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Phase relations in the Me_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems, where Me = Li, K, Tl, Rb, Cs

The Me_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems where Me = Li, K, Tl, Rb, Cs were studied in the subsolidus region using an X-ray powder diffraction. Quasi-binary joins were revealed, and triangulation carried out. The formation of ternary molybdates $Me_5InHf(MoO_4)_6$ for Me = K, Tl, Rb, Cs and $Me_2InHf_2(MoO_4)_{6.5}$ for Me = Rb, Cs was established.

Keywords: phase relations, triangulation, solid-phase reactions, X-ray phase diffraction, molybdates.

Introduction

Ternary molybdates attract attention due to their catalytic and ionexchange properties and the diversity of their crystal structures. The MoO_6 octahedra are usually highly distorted because of the relatively small effective radius of the Mo^{6+} ion in the oxygen environment, which is favorable for the formation of low-symmetry crystal structures.

Systematic studies of multicomponent systems allow obtaining the large amount of data which make it possible to identify regularities of the phase formation in related systems. In our previous works, the phase equilibria in the Me_2MoO_4–$R_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Me = Rb, Cs; R — trivalent metals) systems were studied [1, 2].

The purpose of this work was to establish the phase formation in the Me_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems where Me = Li, K, Tl, Rb, Cs.

Experimental

Subsolidus phase relations in the Me_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Me = Li, K, Tl, Rb, Cs) systems were studied within the temperature range 450–550 °C using the intersecting joins method.

The correspondent molybdates of lithium, potassium, thallium, rubidium, cesium, indium and hafnium were used as starting components for studying the phase equilibria in the Me_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Me = Li, K, Tl, Rb, Cs) systems. In order to avoid MoO_3 losses due to the sublimation, annealing was started at 400 °C. Synthesis of thal-

lium molybdate Tl_2MoO_4 was performed according to the following reaction:

$$Tl_2O_3 + MoO_3 \rightarrow Tl_2MoO_4 + O_2\uparrow$$
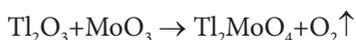
while the temperature was gradually increased in the range of 400–550 °C for 50 h.

Binary alkali molybdates Me_2MoO_4 (Me = Li, K, Rb, Cs) were synthesized by the solid-state reaction using stoichiometric mixtures of alkali carbonates or nitrates with molybdenum trioxide for 80–100 h.

Hafnium molybdate was prepared by step annealing of stoichiometric mixtures of HfO_2 and MoO_3 within the temperature range 400–700 °C for 100–150 h. Indium molybdate was synthesized from indium oxide (III) In_2O_3 and molybdenum oxide (VI) MoO_3 by solid-state reaction at 500–700 °C.

X-ray powder diffraction (XRD) measurements were performed using a Bruker D8 Advance diffractometer (Bragg — Brentano geometry, Cu Kα radiation, secondary monochromator, maximum angle 2θ = 100°, scan step 0.02°).

Results and discussion

Information about the known phases in the side quasi-binary systems, which formed studied quasi-ternary Me_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Me = Li, K, Tl, Rb, Cs) systems, required for triangulation, was taken from the literature. According to Solodovnikov et al. [3], the Li_2MoO_4–$Hf(MoO_4)_2$ system contains a lithium hafnium molybdate $Li_{10-4x}Hf_{2+x}(MoO_4)_9$ (0.21 ≤ x ≤ 0.68). Two types of double molybdates, $Me_8Hf(MoO_4)_6$ and $Me_2Hf(MoO_4)_3$ (Me = K, Tl, Rb, Cs), are formed inside the Me_2MoO_4–$Hf(MoO_4)_2$ systems [4–6]. An existence of the double molybdates, namely: $Li_3In(MoO_4)_3$, $MeIn(MoO_4)_2$ (Me = Li, K, Tl, Rb, Cs), and $Me_5In(MoO_4)_4$ (Me = Tl, Rb) was confirmed in the Me_2MoO_4–$In_2(MoO_4)_3$ systems [7–10]. No intermediate compounds were found inside the $In_2(MoO_4)_3$–$Hf(MoO_4)_2$ system [11].

Taking into account the aforementioned data, the phase formation in the Me_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Me = Li, K, Tl, Rb, Cs) systems were studied by means of so-called "intersection joins method". Within this approach, we analyzed the XRD results for the samples representing the intersection points of the joins that connect the starting components and phases inside the quasi-binary systems. This makes it possible to establish the quasi-binary joins and, as a result, to implement the triangulation of the system. Since the phase relations in the K_2MoO_4–$In_2(MoO_4)_3$ and Cs_2MoO_4–$In_2(MoO_4)_3$ systems enriched by either potassium molybdate or by cesium molybdate were found to be non-quasibinary, the studies of the Me_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Me = K, Cs) systems were limited to the $Hf(MoO_4)_2$–$Me_8Hf(MoO_4)_6$–$MeIn(MoO_4)_2$–$In_2(MoO_4)_3$ (Me = K, Cs) regions. The results obtained are presented in Fig. 1 and Fig. 2.

All systems under investigation can be categorized into three groups depending on the phase compositions of the binary subsystems and triple molybdates. The first group comprises the Li_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ simple eutectic system without intermediate phases inside. The second group consists of the Me_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems where Me = K and Tl, with one intermediate phase, denoted in Fig. 1 as S — $Me_5InHf(MoO_4)_6$ (5:1:2 mole ratio). The third group includes the Me_2MoO_4–

In$_2$(MoO$_4$)$_3$–Hf(MoO$_4$)$_2$ systems where (Me = Rb, Cs), with two intermediate phases: S$_1$ – Me$_5$InHf(MoO$_4$)$_6$ (5:1:2 mole ratio) and S$_2$ — Me$_2$InHf(MoO$_4$)$_6$ (2:1:4 mole ratio).

Single-phase samples of Me$_5$InHf(MoO$_4$)$_6$ (Me = K, Tl, Rb, Cs)
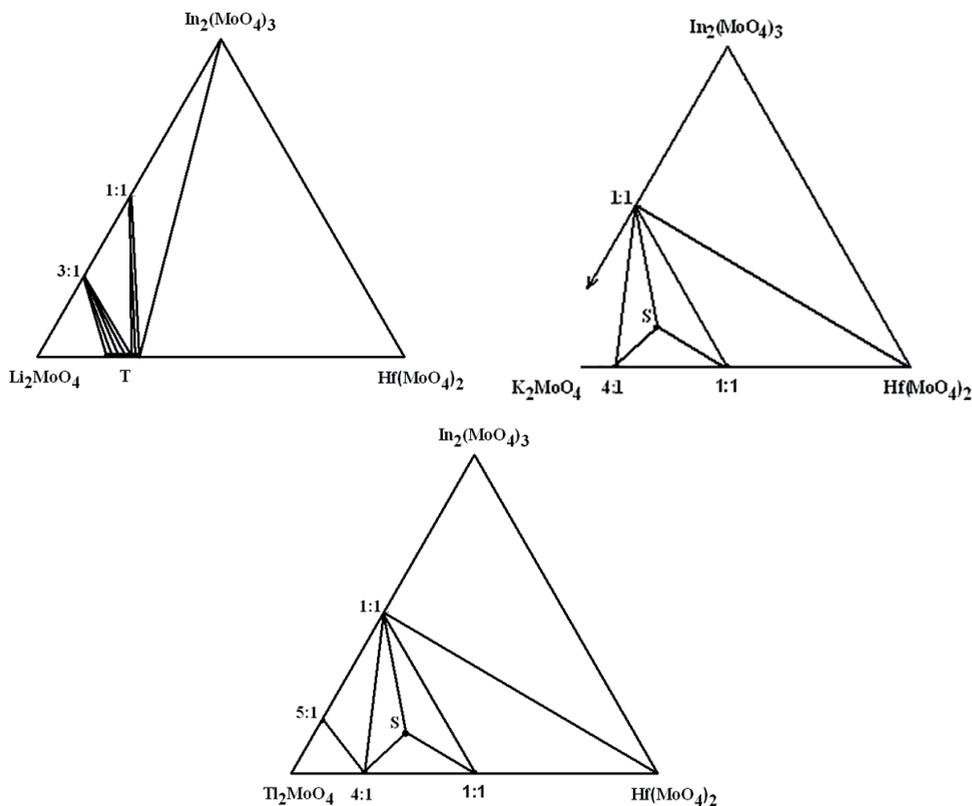
Fig. 1. Subsolidus phase relations in the Me$_2$MoO$_4$–In$_2$(MoO$_4$)$_3$–Hf (MoO$_4$)$_2$ (Me = Li, K, Tl) systems: S – Me$_5$InHf(MoO$_4$)$_6$ (5:1:2 mole ratio)
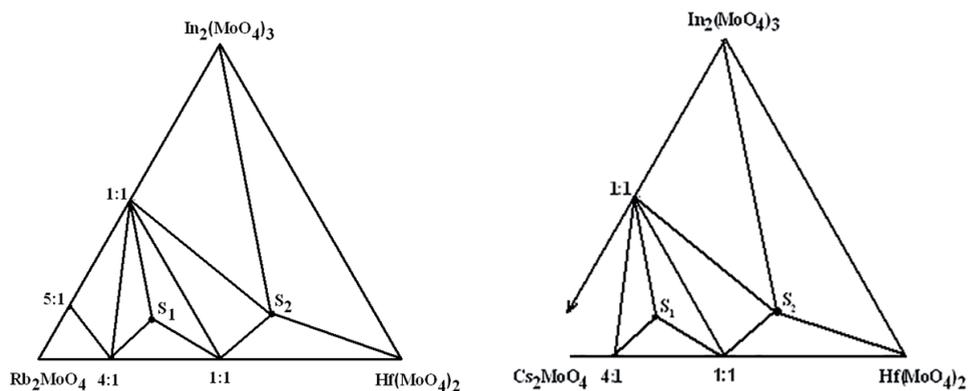
Fig. 2. Subsolidus phase relations in the Me$_2$MoO$_4$–In$_2$(MoO$_4$)$_3$–Hf(MoO$_4$)$_2$ (Me = Rb, Cs) systems: S$_1$ – Me$_5$InHf (MoO$_4$)$_6$ (5:1:2 mole ratio); S$_2$ — Me$_2$InHf(MoO$_4$)$_6$ (2:1:4 mole ratio)

and $Me_2InHf(MoO_4)_6$ (Me = Rb, Cs) were prepared by annealing the stoichiometric mixtures of quasi-binary molybdates at 450–600 °C for 80–100 h. Ternary molybdates $Me_5InHf(MoO_4)_6$ (Me = K, Tl, Rb, Cs) and $Me_2InHf(MoO_4)_6$ (Me = Rb, Cs) are insoluble in water and usual organic solvents, but were found to be soluble in HCl aqueous solution.

The ternary molybdates $Me_5InHf(MoO_4)_6$ (Me = K, Tl, Rb, Cs) are located inside the triangle that is formed by the double molybdates $MeR(MoO_4)_2$, $Me_8Hf(MoO_4)_6$ and $Me_2Hf(MoO_4)_3$ in its vertices.

The number of phases formed in the systems under consideration increases as the size of the singly charged alkali cation increases. The only exception is thallium-containing system. A distinctive feature of thallium is that it combines properties of alkali metals, such as potassium, rubidium, and cesium, together with those related to heavy metals, such as copper (I), silver, and lead [12].

The single crystals of new ternary potassium indium hafnium molybdate $K_5InHf(MoO_4)_6$ were grown by fluxed-melt crystallization with spontaneous nucleation [13]. The composition and crystal structure of as-grown single crystals were refined using X-ray diffraction data (a CAD-4 automated diffractometer, Mo Kα radiation, 1498 reflections, R = 0.0252). The crystal structure was solved as trigonal with the following unit cell parameters: a = 10.564 (1) Å, c = 37.632 (4) Å, V = 3637.0 (6) Å^3, Z = 6, space group R$\bar{3}$c. A three-dimensional mixed framework of the structure is formed by Mo tetrahedra and two independent (In, Hf) octahedra, which are connected through the shared vertices. Two types of potassium atoms occupy the large voids within the framework. The dis-

tribution of In^{3+} and Hf^{4+} cations over two different sites was refined as presented in the caption for Fig. 3.

Fig. 4 illustrates the IR and Raman spectra for the triple rubidium indium
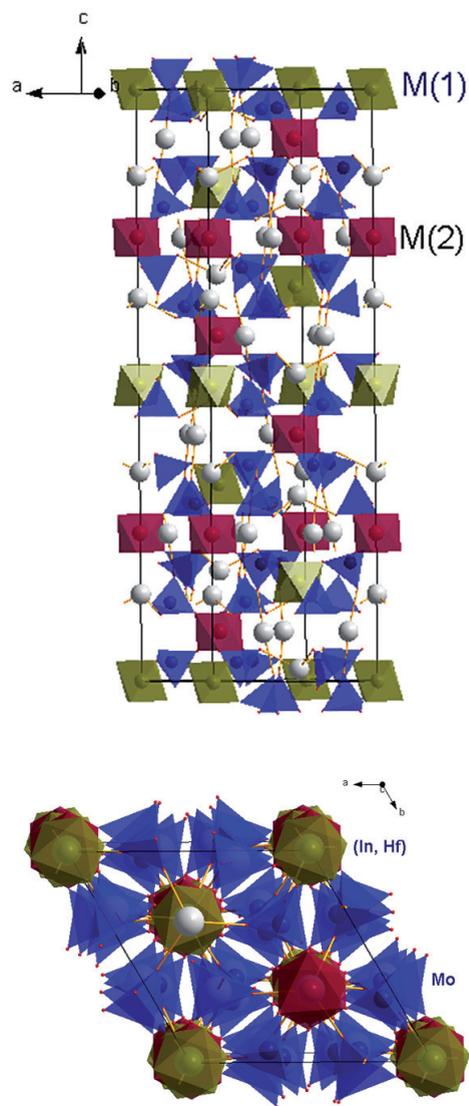

Fig. 3. Mixed framework of MoO_4 tetrahedra (blue color) and two types of octahedra (In, Hf)O_6 in the $K_5InHf(MoO_4)_6$ crystal structure. M(1) = 0.413(1)Hf + 0.587(1)In (olive color); M(2) = 0.587(1)Hf + 0.413(1)In (burgundy color)
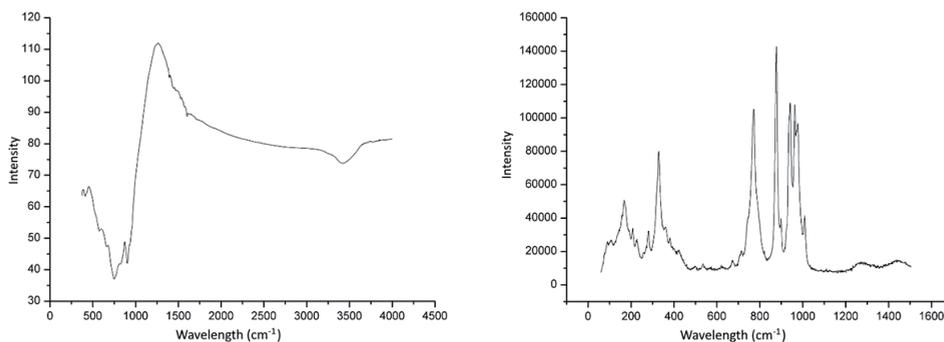
Fig. 4. IR and Raman spectra of $Rb_2InHf_2(MoO_4)_{6.5}$

hafnium molybdate $Rb_2InHf_2(MoO_4)_{6.5}$. Since the oscillation frequencies in the IR and Raman spectra differ from each other, one can assume that ternary molybdate $Rb_2InHf_2(MoO_4)_{6.5}$ and its analogues are centrosymmetric.

Conclusions

The phase equilibria in quasi-ternary salt systems were studied; six new compounds were identified inside the studied systems. The phase relations in the $Me_2MoO_4–In_2(MoO_4)_3–Hf(MoO_4)_2$ (Me = Li, K, Tl, Rb, Cs) systems are influenced by the size factor and the nature of the singly charged alkali cation.

Acknowledgements

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