Bazarova Zh. G., Grossman V. G., Bazarov B. G.,
Tushinova Yu. L., Chimitova O. D., Bazarova Ts. T.
Chimica Techno Acta. 2017. Vol. 4, No. 4. P. 224–230.
ISSN 2409–5613

DOI: 10.15826/chimtech/2017.4.4.03

Zh.G. Bazarova[1,2], V.G. Grossman[1], B.G. Bazarov[1,2],
Yu.L. Tushinova[1,2], O.D. Chimitova[1], Ts.T. Bazarova[1]
[1]Baikal Institute of Nature Management,
Siberian Branch of Russian Academy of Sciences,
8 Sakh'yanovoi St., Ulan-Ude, 670047, Russian Federation
[2]Buryat State University,
24a SmolinaSt., Ulan-Ude, 670000, Russian Federation
e-mail: jbaz@binm.ru

Phase diagrams for the M_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems, where M = Li–Cs, Tl and Ln = La–Lu

In this paper, the results of systematic studies of complex molybdate systems M_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (M = Li–Cs, Tl; Ln = La–Lu) are presented. Subsolidus phase diagrams of ternary systems were constructed and new triple molybdates were obtained. The optimum synthesis conditions for poly- and monocrystalline form were determined. According to single-crystal data, the structure of one of the representatives of triple molybdates was determined.

Keywords: phase equilibria, synthesis, systems, lithium, sodium, potassium, rubidium, cesium, thallium, lanthanides, hafnium, crystal structure.

Received: 17.11.2017; accepted: 06.12.2017; published: 25.12.2017.

Introduction

The molybdates containing tetrahedrally coordinated anions MoO_4^{2-} are among the most exciting objects in inorganic and crystal chemistry. Special attention has been paid to the molybdates that include luminescent elements, such as Ce, Pr, Eu, Tb, Tm, in their composition. These compounds can be used as phosphors for white light emitting diodes. Currently, numerous studies had been undertaken that aim to search for new effective phosphors for the creation of WLED. These phosphors should possess high stability, compactness, high luminescence efficiency when excited by near UV, long lifetime and low cost. Luminescent materials containing rare-earth elements are also within the scope of such studies [1–3]. In this paper, we present results on the study of phase equilibria in ternary molybdate systems containing single-, three- and tetravalent elements, as well as data on the crystal structure of complex molybdate structural types.

Experimental

Reagents Li_2MoO_4 ("pure" grade), $Na_2MoO_4\cdot 2H_2O$ ("pure for analysis" grade), K_2MoO_4 ("pure" grade), Cs_2MoO_4 ("pure" grade), Rb_2CO_3 ("chemically pure" grade), Tl_2O_3 ("chemically pure" grade), MoO_3 ("chemically pure" grade), HfO_2 ("chemically pure" grade), and rare earth oxides of 99.9% purity were used as starting materials. $Hf(MoO_4)_2$ and $Ln_2(MoO_4)_3$ were synthesized by the solid state method. The annealing had started at 400–500 °C with the following temperature increase up to 800 °C in order to prevent MoO_3 losses due to its high volatility. The total calcination time was 100–150 h. Rb_2MoO_4 was prepared within the temperature range 350–650 °C during 100 h. Tl_2MoO_4 was synthesized during 50 h firing starting at 400 °C with final temperature equal to 550 °C. The samples were regrinded after each 24 h in the course of annealing in order to reach better homogeneity.

The phase formation inside a subsolidus region of the ternary salt systems M_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (M = Li–Cs, Tl; Ln = La–Lu) in air were studied using the intersecting joins method. The phase composition of the samples was monitored by X-ray diffraction (XRD) measurements using Bruker D8 Advance diffractometer (Cu Kα radiation, VANTEC-1, maximum angle $2\theta=100°$, scan step 0.01–0.02°). Primary fitting of the diffraction patterns was made using PROFAN software from the CSD package.

Results and discussion

The data concerning phase equilibrium for the side systems of studied triangles (quasi-ternary systems) M_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (M = Li–Cs, Tl; Ln = La–Lu) are taken from the literature. The phase formation in the quasi-binary Li_2MoO_4–$Ln_2(MoO_4)_3$ systems was described in paper [4] in details. The aforementioned systems can be divided into two groups. The first group includes systems with Ln = La–Tb in which two intermediate phases $LiLn_5(MoO_4)_8$ and $LiLn(MoO_4)_2$ possess a significant homogeneity range. The second group includes the systems with Ln = Dy–Lu. Inside these systems two intermediate compounds that did not exhibit any noticeable homogeneity ranges were detected: $LiLn(MoO_4)_2$ and $Li_7Ln_3(MoO_4)_8$.

Two intermediate compounds with the constituents mole ratio of 5:1 and 1:1 were detected inside the quasi-binary Na_2MoO_4–$Er_2(MoO_4)_3$ systems similarly to the K_2MoO_4–$Ln_2(MoO_4)_3$ (Ln = La, Tb, Dy, Er), M_2MoO_4–$Ln_2(MoO_4)_3$ (M = Tl, Rb; Ln = La–Lu) systems [4–8]. Additionally to those two one more intermediate phase with the constituents mole ratio 1:5 was found to exist inside the Na_2MoO_4–$Ln_2(MoO_4)_3$ (Ln = Nd, Sm) and K_2MoO_4–$Sm_2(MoO_4)_3$ systems [4, 5].

The phases formed inside the cesium-containing rare-earth molybdate systems included those with the constituents mole ratio 3:1 and 1:1 with Ln = Nd, whereas the systems with Ln = Sm, Tb, Er revealed only 1:1 compound [4, 5].

Lithium hafnium molybdate with the significant homogeneity range $Li_{10-4x}Hf_{2+x}(MoO_4)_9$ ($0.21 \le x \le 0.68$) was formed in the Li_2MoO_4–$Hf(MoO_4)_2$ system [9], but in the oxide systems with larger alkali earth metals M_2MoO_4–$Hf(MoO_4)_2$ (M = K, Tl, Rb, Cs) two types of compounds were confirmed – $M_8Hf(MoO_4)_6$ and $M_2Hf(MoO_4)_3$ [10–13]. It should be noted that Na-containing system slightly differs from the aforementioned ones. It was found that along with phases with the constituents mole ratios equal to 4:1 and 1:1 one more compound is formed with the 3:1 composition.

The phases that were isolated in the $Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems are $Ln_2Hf_3(MoO_4)_9$ (Ln = La–Tb), $Ln_2Hf_2(MoO_4)_7$ (Ln = Sm–Ho), and $Ln_2Hf(MoO_4)_5$(Ln = Er–Lu) [14].

The phase diagrams for various molybdate systems are shown in Fig. 1–6, and the corresponding phase compositions are listed in Table 1.

No new compounds were detected in the lithium-containing and sodium-containing systems [15, 16]. In contrast, the new compounds listed in Table 1 and shown in Fig. 3–6 were confirmed in the M_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (M = K, Rb, Tl, Cs; Ln = La–Lu) systems [14, 17, 18].

The molybdates with the composition $K_5LnHf(MoO_4)_6$ were identified in the systems with Ln = Sm–Lu.

Two types of compounds, namely $M_5LnHf(MoO_4)_6$ (5:1:2) and $M_2LnHf_2(MoO_4)_{6.5}$ (2:1:4), were isolated in the Tl_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Ln = Ce–Lu) and Rb_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Ln = Ce–Lu) systems. In case of the Tl-containing systems, for Ln = Ce–Nd one more phase except those mentioned above had been obtained – $TlLnHf_{0.5}(MoO_4)_3$ (1:1:1).

The phase with composition $Cs_2LnHf_2(MoO_4)_{6.5}$ (2:1:4) was found to

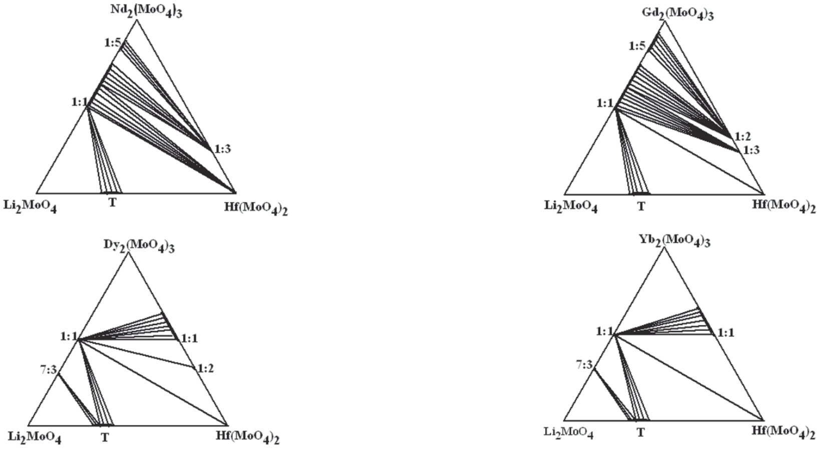


Fig. 1. Subsolidus phase diagrams of the Li_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems (T – $Li_{10-4x}Hf_{2+x}(MoO_4)_9$, $0.21 \le x \le 0.68$; shaded double-phase equilibrium region) [15]

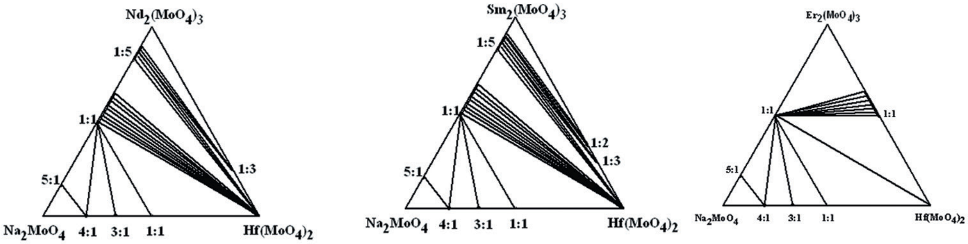


Fig. 2. Subsolidus phase diagrams of the Na_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems; shaded double-phase equilibrium region [16]

exist in the Cs-containing rare earth molybdates with Ln = Pr–Lu.

The systems M_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (M = K, Rb, Tl, Cs; Ln = La–Lu) are characterized by the formation of a different number of phases with varying homogeneity ranges with respect to the lanthanide elements. One can see that $M_5LnHf(MoO_4)_6$ (M = K, Tl, Rb) compounds were formed if the size difference for the single charged M^+ cation and rare earth element cation Ln^{3+} lies in the range of 0.682 Å ≤ $r(M^+)_{(CN=12)}$–$r(Ln^{3+})_{(CN=6)}$ ≤ 0.859 Å [19]. In the case of M^+ = Li^+, Na^+, Cs^+ such radii difference lies outside this range. As a result, formation of $M_5LnHf(MoO_4)_6$ compounds for these cations is impossible.

If the size difference for the single charged M^+ cation and rare earth element cation Ln^{3+} lies in the range 0.839 Å ≤ $r(M^+)_{(CN=12)}$ – $r(Ln^{3+})_{(CN=6)}$ ≤ 1.019 Å, it

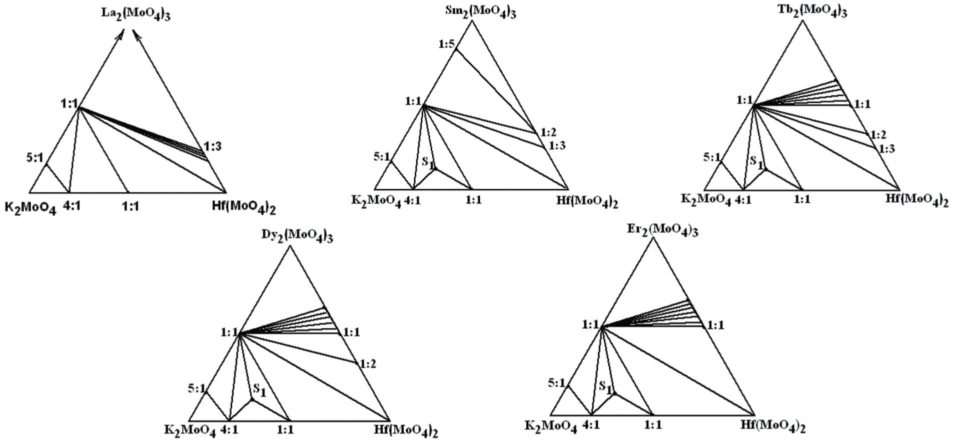


Fig. 3. Subsolidus phase relations in the K_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems (S_1–$K_5LnHf(MoO_4)_6$ (5:1:2); shaded double-phase equilibrium region) [14]

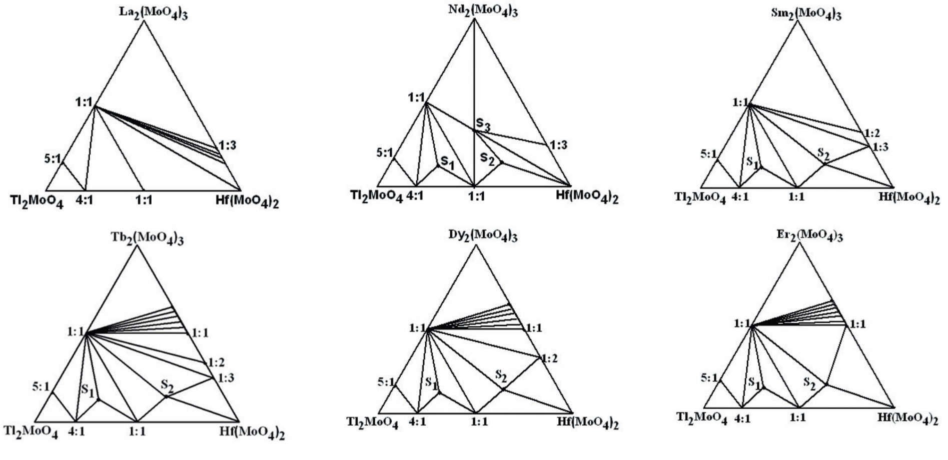


Fig. 4. Subsolidus phase diagrams for the Tl_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems where Ln = La–Lu. Notations: S_1–$Tl_5LnHf(MoO_4)_6$ (5:1:2), S_2–$Tl_2LnHf_2(MoO_4)_{6.5}$ (2:1:4), and S_3–$TlLnHf_{0.5}(MoO_4)_3$ (1:1:1); shaded double-phase equilibrium region [17]

Table 1

Compositions of triple molybdates in the M_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (M = Li–Cs, Tl; Ln = La–Lu) systems

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LiHf														
NaHf														
KHf					$K_5LnHf(MoO_4)_6$									
TlHf		$Tl_5LnHf(MoO_4)_6$												
		$Tl_2LnHf_2(MoO_4)_{6.5}$												
		$TlLnHf_{0.5}(MoO_4)_3$												
RbHf		$Rb_5LnHf(MoO_4)_6$												
		$Rb_2LnHf_2(MoO_4)_{6.5}$												
CsHf			$Cs_2LnHf(MoO_4)_{6.5}$											

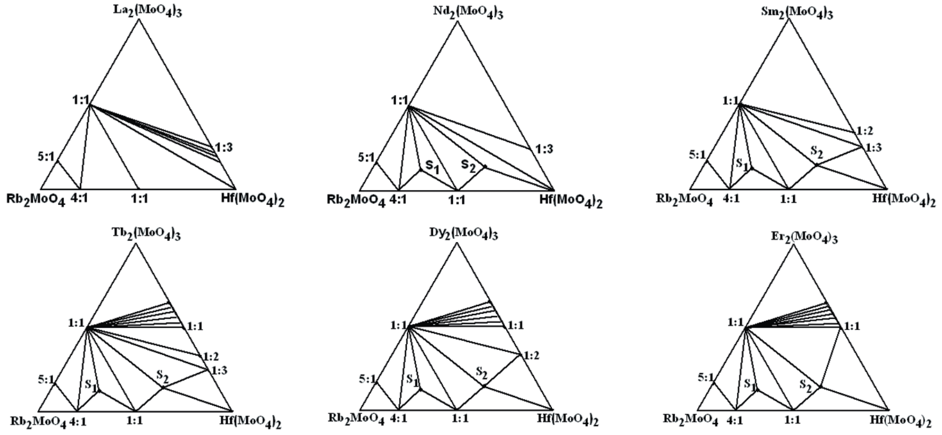
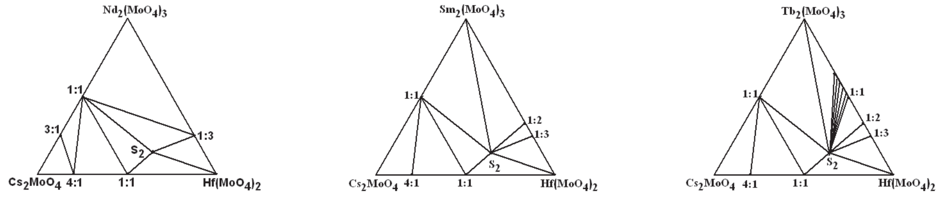


Fig. 5. Subsolidus phase diagrams for the Rb_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems where Ln = La–Lu. Notations: S_1–$Rb_5LnHf(MoO_4)_6$ (5:1:2) and S_2–$Rb_2LnHf_2(MoO_4)_{6.5}$ (2:1:4); shaded double-phase equilibrium region [18]



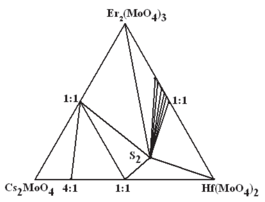


Fig. 6. Subsolidus phase relations in the Cs_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems (S_2–$Cs_2LnHf_2(MoO_4)_{6.5}$ (2:1:4); shaded double-phase equilibrium region)

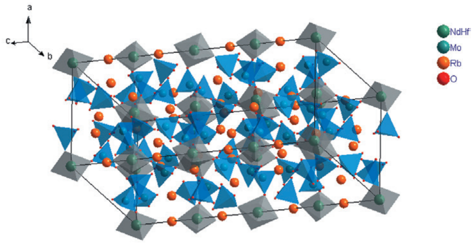


Fig. 7. Crystal structure fragment for $Rb_5NdHf(MoO_4)_6$

makes a formation of the $M_2LnHf_2(MoO_4)_{6.5}$ molybdates possible. The complex molybdates $M_5LnHf(MoO_4)_6$ (M = K, Tl, Rb) are isostructural to the earlier grown single crystals of $Rb_5LnHf(MoO_4)_6$ (Ln = Nd, Eu, Er), which possess the trigonal structure with $R\bar{3}c$ space group [18]. Three-dimensional framework of this structure is built of the consequently alternating MoO_4 tetrahedra and (Ln, Hf)O_6 octahedra linked with each other through the common O-vertices. One of the structural peculiarities for this class of compounds is a random distribution of Ln^{3+} and Hf^{4+} cations over two crystallographic sites with various distribution coefficients. Rubidium cations fill two types of large cavities in the framework, forming differently oriented channels of a large diameter. It gives good expectations for the fast ionic transport in such structures (Fig. 7).

Unfortunately, we have failed to prepare single crystals of $M_2LnHf_2(MoO_4)_{6.5}$ (2:1:4) and $TlLnHf_{0.5}(MoO_4)_3$ (1:1:1) in the condition used in the present work.

Acknowledgements

This work was carried out according to the state assignment BINM SB RAS (project No. 0339-2016-0007.). This work was supported by the Comprehensive Program of Basic Research SB RAS No II.2 «Integration and Development» (project No. 0339-2015-0039).

References

1. Haque M, Lee HI, Kim DK. Luminescent properties of Eu^{3+}-activated molybdate-based novel red-emitting phosphors for LEDs. *J Alloys Compd.* 2009;481:792–6. DOI:10.1016/j.jallcom.2009.03.083.
2. Haque M, Kim DK. Luminescent properties of Eu^{3+} activated $MLa_2(MoO_4)_4$ based (M = Ba, Sr and Ca) novel red-emitting phosphors. *Mater Lett.* 2009;3:793–6. DOI:10.1016/j.matlet.2009.01.018.
3. Liang Y, Noh HM, Ran W, Park SH, Choi BC, Jeong JH, Kim KH. The design and synthesis of new double perovskite (Na, Li)YMg(W, Mo)O_6: Eu^{3+} red phosphors for white light-emitting diodes. *J Alloys Compd.* 2017;716:56–64. DOI:10.1016/j.jallcom.2017.05.027.
4. Evdokimov AA, Efremov VA, Trunov VK, Kleyman IA, Tananaev IV. Soedineniya redkozemel'nykh elementov. Molibdaty, vol'framaty [Rare-earth elements' compounds. Molibdates, wolframates]. Moscow: Nauka; 1991. 267 p. Russian.
5. Trunov VK, Efremov VA, Velikodny Yu A. [Crystal chemistry and properties of double molybdates and tungstates.] Leningrad (USSR): Nauka; 1986. 173 p. Russian.
6. Basovich OM. [New phases in M_2MoO_4–$Ln_2(MoO_4)_3$ (M = Ag, Tl) and Li_2MoO_4–M_2MoO_4–$Ln_2(MoO_4)_3$ (M = K, Rb, Tl) systems] [dissertation]. Irkutsk (Russia); 2006. Russian.

7. Spitsyn VI, Trunov VK. [New data on double tungstates and molybdates of composition MeLn$(EO_4)_2$]. [*Reports of the Academy of Sciences of the USSR*]. 1969;185(4):854–5. Russian.
8. Savel'eva MV, Shakhno IV, Plyushchev VE. [Synthesis and properties of molybdates of alkaline and some rare-earth elements]. *Izv AN SSSR: Inorg Mat.* 1970;6(9):1665–9. Russian.
9. Solodovnikov SF, Balsanova LV, Bazarov BG, Zolotova ES, Bazarova Zh G. Phase formation in the Rb_2MoO_4–Li_2MoO_4–$Hf(MoO_4)_2$ system and the crystal structure of $Rb_5(Li_{1/3}Hf_{5/3})(MoO_4)_6$. *Russ J Inorg Chem.* 2003;48(7):1084–8.
10. Zolotova ES. [Synthesis and physico-chemical properties of double molybdates of alkali and tetravalent elements] [dissertation]. Novosibirsk (Russia); 1986. Russian.
11. Klevtsov PV, Zolotova ES, Glinskaya LA, Klevtsova RF. Synthesis, thermal stability and crystal structure of rubidium double molybdates with zirconium and hafnium. *Russ J Inorg Chem.* 1980;25(7):1844–50.
12. Bazarov BG, Bazarova TsT, Fedorov KN, Bazarova ZhG, Klevtsova RF, Glinskaya LA. Systems Tl_2MoO_4–$E(MoO_4)_2$ where E = Zr, Hf and crystal structure of $Tl_8Hf(MoO_4)_6$. *Russ J Inorg Chem.* 2006;51(5):794–9. DOI:10.1134/S0036023606050184.
13. Klevtsova RF, Antonova AA, Glinskaya LA. The crystal structure of $Cs_2Hf(MoO_4)_3$. *Crystallography.* 1980;25(1):161–4.
14. Romanova EYu. [New double and triple molybdates in the $Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ and K_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Ln = La–Lu, Y) systems] [dissertation]. Irkutsk (Russia); 2007. Russian.
15. Grossman VG, Bazarov BG, Tushinova YuL, Bazarova Zh G. Phase equilibria in the Li_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Ln = La–Lu) systems. *Russ J Inorg Chem.* 2015;51(4):351–4. DOI:10.1134/S0020168515030061.
16. Tushinova YuL, Bazarova TsT, Bazarov BG. [Phase relations in the Na_2MoO_4–$Ln_2(MoO_4)_3$–$Zr(MoO_4)_2$ (Ln = Nd, Sm, Er, Lu)]. *Vestnik buryatskogo gosudarstvennogo universiteta* [*Bulletin of Buryat State University*]. 2014;3:3–6. Russian.
17. Grossman VG, Bazarov BG, Bazarova Zh G. Subsolidus phase diagrams for the Tl_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems, where Ln = La–Lu. *Russ J Inorg Chem.* 2008;53(11):1788–94. DOI:10.1134/S003602360811020X.
18. Chimitova OD. [Phase equilibrium, crystalline structures and electrical properties of new triple molybdates in the Rb_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ (Ln = La–Lu) systems] [dissertation]. Krasnoyarsk (Russia); 2008. Russian.
19. Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* 1976; A32:751–67. DOI:10.1107/S0567739476001551.

Cite this article as:

Bazarova ZhG, Grossman VG, Bazarov BG, Tushinova YuL, Chimitova OD, Bazarova TsT. Phase diagrams for the M_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems, where M = Li–Cs, Tl and Ln = La–Lu. *Chimica Techno Acta*. 2017;4(4):224–30. DOI:10.15826/chimtech/2017.4.4.03.