Synthesis and X-ray Diffraction and IR Spectroscopy Studies of Ternary Molybdates Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$ (R = La–Lu, Y)

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Abstract—Ternary molybdates Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$ (R = La–Lu, Y) were synthesized by the solid-phase method. Their unit cell parameters were determined and IR spectra were assigned. The compounds are isomorphic to each other and crystallize in the monoclinic system (space group C2/c).

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A considerable interest in synthesis and studies of complex molybdates and tungstates has been held for more than 30 years. This is due to their unique spectral-luminescence and ferroelectric properties, catalytic activity, good ionic conductivity, thermal and chemical phase stabilities [1, 2].

Combination of the above-listed physicochemical properties of molybdates and tungstates stimulates intensive theoretical and experimental studies of this group of inorganic compounds.

The aim of this work was to study phase formation in the subsolidus region of the Li$_2$MoO$_4$–BaMoO$_4$–R$_2$(MoO$_4$)$_3$ systems and to synthesize and study the ternary molybdates by X-ray diffraction and IR spectroscopy.

EXPERIMENTAL

The initial components for studying phase formation in the Li$_2$MoO$_4$–BaMoO$_4$–R$_2$(MoO$_4$)$_3$ systems were Li$_2$MoO$_4$, BaMoO$_4$, and R$_2$(MoO$_4$)$_3$, which were presynthesized from Li$_2$CO$_3$, BaO, R$_2$O$_3$, and MoO$_3$ by the solid-phase method in a temperature range of 400–650°C with repeated intermediate grindings in every 20–30 h. The annealing time at each temperature was 100–120 h. After annealing, samples were slowly cooled with the oven. Nonequilibrated samples were additionally annealed, and equilibrium was considered to be attained when the phase composition of the sample remained constant after two successive annealings. The syntheses products were identified by X-ray powder diffraction in a FR-552 camera-monochromator (CuK$_\alpha$ radiation, Ge inner standard). X-ray diffraction patterns were treated using the Rentgen program package. Vibrational spectra of polycrystalline Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$ samples were recorded as mineral oil mulls and KBr pellets on Bruker FT-IR and Specord M-80 spectrophotometers with the use of laser excitation in a near-IR range (1.06 nm, reflection geometry, resolution of 3–5 cm$^{-1}$). Isotope-substituted (Li) samples were prepared using Li$_2$CO$_3$ with 90.5%-content of the major isotope as the starting reagent.

Differential thermal analysis was carried out on a MOM OD-103 derivatograph at a heating rate of 10 K/min (sample weights were 0.3–0.4 g).

Interactions in the Li$_2$MoO$_4$–BaMoO$_4$–R$_2$(MoO$_4$)$_3$ systems were studied in the range of 400–900°C. In the terminal double Li$_2$MoO$_4$–R$_2$(MoO$_4$)$_3$ system, molybdates of the compositions 1 : 1, 1 : 5 for R = La–Tb, and 1 : 1, 1 : 3 for R = Dy–Lu and Y with scheelite-type structures were found [1]. Double molybdates LiR(MoO$_4$)$_2$ have a disordered tetragonal structure of scheelite (space group I4$_1$/a). Structure solution for LiR$_3$(MoO$_4$)$_8$ has confirmed the conclusion on a partial disorder of lithium and rare-earth atoms in the scheelite structure. The layered structure of Li$_2$R$_3$(MoO$_4$)$_8$ (space group $P\bar{1}$) is built of layers of M eight-vertex polyhedra ($M = 0.75R + 0.25Li$), which share edges and have common vertices with adjacent MoO$_4$ tetrahedra.

In the BaMoO$_4$–R$_2$(MoO$_4$)$_3$ system, BaR$_4$(MoO$_4$)$_4$ molybdates with wide homogeneity regions were synthesized. The molybdates belong to two structural types: monoclinic (space group C2/c) for R = Ce–Dy and triclinic (space group $P\bar{1}$) for Ho–Lu and Y [3]. In BaR$_3$(MoO$_4$)$_4$ compounds having monoclinic and triclinic structures, honeycomb layers with small variations are formed. Molybdenum atoms have a tetrahedral coordination; R atoms are in the centers of eight-vertex polyhedra; and Ba atoms have the coordination number 10 and reside between the layers formed by Mo and R polyhedra [1].

The study of the Li$_2$MoO$_4$–BaMoO$_4$–R$_2$(MoO$_4$)$_3$ system was carried out in two stages. First, we studied the phase compositions that correspond to the intersection points of the sections radiating from neutral and double molybdates formed in the Li$_2$MoO$_4$–BaMoO$_4$–R$_2$(MoO$_4$)$_3$ system.
R$_2$(MoO$_4$)$_3$ and BaMoO$_4$–R$_2$(MoO$_4$)$_3$ boundary binary systems. The Li$_2$MoO$_4$–Ba(MoO$_4$)$_2$ system is eutectic. At the second stage, we studied the quasi-binary sections revealed; this allowed us to perform triangulation of the systems (Fig. 1).

![Fig. 1. Phase equilibria (at 700°C) in (a) LiMoO$_4$–BaMoO$_4$–Sm$_2$(MoO$_4$)$_3$ and (b) LiMoO$_4$–BaMoO$_4$–Y$_2$(MoO$_4$)$_3$ systems.](image)

The interactions in the BaMoO$_4$–LiR(MoO$_4$)$_2$ sections were studied in most detail (in 1–2 mol % steps); here, Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$ ternary molybdates were found to be formed at 650–700°C for all the rare-earth elements including yttrium. To achieve equilibrium, the reaction mixtures were annealed for 120–140 h with intermediate homogenization.

The systems studied are divided in two groups due to different phase transformations: (i) for R = La–Tb and (ii) R = Dy–Ly and Y. This difference is caused by different phase compositions in the Li$_2$MoO$_4$–R$_2$(MoO$_4$)$_3$ boundary systems. For the systems with R = La–Tb, the quasi-binary sections are Li$_3$MoO$_4$–Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$, BaMoO$_4$–Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$, Ba$_3$(MoO$_4$)$_4$–Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$, Ba$_5$(MoO$_4$)$_4$–Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$, Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$–LiR$_5$(MoO$_4$)$_8$, and Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$–LiR$_5$(MoO$_4$)$_8$ (Fig. 1a). In the systems of the second group (R = Dy–Ly and Y), phase equilibria at 700°C have the following quasi-binary sections: Li$_2$MoO$_4$–Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$, Li$_7$R$_3$(MoO$_4$)$_8$–Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$, BaMoO$_4$–Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$, Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$–LiR$_5$(MoO$_4$)$_8$, and Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$–LiR$_5$(MoO$_4$)$_8$ (Fig. 1b). X-ray powder diffraction showed that 18–20% of BaMoO$_4$ is dissolved in ternary molybdates, and the solubility of the Ba$_3$(MoO$_4$)$_4$ ternary molybdate is less than 5–7 mol %. The solubility of LiR$_5$(MoO$_4$)$_8$ in Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$ is 10–12 mol %, and no more than 8–10 mol % of Li$_3$Ba$_2$R$_3$(MoO$_4$)$_8$ is dissolved in Li$_2$MoO$_4$.

The T–x diagram of the BaMoO$_4$–LiSm(MoO$_4$)$_2$ section (Fig. 2) was constructed. The eutectic composition is 82% of LiSm(MoO$_4$)$_2$; the melting point is 920°C. The homogeneity region based on Li$_3$Ba$_2$Sm$_3$(MoO$_4$)$_8$ extends over 28 mol %. According to X-ray powder diffraction data, Li$_3$Ba$_2$Sm$_3$(MoO$_4$)$_8$ dissolves 11 mol % of BaSm$_2$(MoO$_4$)$_4$ and 10 mol % of

![Fig. 2. T–x diagram of the LiSm(MoO$_4$)$_2$–BaMoO$_4$ section; (I) LiSm(MoO$_4$)$_2$, (II) Li$_3$Ba$_2$Sm$_3$(MoO$_4$)$_8$, and (III) BaMoO$_4$.](image)