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Phase formation in the systems Li_2MoO_4–K_2MoO_4–$Ln_2(MoO_4)_3$ (Ln = La, Nd, Dy, Er) and properties of triple molybdates $LiKLn_2(MoO_4)_4$

O.M. Basovich[a], E.G. Khaikina[a,*], S.F. Solodovnikov[b], G.D. Tsyrenova[a]

[a]*Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Sciences, Sakh'yanova Street 6, Ulan-Ude, 670047 Buryat Republic, Russia*

[b]*Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Akad. Lavrent'ev Ave. 3, Novosibirsk 630090, Russia*

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Abstract

Subsolidus phase relations in the systems Li_2MoO_4–K_2MoO_4–$Ln_2(MoO_4)_3$ (Ln = La, Nd, Dy, Er) were determined. Formation of $LiKLn_2(MoO_4)_4$ was confirmed in the systems with Ln = Nd, Dy, Er at the $LiLn(MoO_4)_2$–$KLn(MoO_4)_2$ joins. No intermediate phases of other compositions were found. No triple molybdates exist in the system Li_2MoO_4–K_2MoO_4–$La_2(MoO_4)_3$. The join $LiLa(MoO_4)_2$–$KLa(MoO_4)_2$ is characterized by formation of solid solutions.

Triple molybdates $LiKLn_2(MoO_4)_4$ for Ln = Nd–Lu, Y were synthesized by solid state reactions (single phases with ytterbium and lutetium were not prepared). Crystal and thermal data for these molybdates were determined. Compounds $LiKLn_2(MoO_4)_4$ form isostructural series and crystallized in the monoclinic system with the unit cell parameters $a = 5.315$–5.145 Å, $b = 12.857$–12.437 Å, $c = 19.470$–19.349 Å, $\beta = 92.26$–$92.98°$. When heated, the compounds decompose in solid state to give corresponding double molybdates. The dome-shaped curve of the decomposition temperatures of $LiMLn_2(MoO_4)_4$ has the maximum in the Gd–Tb–Dy region.

While studying the system Li_2MoO_4–K_2MoO_4–$Dy_2(MoO_4)_3$ we revealed a new low-temperature modification of $KDy(MoO_4)_2$ with the triclinic structure of α-$KEu(MoO_4)_2$[1] ($a = 11.177(2)$ Å, $b = 5.249(1)$ Å, $c = 6.859(1)$ Å, $\alpha = 112.33(2)°$, $\beta = 111.48(1)°$, $\gamma = 91.30(2)°$, space group $P\bar{1}$, $Z = 2$).

Keywords: Rare-earth elements; Triple molybdates; Double molybdates; Phase relations; Polymorphism; X-ray diffraction; Thermal analysis

1. Introduction

Existence of the extensive family of the isostructural triple molybdates $LiMR_2(MoO_4)_4$ (M = K, Tl, Rb; R = Bi, Ln) was early reported in [1–4]. Their stability fields shift toward larger R^{3+} cations along with increasing M^+ radius and include Bi, Nd–Lu, Y for the potassium-containing series; Bi, Ce–Eu for the thallium-containing row, and Bi, La–Eu for the rubidium-containing one. The most extensive group of the $LiMR_2(MoO_4)_4$ family is the potassium-containing compounds (13 of 26 representatives). However, whereas information on phase formation in the systems Li_2MoO_4–M_2MoO_4–$R_2(MoO_4)_3$ (M = Tl, Rb) is rather completed [4–6], data for M = K are limited by the system containing bismuth [4].

To fill this gap we undertook the investigation of phase relations in a number of the systems Li_2MoO_4–K_2MoO_4–$Ln_2(MoO_4)_3$ that allowed us to observe a pattern of their changes depending on the nature of a rare-earth element.

*Corresponding author. Fax: +7 3012 434753.
E-mail address: ekha@binm.bsc.buryatia.ru (E.G. Khaikina).

[1]Hereinafter, α refers to a low-temperature modification.

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Numerous publications are devoted to phase relations in the boundary binary systems of such triple systems. The phase diagram of the system Li_2MoO_4–K_2MoO_4 was constructed in [7,8]. According to these data the system is characterized by formation of the only intermediate phase $LiKMoO_4$ crystallizing in four polymorphous modifications [9]. Phase equilibria in the systems M_2MoO_4–$Ln_2(MoO_4)_3$ (M = Li, K) are rather complex and change significantly depending on the rare-earth element and the structure of its normal molybdate.

In the systems Li_2MoO_4–$Ln_2(MoO_4)_3$ (Ln = La–Tb) between $Ln_2(MoO_4)_3$ and $LiLn(MoO_4)_2$ with distorted and undistorted scheelite structures, respectively, intermediate phases were found which have an approximate composition $LiLn_5(MoO_4)_8$ with monoclinic scheelite superstructures and wide homogeneity regions. Homogeneity regions of the compounds with an approximate 1:1 composition are also significant. Solid solutions on the base of 1:1 and 1:5 compounds are decomposed peritectically. Subsolidus phase transitions of these compounds are not revealed [10], except of $LiLa(MoO_4)_2$ undergoing an irreversible polymorphous transformation [10,11]. Only β-$LiLa(MoO_4)_2$ possessing the tetragonal scheelite-type structure forms solid solutions [12]. The authors of the latter work suppose that α-$LiLa(MoO_4)_2$ has no appreciable homogeneity region. No intermediate phases were revealed in the lithium containing systems with Ln = Dy–Lu, Y [10] in the range of 50–100 mol% $Ln_2(MoO_4)_3$. Formation of incongruently melting compounds $LiLn(MoO_4)_2$ and $Li_7Ln_3(MoO_4)_8$ with neither noticeable homogeneity regions, nor polymorphism was established. In the system Li_2MoO_4–$Dy_2(MoO_4)_3$, the monotectic reaction $L_2 \leftrightarrow L_1 + \beta$-$Dy_2(MoO_4)_3$ was detected within the range 40–50 mol% Li_2MoO_4.

The systems K_2MoO_4–$Ln_2(MoO_4)_3$ are characterized by formation of a greater number of double molybdates such as $K_5Ln(MoO_4)_4$ and $KLn(MoO_4)_2$ [13–15]. Compounds $K_5Ln(MoO_4)_4$ have no distinct homogeneity regions. While there is a significant structural similarity between $KLn(MoO_4)_2$ and $Ln_2(MoO_4)_3$ based on the scheelite-type structure, 1:1 compounds possess rather extensive homogeneity regions. In this case, as well as in the analogous lithium–lanthanide systems, formation of scheelite-type solid solutions on the base of the phases with an approximate 1:5 composition was determined. When studying the systems with neodymium and europium [13,14] double molybdates $KLn_5(MoO_4)_8$ were obtained. The authors of [13] suggest that $KLn_5(MoO_4)_8$ should exist for the other rare-earth elements forming simple and double molybdates of a 1:1 composition with scheelite-like structures. Nevertheless, despite of scheelite-like structures of $KLa(MoO_4)_2$ and $La_2(MoO_4)_3$, the existence of a similar phase in the potassium–lanthanum system is still uncertain. As it was shown in [15], where T–x diagram of the system K_2MoO_4–$La_2(MoO_4)_3$ was constructed using X-ray powder diffraction and thermal analysis, the obtained results suggested a possible formation of both the intermediate 1:5 phase and the extended solid solution on the base of α-$KLa(MoO_4)_2$. According to [15], only preparation and XRD study of single crystals containing 50 and 83 mol% $La_2(MoO_4)_3$, as well as comparing the types of their superstructures allow us to make the unequivocal conclusion about existence of the 1:5 phase and the character of the phase diagram of this system. In [16,17], the crystals of α- and β-$KLa(MoO_4)_2$ were obtained with hydrothermal crystallization, but their complete structure study was not conducted. The authors of [17] determined that the higher stability limit of the α-modification lies within 560 and 565 °C and indexed the powder pattern of this modification in a body-centered monoclinic subcell with the parameters $a = 5.437(1)$ Å, $b = 12.205(2)$ Å, $c = 5.417(1)$ Å, $\beta = 90.05(1)^\circ$. However, they failed to index a group of the first superstructure reflections. No information on the synthesis of single crystals of $KLa_5(MoO_4)_8$ and its crystal structure is available in literature.

This paper presents results of our studies of subsolidus phase formation in the systems Li_2MoO_4–K_2MoO_4–$Ln_2(MoO_4)_3$ (Ln = La, Nd, Dy, Er) and physicochemical properties of triple molybdates $LiKLn_2(MoO_4)_4$ for Ln = Nd–Lu, Y.

2. Experimental

As starting materials molybdenum trioxide, lithium and potassium carbonates (all reagent grade) and rare-earth oxides with content of the major substance more than 99.9% were taken. Molybdates M_2MoO_4 (M = Li, K) and $Ln_2(MoO_4)_3$ were prepared by solid-state reactions. To avoid a loss of MoO_3 due to its evaporation, annealing was started from 500 °C, stepwise increasing temperature up to 650 °C (to prepare M_2MoO_4) or 750 °C (to obtain rare-earth molybdates). Total duration of solid-state synthesis was 70 h. For better reactivity, the reaction mixtures were ground with ethanol in agate mortars in each 15 h of annealing.

The investigations of interaction in the ternary salt systems were carried out by the "intersecting joins" method [18,19]. The method is based on determination of phase compositions of the interception points of all joins connecting the composition points of the components, binary and ternary compounds. Using X-ray powder diffraction we revealed quasibinary sections to construct triangulated phase diagrams of the systems Li_2MoO_4–K_2MoO_4–$Ln_2(MoO_4)_3$.

X-ray diffraction analysis (XRD) was performed on a diffractometer DRON-UM1 (Cu$K\alpha$-radiation). In the most important cases such as determining homogeneity