reaction products enter the Na₃ClMoO₄-Na₃ClWO₄-SrMoO₄-SrWO₄ simplex. The overall reaction equation will be

$$3Na_2MoO_4 + 3Na_2WO_4 + 2SrCl_2 = 2Na_3ClMoO_4 + 2Na_3ClWO_4 + SrMoO_4 + SrWO_4.$$
(9)

The overall reaction can be decomposed to the following simpler reactions to produce double compounds and ss:

$$3Na_2MoO_4 + SrCl_2 = SrMoO_4 + 2Na_3ClMoO_4, (10)$$

$$3Na_2WO_4 + SrCl_2 = SrWO_4 + 2Na_3ClWO_4, \quad (11)$$

$$SrMoO_4 + SrWO_4 = 2SrMo_{0.5}W_{0.5}O_4,$$
 (12)

$$2Na_{3}CIMoO_{4} + 2Na_{3}CIWO_{4}$$

$$= 4Na_{3}CIMo_{0.5}W_{0.5}O_{4}.$$
(13)

The crystallizing phases will be two ss: $Na_3Cl-Mo_{0.5}W_{0.5}O_4$ and $SrMo_{0.5}W_{0.5}O_4$.

Set the initial batch contains four salts: $3SrCl_2 + 7Na_2MoO_4 + 2NaCl + 2Na_2WO_4$. Combining the last two salts into the compound Na_3ClWO_4 , we obtain $3SrCl_2 + 7Na_2MoO_4 + 2Na_3ClWO_4$.

(1) Let us consider the NaCl-SrCl₂-SrMoO₄-SrWO₄ simplex.

The equation in the general form will be

$$3SrCl_{2} + 7Na_{2}MoO_{4} + 2Na_{3}ClWO_{4}$$

= xNaCl + zNa_{2}MoO_{4} + tSrWO_{4}. (14)

Equating the factors at ions in the right-hand and left-hand parts of the equation, we obtain:

$$\begin{cases} Na^{+} = 19 = x \\ Sr^{2+} = 3 = z + t \\ Cl^{-} = 8 = x + y \\ MoO_{4}^{2-} = 7 = z \\ WO_{4}^{2-} = 2 = t \end{cases}$$

Solve this set of linear equations to obtain the factors in the right-hand part of the equation: x = 19, z = 7, t = 2, and y = -1. Therefore, since one factor is negative, this simplex is not implemented.

(2) Let us proceed with the NaCl–SrMoO₄– SrWO₄–Na₃ClMoO₄–Na₃ClWO₄ simplex.

Write the equation

$$3SrCl_{2} + 7Na_{2}MoO_{4} + 2Na_{3}ClWO_{4}$$

$$\rightleftharpoons xNaCl + ySrMoO_{4} + zSrWO_{4}$$
(15)

$$+ tNa_{3}ClMoO_{4} + pNa_{3}ClWO_{4}.$$

Equating the factors at ions in the left-hand and right-hand parts of the equation, we have:

$$\begin{cases} Sr^{2+} = 3 = y + z \\ Na^{+} = 18 = x + t + p \\ MoO_{4}^{2-} = 6 = y + t \\ WO_{4}^{2-} = 2 = z + p \\ CI^{-} = 8 = x + t + p \end{cases}$$

In order to correctly determine the factors at $SrMoO_4$ and $SrWO_4$, Na_3ClMoO_4 , and Na_3ClWO_4 in the right-hand part of the equation, we need to consider the factors at MoO_4^{2-} and WO_4^{2-} together:

$$y + z = 3;$$
 MoO₄²⁻ + WO₄²⁻ = 8 = (y + t) + (z + p),

$$Na^+ = (Na_3ClMoO_4 + Na_3ClWO_4) = t + p = 6; x = 12.$$

Since all factors are positive, the reaction products enter the simplex. The MoO_4^{2-}/WO_4^{2-} ions that enter continuous ss phases are in the ratio 7/2, so the compositions of molybdates and tungstates will correspond to the mole fractions: 7/9 for MoO_4^{2-} and 2/9 for WO_4^{2-} . So, the overall phase reaction is

$$3SrCl_{2} + 7Na_{2}MoO_{4} + 2Na_{3}ClWO_{4}$$

= 3SrCl_{2} + 7Na_{2}MoO_{4} + 2NaCl + Na_{2}WO_{4}
= 2NaCl + 3(7/9SrMoO_{4} + 2/9SrWO_{4})
+ 6(7/9Na_{2}MoO_{4} + 2/9Na_{2}WO_{4}). (16)

Check the determination of factors:

$$\begin{cases} Na^{+} = 2 + 6\left(3\frac{7}{9} + 3\frac{2}{9}\right) = 2 + \frac{48}{3} + \frac{12}{3} = 20\\ Cl^{-} = 2 + 6\left(\frac{7}{9} + \frac{2}{9}\right) = 8\\ Sr^{2+} = 3\left(\frac{7}{9} + \frac{2}{9}\right) = 3\\ MoO_{4}^{2-} = 3\frac{7}{9} + 6\frac{7}{9} = 7\\ WO_{4}^{2-} = 3\frac{2}{9} + 6\frac{2}{9} = 2 \end{cases}$$

The phases crystallizing from melt by reaction (16) will be

 $NaCl + SrMo_{7/9}W_{2/9}O_4 + Na_2Mo_{7/9}W_{7/9}O_4.$

Chemical interactions for mixtures of five and six initial salts are described in a similar manner (Eqs. (17)-(19)).

The initial composition is comprised of five salts: $5SrCl_2 + 3SrWO_4 + 7Na_2MoO_4 + 2Na_3CIMoO_4 + 11Na_3CIWO_4$.

$$5SrCl_{2} + 3SrWO_{4} + 7Na_{2}MoO_{4} + 2Na_{3}ClMoO_{4} + 11Na_{3}ClWO_{4} = 8NaCl + 8(9/23SrMoO_{4} + 14/23SrWO_{4}) + 15(9/23Na_{3}ClMoO_{4} + 14/23Na_{3}ClWO_{4}),$$
(17)

$$5SrCl_{2} + 3SrWO_{4} + 7Na_{2}MoO_{4} + 2Na_{3}ClMoO_{4} + 11Na_{3}ClWO_{4} = 8NaCl + 8SrMo_{9/23}W_{14/23}O_{4}$$
(18)
+ 15Na_{3}ClMo_{9/23}W_{14/23}O_{4}.

The phases crystallizing from melt are NaCl and $SrMo_{9/23}W_{14/23}O_4 + Na_3ClMo_{9/23}W_{14/23}O_4$. The reaction products enter the NaCl-SrMoO₄-SrWO₄-Na_3ClMoO₄-Na_3ClWO₄ simplex.

The initial composition is comprised of six salts: $2NaCl + 2SrCl_2 + 5Na_2MoO_4 + 6Na_2WO_4 + 2SrMoO_4 + 2SrWO_4$.

$$2NaCl + 2SrCl_{2} + 5Na_{2}MoO_{4} + 6Na_{2}WO_{4}$$

+ 2SrMoO_{4} + 2SrWO_{4} = Na_{2}MoO_{4}
+ 2Na_{2}WO_{4} + 3Na_{3}ClMoO_{4} + 3Na_{3}ClWO_{4}
+ 3SrMoO_{4} + 3SrWO_{4}. (19)

The predicted composition of crystallizing phases is the following: $Na_2Mo_{1/3}W_{2/3}O_4$, $Na_3ClMo_{0.5}W_{0.5}O_4$ and $SrMo_{0.5}W_{0.5}O_4$. The reaction products enter the Na_2MO_4 - Na_2WO_4 - Na_3ClMoO_4 - Na_3ClWO_4 - $SrMoO_4$ - $SrWO_4$ simplex.

The $\Delta_f G_{298}^{\circ}$ values of the precursors were used to calculate the $\Delta_r G_{298}^{\circ}$ of exchange reactions (4)–(6) (Table 1). In view of the $\Delta_r G_{298}^{\circ}$ values and the heats of reactions $\Delta_r H_{298}^{\circ}$ found in [9], the Na⁺,Sr²⁺||Cl⁻,MoO₄²⁻ and Na⁺,Sr²⁺||Cl⁻,WO₄²⁻ systems can be classified as irreversible reciprocal systems (according to [19, 20]) where equilibrium is shifted toward the stable salts NaCl + SrMoO₄ and NaCl + SrWO₄. The liquidi of the Na⁺,Sr²⁺||Cl⁻,MoO₄²⁻ and Na⁺,Sr²⁺||Cl⁻,WO₄²⁻ systems prove the irreversibility of exchange reactions with the dominant SrMoO₄ and SrWO₄ crystallization fields.

RESULTS AND DISCUSSION

Interactions of Salts in Na^+ , $Sr^{2+}||Cl^-$, $MoO_4^{2-}(WO_4^{2-})$,

 $Na^+, Sr^{2+} || Cl^-, MoO_4^{2-}, WO_4^{2-}$ Reciprocal Systems

We have studied interactions in homogenized powder mixtures comprised of 0.5 eqv. fractions $Na_2MoO_4 +$ 0.5 eqv. fractions $SrCl_2$, 0.5 eqv. fractions $Na_2WO_4 +$ 0.5 eqv. fractions $SrCl_2$, and 0.25 eqv. fractions $Na_2MoO_4 +$ 0.25 eqv. fractions $Na_2WO_4 +$ 0.5 eqv. fractions $SrCl_2$ under programmed heating to 800°C:

(1) $2.0592 \text{ g Na}_2\text{MoO}_4 + 1.5853 \text{ g SrCl}_2$ (Fig. 2);

(2) $2.9383 \text{ g Na}_2\text{WO}_4 + 1.5853 \text{ g SrCl}_2$ (Fig. 3); and

(3) 1.0296 g Na_2MoO_4 + 1.4641 g Na_2WO_4 + 1.5853 g SrCl₂ (Fig. 4).

X-ray powder diffraction patterns for mixtures that were annealed for 15 min at 600° C and then quenched in ice appear in Figs. 5–7.

When homogenized powder mixture (1) is heated (Fig. 2), the first endotherm at 457.2°C corresponds to the α/β polymorphic transition in Na₂MoO₄.

The onset temperature of the exothermic reaction (541.5°C) is 16.5°C lower than the melting temperature of the low-melting eutectic (558°C) in the NaCl– SrCl₂–SrMoO₄ subsystem. Na₃ClMoO₄ formation gives rise to an insignificant second endotherm at 635.8°C, whose temperature is 10.8°C higher than the ternary eutectic melting temperature (625°C) in the NaCl–SrMoO₄–Na₃ClMoO₄ stable triangle.

System	Gibbs energy of the chemical exchange reaction, $-\Delta_r G_{298}^{\circ}$, kJ	Conversion point (line)	Stable diagonal (triangle)
$Na^+, Sr^{2+} \ Cl^-, MoO_4^{2-}$	90.468	С	NaCl–SrMoO ₄
$Na^+, Sr^{2+} \ Cl^-, WO_4^{2-}$	90.482	F	NaCl–SrWO ₄
$Na^+, Sr^{2+} \ MoO_4^{2-}, WO_4^{2-} \ $	0.014	D	Na ₂ MoO ₄ -SrWO ₄
$Na^+,Sr^{2+}\ Cl,MoO_4^{2-},WO_4^{2-}$	180.95	0.5C + 0.5F	$NaCl + SrWO_4 + SrMoO_4$

Table 1. Gibbs energies for exchange reactions in ternary reciprocal systems and the Na^+ , $Sr^{2+} \|Cl^-$, MoO_4^{2-} , WO_4^{2-} quaternary reciprocal system

The temperature of the third endotherm (775.3°C) is close to the saddle eutectic temperature on the NaCl–SrMoO₄ stable diagonal (8.7°C lower). On the cooling curve for mixture (1) (Fig. 2), the exotherm temperature (781.1°C) differs by 2.9°C from the saddle point temperature. The exotherm temperature (623.6°C) is close to the ternary eutectic temperature (625°C) in the NaCl–SrMoO₄–Na₃ClMoO₄ subsystem.

On the heating curve for a homogenized powder mixture of composition (2) (Fig. 3), the exotherm temperature (562.3°C) is 9.2°C higher than the ternary eutectic melting temperature in the NaCl– SrCl₂–SrWO₄ subsystem. The temperature of the second endotherm (660.3°C) is 3.3°C higher than the ternary eutectic melting temperature in the NaCl– SrWO₄–Na₃ClWO₄ stable triangle. 787.2°C is the onset temperature of the endotherm whose temperature is 2.2°C higher than the saddle point temperature on the NaCl–SrWO₄ stable diagonal. The exotherm on the cooling curve (Fig. 3) has the temperature (791.5°C) 6.5°C higher than the melting temperature of the saddle point on the NaCl–SrWO₄ quasi-binary side. The insignificant exotherm at 660.1 °C has a temperature 3.1 °C higher than the ternary eutectic melting temperature in the NaCl–Na₃ClWO₄–SrWO₄ subsystem.

The heating and cooling curves for mixture (3) (Fig. 4) feature endotherms with temperatures close to the temperatures for mixtures (1) and (2). The first endotherm nearly coincides with the endotherm on the heating curve of SrCl₂-Na₂MoO₄ mixtures and corresponds to the α/β phase transition in Na₂MoO₄. The onset temperature of the exotherm (542.6°C) falls in the range between the temperatures of exotherms on the DTA curves for mixtures (1) and (2) (541.5 -562.3°C). The second endotherm at 639.3°C (due to $Na_3ClMo_xW_{1-x}O_4$ phase formation) corresponds to the melting temperature of the mixture whose composition corresponds to the figurative point on the monovariant curve that connects the ternary eutectic points with melting temperatures of 625°C (in the NaCl-SrMoO₄-Na₃ClMoO₄ phase triangle) and 657°C (in the NaCl-Na₃ClWO₄-SrWO₄ phase trian-



Fig. 2. DTA (1) heating and (2) cooling curves for $SrCl_2 + Na_2MoO_4$ reaction mixtures.



Fig. 3. DTA (1) heating and (2) cooling curves for $SrCl_2 + Na_2WO_4$ reaction mixtures.



Fig. 4. DTA (1) heating and (2) cooling curves for $SrCl_2 + Na_2MoO_4 + Na_2WO_4$ reaction mixtures.

gle). The third endotherm at 780.5°C also falls in the range from 775.5 to 787.2°C. The cooling curve features two exotherms whose temperatures also fall in the range for mixtures (1) and (2).

Theoretically, the cooling curves for the alloys that correspond to compositions (1) and (2) should each feature two events due to the crystallization of SrEO₄ (E = Mo, W) and NaCl. Due to the divergence of liquidus peaks and the compositions of solid phases, however, the liquidus peaks corresponding to mixtures C and F shift along the $Na_2EO_4 \rightarrow SrCl_2$ unstable diagonal in the direction of the SrCl₂ corner. It is for this reason that the cooling curves of mixtures feature thermal events due to the crystallization of three phases: $SrMo_xW_{1-x}O_4 + NaCl + Na_3ClMo_xW_{1-x}O_4$. Compounds Na₃ClMoO₄ and Na₃ClWO₄ as if "push out" liquidus peaks from the NaCl-SrEO₄ and $D_1(D_2)$ -SrEO₄ stable secants into the NaCl-SrCl₂-SrEO₄ and Na_2EO_4 -SrEO₄-D₁ (D₂) simplexes, as proved by DTA heating and cooling data (Figs. 2-4) and XRD (Figs. 5-8).

Thus, ion-exchange reactions and reactions producing double compounds occur in ternary reciprocal systems, and their occurrence is now supported experimentally.



Fig. 5. X-ray powder diffraction pattern for a reacted $SrCl_2 + Na_2MoO_4$ mixture: (1) NaCl, (2) $SrMoO_4$, and (3) Na_3ClMoO_4 .



Fig. 6. X-ray powder diffraction pattern for a reacted Na₂WO₄ + SrCl₂ mixture: (1) NaCl, (2) SrWO₄, and (3) Na₃ClWO₄.

CONCLUSIONS

(1) The description of chemical interactions in three-component and four-component reciprocal systems in terms of ion balance is consistent with the description by the conversion method, and they complement each other. The advantage of the conversion method is that exothermic reactions can be used to synthesize substances and mixtures from unstable products. The advantage of the ion-balance method is the option to determine the simplex into which the products will enter after the chemical reaction between various combinations of the initial components and double compounds.

(2) We have studied chemical interactions in $Na_2MoO_4 + SrCl_2$, $Na_2WO_4 + SrCl_2$, and $Na_2MoO_4 + Na_2WO_4 + 2SrCl_2$ batches. The heating (cooling) curves for the mixtures gave us the onset temperatures of exothermic exchange reactions in Na^+ , $Sr^{2+}||Cl^-$, MoO_4^{2-} ; Na^+ , $Sr^{2+}||Cl^-$, WO_4^{2-} ; and Na^+ , $Sr^{2+}||Cl^-$, MoO_4^{2-} , WO_4^{2-} ; systems; and they allowed us to elucidate the lowest ternary eutectic temperatures, the melting temperatures of the alloys corresponding to the saddle points



Fig. 7. X-ray powder diffraction pattern for a reacted $Na_2MoO_4 + Na_2WO_4 + 2SrCl_2$ mixture: (1) NaCl, (2) SrMo_xW_{1-x}O₄, and (3) $Na_3ClMo_xW_{1-x}O_4$.

on NaCl–SrEO₄ stable diagonals, and liquidus temperatures.

(3) Due to high melting temperatures, the liquidus is represented by dominant $SrEO_4$ crystallization fields in the Na⁺, $Sr^{2+} ||Cl^-, EO_4^{2-}$ (E = Mo, W) systems. The Na⁺, $Sr^{2+} ||MoO_4^{2-}, WO_4^{2-}$ ternary reciprocal system and the Na⁺, $Sr^{2+} ||Cl^-, MoO_4^{2-}, WO_4^{2-}$ four-component reciprocal system are dominated by the $SrMo_xW_{1-x}O_4$ ss volume.

(4)
$$Na^+, Sr^{2+} \| MoO_4^{2-}, WO_4^{2-} \text{ and } Na^+, Sr^{2+} \| Cl^-,$$

 MoO_4^{2-} , WO_4^{2-} salt melts can be used to prepare Mo-W alloys or for $SrMo_xW_{1-x}O_4$ crystal growth.



Fig. 8. Peak displacement scheme in the liquidus: $C(F) \rightarrow C'(F')$ and $K_1 \rightarrow (K'_1)$.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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