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Solid-phase chemical transformations in molybdate systems

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The ternary salt systems M_2MoO_4—$AMoO_4$—$Zr(MoO_4)_2$ (M = K, Tl; A = Mg, Mn, Ni, Co, Cu, Zn, Cd) in a sub-solidus region were studied. New ternary molybdates with the $M_5A_{0.5}Zr_{1.5}(MoO_4)_6$ and $MA_{0.5}Zr_{0.5}(MoO_4)_2$ compositions were synthesized by solid-phase reactions in these systems. The crystallographic and thermal characteristics of the compounds were found. The electrical properties of potassium—manganese—zirconium molybdates were studied.

Key words: ternary molybdates of uni-, bi-, and tetravalent elements, crystallographic, thermal and electrical properties.

Molybdates are promising materials due to their high ionic and electron conductivity, luminescence, and Seignette- and piezoelectric and catalytic properties.[1,2] Data on ternary molybdates containing potassium (thallium) and doubly- and quadruply charged cations have been unavailable in the literature up to the beginning of our investigations. Previously,[3] we have studied the ternary salt systems K_2MoO_4—$Mg(Mn)MoO_4$—$Zr(MoO_4)_2$ and have found the formation of molybdates with three various cations each, of the following compositions: $K_5A_{0.5}Zr_{1.5}(MoO_4)_6$ (**1**) and $KA_{0.5}Zr_{0.5}(MoO_4)_2$ (**2**) (A = Mg, Mn). Single crystals of the molybdates containing magnesium have been prepared and their structures have been determined.[4,5] The octahedral coordination of Zr and Mg and the statistical interreplacement are typical of these molybdates.

The goal of this work is a search for new compounds containing other bivalent metals (Co, Ni, Cu, Zn, Cd). For this purpose, we studied the systems M_2MoO_4—$AMoO_4$—$Zr(MoO_4)_2$ (M = K, A = Co, Ni, Zn, Cu, Cd; M = Tl, A = Mg, Mn, Co, Ni, Cu, Zn, Cd). Phase equilibria in these systems were not studied previously.

Results and Discussion

Binary systems that are the sides of the concentration triangle have been studied in detail. Compounds with 4 : 1 and 1 : 1 component ratios are formed in the K_2MoO_4—$Zr(MoO_4)_2$ system,[6] and compounds with 2 : 1 and 1 : 2 compositions which are crystallized in the structural types of $K_4Mg(MoO_4)_3$,[7] $K_4Zn(MoO_4)_3$,[11] $K_2Zn_2(MoO_4)_3$,[8] and $K_2Mg_2(MoO_4)_3$,[10] are formed in the K_2MoO_4—$AMoO_4$ (A = Mg, Mn, Co, Ni, Cu, Zn) system.[1,2,7—11] The molybdates $K_2A(MoO_4)_2$ (A = Mg, Ni)[12,13] and $K_2Cu_3(MoO_4)_4$[14] are also known. Later compounds of

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2 : 1 (A = Mn, Cd), 1 : 2 (Mn), and nearly 1 : 1 (Cd) compositions were prepared.[15,16]

Molybdates of 2 : 1 (A = Cu, Zn) and 1 : 2 (A = Mg, Mn, Co, Ni, Zn) compositions are formed in Tl_2MoO_4—$AMoO_4$ systems.[17] We found that molybdates with 4 : 1 and 1 : 1 (Zr) and 2 : 1 (Cd) component ratios were formed in the Tl_2MoO_4—$Zr(MoO_4)_2$ and Tl_2MoO_4—$CdMoO_4$ systems.

Our studies showed that solid solutions containing up to 5—7 mol.% of the low-temperature β-$Zr(MoO_4)_2$ modification were formed in the K_2MoO_4—$Zr(MoO_4)_2$ and $AMoO_4$—$Zr(MoO_4)_2$ systems. The peculiarity of interaction in $Zr(MoO_4)_2$ containing systems is that the low-temperature monoclinic modification is always formed under annealing regardless of the nature of the starting zirconium molybdate (low-temperature (β)-modification or high-temperature (α)-modification).

The ternary salt systems containing potassium can be divided into two groups with respect to the phase composition: the first group includes the systems in which two ternary Co and Ni molybdates form (Fig. 1) and the second group includes the systems in which only one compound forms (see Fig. 1). The systems with Cu and Cd belong to the second group.

Study of the solid-state interaction between the starting compounds showed that the ternary molybdates were formed at various molar ratios of the components.

Compounds of the **1** composition are formed in the systems containing Mg and Cd molybdates and the transition elements (A = Mn, Ni, Co, Cu, Zn). Molybdates **2** (A = Mg, Mn,[3] Co, Zn) are formed in the systems containing Mg, Mn, Co, and Zn molybdates along with compounds of the **1** composition. In the thallium systems, similar compounds are formed (Tables 1 and 2, Fig. 2) along with molybdates **2** containing Ni and Cd.

The data of XRD and vibrational spectroscopy showed that all compounds of the same overall formula are isostructural. The powder diffractograms of the compounds were indexed on the basis of the diffractograms of the single crystals of magnesium ternary molybdates of various compositions (see Tables 1, 2).

According to the XRD data, the formation of **2** in the stoichiometric mixtures of K, Mn (Mg), and Zr

Table 1. Crystallographic and thermal characteristics of ternary molybdates

Compound	Space group	Parameters of unit cell/Å		M.p. /°C
		a	*c*	
$K_5Mg_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.576(1)	37.511(3)	640
$K_5Mn_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.584(1)	37.576(3)	650
$K_5Ni_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.555(1)	37.442(5)	650
$K_5Co_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.572(1)	37.501(5)	660
$K_5Zn_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.573(1)	37.490(4)	610
$K_5Cd_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.621(1)	37.682(5)	480
$K_5Cu_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.555(1)	37.424(7)	470
$KMg_{0.5}Zr_{0.5}(MoO_4)_2$	$P\bar{3}m1$	5.763(1)	7.187(1)	650
$KMn_{0.5}Zr_{0.5}(MoO_4)_2$	$P\bar{3}m1$	5.771(2)	7.247(1)	670
$KCo_{0.5}Zr_{0.5}(MoO_4)_2$	$P\bar{3}m1$	5.670(3)	7.235(1)	630
$KZn_{0.5}Zr_{0.5}(MoO_4)_2$	$P\bar{3}m1$	5.669(4)	7.231(1)	620
$Tl_5Mg_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.631(1)	37.967(8)	580
$Tl_5Mn_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.657(1)	38.078(8)	575
$Tl_5Ni_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.630(1)	37.915(8)	570
$Tl_5Co_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.629(1)	37.957(1)	560
$Tl_5Cu_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.633(1)	37.970(8)	565
$Tl_5Zn_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.634(1)	37.965(9)	570
$Tl_5Cd_{0.5}Zr_{1.5}(MoO_4)_6$	$R\bar{3}c$	10.688(1)	38.223(7)	580

Table 2. Crystallographic and thermal characteristics of thallium molybdates of compositions $TlA_{0.5}Zr_{0.5}(MoO_4)_2$

Compound	Space group	Parameters of unit cell/Å			M.p. /°C
		a	*b*	*c*	
$TlMg_{0.5}Zr_{0.5}(MoO_4)_2$	*Pnam*	14.982(3)	8.816(3)	5.816(1)	740
$TlMn_{0.5}Zr_{0.5}(MoO_4)_2$	*Pnam*	14.969(4)	8.799(2)	5.854(2)	723
$TlNi_{0.5}Zr_{0.5}(MoO_4)_2$	*Pnam*	14.905(4)	8.796(2)	5.789(1)	674
$TlCo_{0.5}Zr_{0.5}(MoO_4)_2$	*Pnam*	14.937(3)	8.791(2)	5.819(1)	684
$TlZn_{0.5}Zr_{0.5}(MoO_4)_2$	*Pnam*	14.933(3)	8.788(2)	5.820(1)	661
$TlCd_{0.5}Zr_{0.5}(MoO_4)_2$	*Pnam*	14.934(5)	8.800(2)	5.940(2)	651

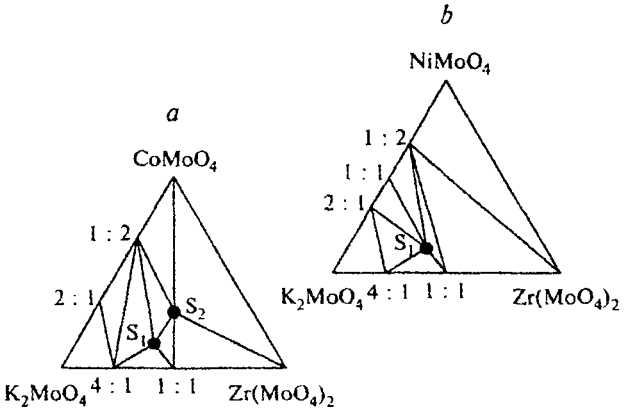

Fig. 1. Schemes of phase ratios in K_2MoO_4—$AMoO_4$—$Zr(MoO_4)_2$ systems (A = Co (*a*), Ni (*b*)).

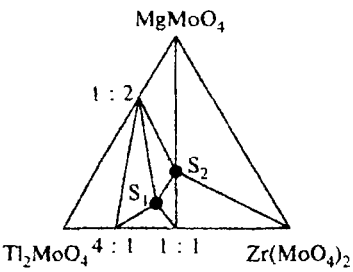

Fig. 2. Scheme of phase ratios in the Tl_2MoO_4—$MgMoO_4$—$Zr(MoO_4)_2$ system.

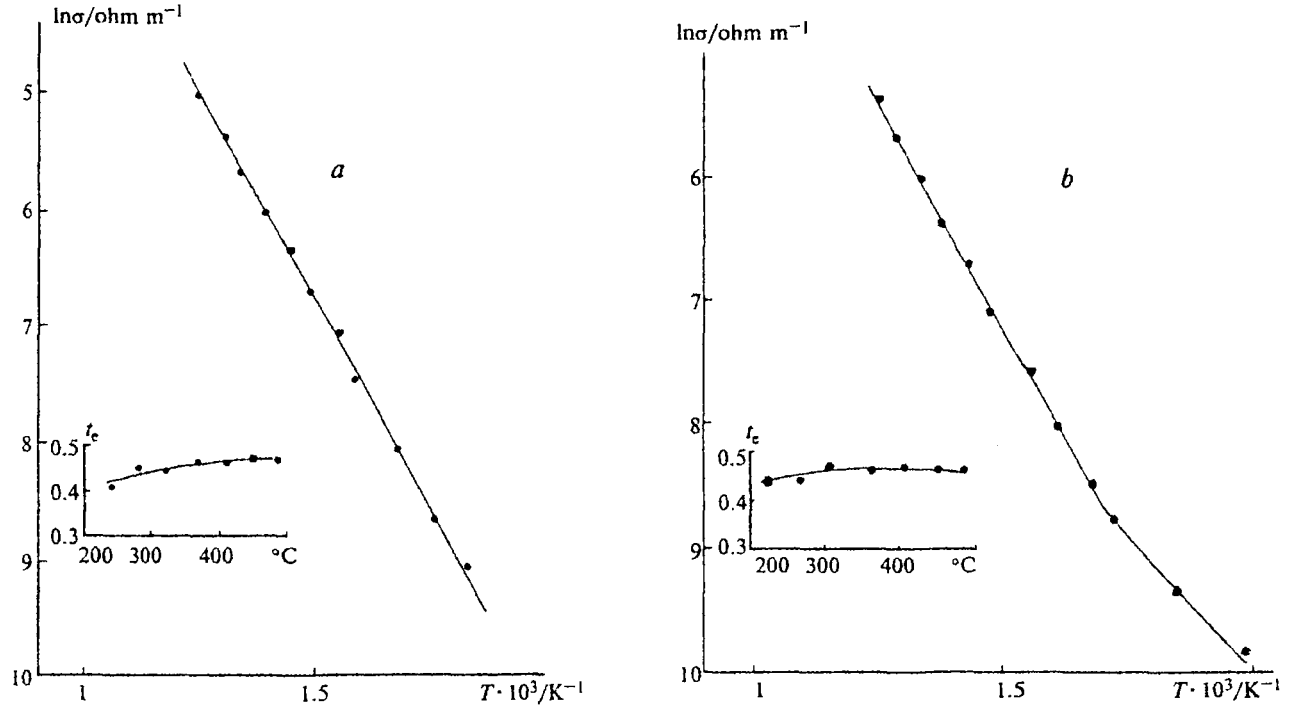

Fig. 3. Temperature dependence of conductivity: $K_5Mn_{0.5}Zr_{1.5}(MoO_4)_6$ (*a*), $KMn_{0.5}Zr_{0.5}(MoO_4)_2$ (*b*).

molybdates can be presented as a sequence of the following reactions:

$$K_2MoO_4 + Zr(MoO_4)_2 \xrightarrow{450-550\ ^\circ C} K_2Zr(MoO_4)_3,$$

$$1/2\ K_2Zr(MoO_4)_3 + 1/2\ MnMoO_4 \xrightarrow{550-600\ ^\circ C} KMn_{0.5}Zr_{0.5}(MoO_4)_2.$$

The ternary molybdates melt incongruently in the temperature range of 470—740 °C and are crystallized in three structural types.

The molybdates under study exhibit a mixed electron-ionic conductivity with predominence of the ionic constituent at high temperatures (Table 3).

Notable are the close values of the activation energy of conductivity E_a for the ternary molybdates and comparable values of the specific conductivity (σ). These facts suggest that current carriers in the molybdates of various compositions are common ions.

Based on the low values of E_a and ionic conductivity, the ternary molybdates (Fig. 3, Table 3) can be classified as solid electrolytes.

Table 3. Electrophysical characteristics of molybdates

Compound	σ/ohm^{-1} m^{-1} (400 °C)	E_a/eV
K_2MoO_4	$1.36 \cdot 10^{-3}$	0.63
$MnMoO_4$	$1.27 \cdot 10^{-3}$	0.47
$Zr(MoO_4)_2$	$7.62 \cdot 10^{-4}$	0.37
$K_2Zr(MoO_4)_3$	$1.87 \cdot 10^{-3}$	0.45
$K_8Zr(MoO_4)_6$	$1.66 \cdot 10^{-3}$	0.52
$K_5Mn_{0.5}Zr_{1.5}(MoO_4)_6$	$1.23 \cdot 10^{-3}$	0.62
$KMn_{0.5}Zr_{0.5}(MoO_4)_2$	$0.79 \cdot 10^{-3}$	0.64
$K_4MnZr_6(4MoO_4)_{15}$	$0.91 \cdot 10^{-3}$	0.63

Note. σ is the conductivity; E_a is the activation energy of conductivity.

Experimental

The starting molybdates of potassium and bivalent elements were prepared at 550—650 °C from the corresponding oxides (carbonates) of potassium, thallium, and bivalent elements and molybdenum trioxide of chemically pure and analytical grades. Zirconium molybdate was prepared by the stepwise annealing of stoichiometric amounts of ZrO_2 and MoO_3 at 250—300, 450—550, and 550—650 °C. The systems were prepared at 5 mol.% intervals and in some cases at 1—1.5 mol.% intervals. Time of annealing was ≥100 h. The achievement of equilibrium was monitored by XRD technique. The reactions in the M_2MoO_4—$AMoO_4$—$Zr(MoO_4)_2$ (A = Co, Ni, Cu, Zn, Cd) systems were studied in a sub-solidus region (550—600 °C) by X-ray diffraction (DRON-UM1, Cu-Kα radiation) and differential thermal analysis (a MOM OD-103 derivatograph) at a heating rate of 10 deg min^{-1}, as well as by IR spectroscopy (a Bruker spectrometer).

The temperature dependences of conductivity σ, dielectric permittivity E, and the tangent of the angle of dielectric losses tgδ were measured on the ceramic samples according to the known procedures.[18] Platinum was used for electric contacts.

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