

## Original articles

Research article

<https://doi.org/10.17308/kcmf.2021.23/3679>Phase formation in the  $\text{Ag}_2\text{MoO}_4\text{–Rb}_2\text{MoO}_4\text{–Hf}(\text{MoO}_4)_2$  systemYu. L. Tushinova<sup>1,2✉</sup>, B. G. Bazarov<sup>1,2</sup>, E. V. Kovtunets<sup>1</sup>, J. G. Bazarova<sup>1</sup><sup>1</sup>Baikal Institute of Nature Management, Siberian Branch of the Russian Academy of Sciences, 6 ul. Sakhyanovoy, Ulan-Ude 670047, Republic of Buryatia, Russian Federation<sup>2</sup>Banzarov Buryat State University, 24a ul. Smolina, Ulan-Ude 670000, Republic of Buryatia, Russian Federation

## Abstract

Systematic studies of the subsolidus structure of ternary molybdate systems allow expanding the representation of ternary molybdates. In this paper we studied the solid phase interaction in the  $\text{Ag}_2\text{MoO}_4\text{–Rb}_2\text{MoO}_4\text{–Hf}(\text{MoO}_4)_2$  system for the first time using X-ray phase analysis.

To determine the quasi-binary sections, we use the method of “intersecting cuts”. It helped to reveal the formation of new  $\text{Rb}_3\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  and  $\text{Rb}_3\text{AgHf}_2(\text{MoO}_4)_6$  phases. We also determined their thermal characteristics using differential scanning calorimetry. The ternary molybdate  $\text{Rb}_3\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  crystallised in the trigonal syngony with the following unit cell parameters:  $a = 10.7117(1)$ ,  $c = 38.5464(5)$  Å (space group R3c, Z = 6). The  $\text{Ag}_2\text{MoO}_4\text{–Rb}_2\text{MoO}_4\text{–Hf}(\text{MoO}_4)_2$  system is characterised by the existence of ten quasi-binary cross sections.

The experimental data obtained in this work complement the information on phase equilibria in condensed ternary systems containing molybdates of tetravalent elements and two different monovalent elements. This provides opportunities for the combination of the compositions of ternary molybdates due to cationic substitutions, which will allow controlling their properties.

**Keywords:** Phase diagram, Triangulation, Solid-state synthesis, Ternary molybdate, Silver molybdate, Rubidium molybdate, Hafnium molybdate, X-ray diffraction analysis

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## 1. Introduction

The study of phase equilibria in multicomponent systems is one of the methods of searching for new complex oxide compounds. In recent decades, molybdates with various combinations of cationic composition have been obtained as a result of the study of ternary molybdate systems [1–4]. This class of substances is still being actively expanded [5–9]. It should be noted that the studies of the properties of the identified ternary molybdates show that their application is promising. For example, the high values of ion conductivity of silver-bearing compounds obtained in [10, 11] allowed classifying them as superionic conductors.

A systematic study of phase equilibria allows obtaining more complete information on the interaction of components and the number of the formed phases, and identifying the general patterns of phase formation in the future. For instance, ternary molybdate systems containing molybdate of a tetravalent element, zirconium or hafnium, as one of the components, were studied in detail in [12–16]. The goal of this work was to study the phase formation in the  $\text{Ag}_2\text{MoO}_4$ – $\text{Rb}_2\text{MoO}_4$ – $\text{Hf}(\text{MoO}_4)_2$  system in the subsolidus region.

## 2. Experimental

We used the following industrial reagents:  $\text{Rb}_2\text{CO}_3$  (extra pure grade),  $\text{HfO}_2$  (chemically pure grade),  $\text{AgNO}_3$  (analytical reagent grade), and  $\text{MoO}_3$  (analytical reagent grade).

To obtain the initial molybdates from stoichiometric mixtures of the corresponding reagents, we used the method of solid-phase synthesis. Stepped annealing of the samples was conducted in a muffle furnace, and the samples were repeatedly ground in an agate mortar in an ethyl alcohol medium. Silver molybdate was obtained with a synthesis temperature of 200–450 °C, the total duration of annealing was 150 hours. Medium rubidium and hafnium molybdates were synthesised in the range of 400–550 °C (rubidium molybdate) and 400–750 °C (hafnium molybdate) for 80–100 hours.

Ternary molybdates with the compositions  $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  and  $\text{Rb}_5\text{AgHf}_2(\text{MoO}_4)_6$  were synthesised from stoichiometric amounts of the reaction mixtures of  $\text{Ag}_2\text{MoO}_4$ ,  $\text{Rb}_2\text{MoO}_4$ , and

$\text{Hf}(\text{MoO}_4)_2$ . The annealing was conducted in the temperature range 290–500 °C with an increase in temperature with steps of 30 °C and repeated grinding of the samples. The time of annealing was 60 hours.

The phase equilibria in the ternary system were studied using the method of “intersecting cuts” [17]. The interaction in the subsolidus area was studied using X-ray and had two stages. During the first stage, we determined the phase composition of the intersection points of all possible cuts connecting the compositions of the components and intermediate phases of the faceting elements. During the second stage, we also studied individual quasi-binary sections of the system and some compositions from the three-phase regions. The achievement of equilibrium was proved by the stabilisation of the phase composition of the samples after several sequential annealings and the mutual consistency of the phase composition allowing triangulating the systems.

X-ray phase analysis (XPA) was performed on a Bruker D8 Advance automatic powder diffractometer ( $\text{CuK}\alpha$  radiation, scanning step 0.01°). The ICDD PDF-2 database was used to analyse the X-ray patterns.

We used the Le Bail method and the TOPAS 4.2 software to process the experimental data and specify the unit cell parameters of the  $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  compound.

Thermal analysis was conducted on an STA 449 F1 Jupiter synchronous thermal analyser manufactured by NETZSCH. The samples were scanned in platinum crucibles in an argon atmosphere with heating and cooling at a rate of 10 °C/min. The weight of the samples was 17–20 mg.

## 3. Results and discussion

Phase equilibria in the  $\text{Ag}_2\text{MoO}_4$ – $\text{Rb}_2\text{MoO}_4$ – $\text{Hf}(\text{MoO}_4)_2$  system were studied taking into account the previous publications on binary faceting systems.

One compound with the  $\text{AgRb}_3(\text{MoO}_4)_2$  composition which melts at 435 °C was formed in the  $\text{Ag}_2\text{MoO}_4$ – $\text{Rb}_2\text{MoO}_4$  binary system [19]. During crystallisation from a solution, single crystals were obtained in a melt, and their composition was determined when decoding the structure

as  $\text{Ag}_{1.19}\text{Rb}_{2.81}(\text{MoO}_4)_2$  [20]. It should be noted a single-phase sample of this composition cannot be synthesised using the method of solid-phase reactions. And the discovered crystal composition is probably limited in terms of silver content and can only be obtained from melt. It was shown that the  $\text{Ag}_{1+x}\text{Rb}_{3-x}(\text{MoO}_4)_2$  samples with  $0 \leq x \leq 0.10$ , which is about 2 mol. %, were single-phase only at limiting subsolidus temperatures [20].

The  $\text{Rb}_2\text{MoO}_4$ – $\text{Hf}(\text{MoO}_4)_2$  binary system is characterised by the presence of two compounds with the  $\text{Rb}_8\text{Hf}(\text{MoO}_4)_6$  and  $\text{Rb}_2\text{Hf}(\text{MoO}_4)_3$  compositions with melting temperatures of 655 and 650 °C respectively [21, 22].

We established that one  $\text{AgRb}_2(\text{MoO}_4)_2$  compound was formed in the  $\text{Ag}_2\text{MoO}_4$ – $\text{Hf}(\text{MoO}_4)_2$  binary system and melted incongruently at 570 °C [23].

When synthesizing double molybdates, we focused on the conditions of their obtaining and melting temperatures mentioned in previous publications.

The formation of new  $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  –  $S_1$  and  $\text{Rb}_3\text{AgHf}_2(\text{MoO}_4)_6$  –  $S_2$  phases was identified when studying phase equilibria in the subsolidus region. It should be noted that reflections of the new  $S_1$  phase were observed on the X-ray patterns of the samples of the supposed section of  $\text{AgRb}_5(\text{MoO}_4)_2$ – $\text{Rb}_2\text{Hf}(\text{MoO}_4)_3$ .

The phase relationships at 430 °C in the triple silver-rubidium-hafnium molybdate system are characterised by the following quasi-binary sections:  $\text{AgRb}_3(\text{MoO}_4)_2$ – $\text{Rb}_8\text{Hf}(\text{MoO}_4)_6$ ,  $\text{Ag}_2\text{MoO}_4$ – $\text{Rb}_8\text{Hf}(\text{MoO}_4)_6$ ,  $\text{Ag}_2\text{MoO}_4$ – $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$ ,  $\text{Ag}_2\text{MoO}_4$ – $\text{Rb}_3\text{AgHf}_2(\text{MoO}_4)_6$ ,  $\text{Hf}(\text{MoO}_4)_2$ – $\text{Rb}_3\text{AgHf}_2(\text{MoO}_4)_6$ ,  $\text{Ag}_2\text{Hf}(\text{MoO}_4)_3$ – $\text{Rb}_3\text{AgHf}_2(\text{MoO}_4)_6$ ,  $\text{Hf}(\text{MoO}_4)_2$ – $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$ ,  $\text{Rb}_2\text{Hf}(\text{MoO}_4)_3$ – $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$ ,  $\text{Rb}_8\text{Hf}(\text{MoO}_4)_6$ – $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$ ,  $\text{Rb}_8\text{Hf}(\text{MoO}_4)_6$ – $\text{Rb}_3\text{AgHf}_2(\text{MoO}_4)_6$ ,  $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$ – $\text{Rb}_3\text{AgHf}_2(\text{MoO}_4)_6$  (Fig. 1). As for the studied conditions, there were no sections radiating from the apex of the triangle where rubidium molybdate was located. Thus, the studied system was divided into nine secondary triangles by ten quasi-binary sections.

Comparing the results with those obtained previously in [24], we should mention some similarity with the phase diagram of the  $\text{Li}_2\text{MoO}_4$ – $\text{Rb}_2\text{MoO}_4$ – $\text{Hf}(\text{MoO}_4)_2$  system despite significant

differences in the faceting elements. For example, a  $\text{RbLiMoO}_4$  composition was observed in the  $\text{Li}_2\text{MoO}_4$ – $\text{Rb}_2\text{MoO}_4$  binary system, while an intermediate phase in the  $\text{Li}_2\text{MoO}_4$ – $\text{Hf}(\text{MoO}_4)_2$  system has a rather extended homogeneity range. The similarity was found during the triangulation of the  $\text{Li}_2\text{MoO}_4$ – $\text{Rb}_2\text{MoO}_4$ – $\text{Hf}(\text{MoO}_4)_2$  system when a part of the stable sections was radiating from the apex of the concentration triangle where lithium molybdates were located. In our case, the sections with the participation of silver molybdate were stable. And in both phase diagrams, there were no stable sections radiating from the apex of the triangle, where rubidium molybdate was located. The differences were observed in the amount of triple molybdates. Triple molybdates with the  $\text{Rb}_5\text{Me}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  and  $\text{Rb}_3\text{MeHf}_2(\text{MoO}_4)_6$  ( $\text{Me} = \text{Li}, \text{Ag}$ ) compositions were found in both systems. However, unlike the lithium system, there was no compound similar to the  $\text{RbLiHf}(\text{MoO}_4)_3$  composition formed in the system with silver molybdate.

The compounds with the similar composition  $\text{Me}_3\text{Me}'\text{Hf}_2(\text{MoO}_4)_6$  were obtained with  $\text{Me} = \text{Na}, \text{K}, \text{Tl}, \text{Rb}$ , and  $\text{Me}' = \text{Li}$  [16]. They were classified using three structure types of binary molybdates. Triple molybdates  $\text{Me}_3\text{LiHf}_2(\text{MoO}_4)_6$  ( $\text{Me} = \text{K}, \text{Rb}$ ) are isostructural to  $\text{KAl}(\text{MoO}_4)_2$ , while  $\text{Na}_3\text{LiHf}_2(\text{MoO}_4)_6$  molybdate is isostructural to  $\text{NaIn}(\text{MoO}_4)_2$ . The diffraction pattern of  $\text{Tl}_3\text{LiHf}_2(\text{MoO}_4)_6$  was indexed with the assumption of the formation of a superstructure of the rhombic  $\text{KIn}(\text{MoO}_4)_2$  with a tripling of the

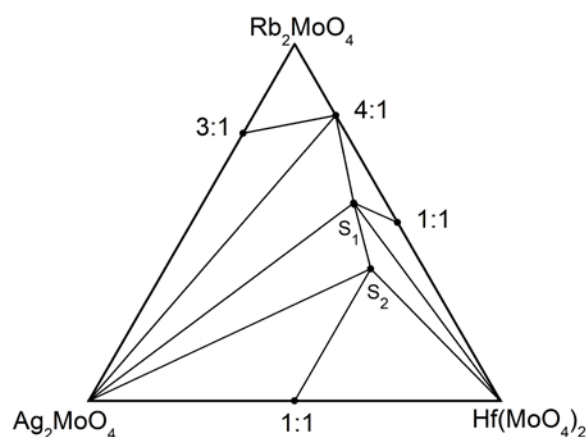


Fig. 1. Phase equilibria in the  $\text{Ag}_2\text{MoO}_4$ – $\text{Rb}_2\text{MoO}_4$ – $\text{Hf}(\text{MoO}_4)_2$  system in the subsolidus region (400–430 °C):  $S_1$ – $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$ ,  $S_2$ – $\text{Rb}_3\text{AgHf}_2(\text{MoO}_4)_6$

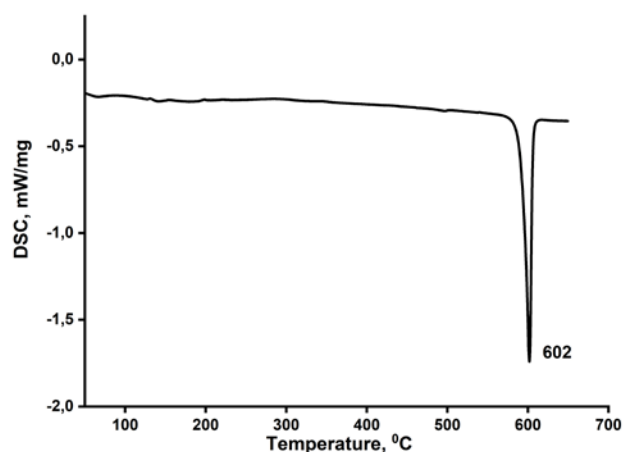
smallest parameter  $c$ . In our case, we still have not found a structural analogue for the phase. Apparently, the change of the cationic composition leads to the formation of a different structure. One endothermic effect corresponding to melting was observed on the DSC curve for the  $\text{Rb}_5\text{AgHf}_2(\text{MoO}_4)_6$  sample (Fig. 2). However, the results of X-ray phase analysis of the cooled melt allowed making the assumption that melting has an incongruent nature.

According to X-ray phase analysis, the synthesised  $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  ternary molybdate was isostructural to the previously studied  $\text{Rb}_5\text{Li}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  which crystallised in the trigonal syngony (space group  $R\bar{3}c$ ,  $Z = 6$ ), and its structure was determined in [24]. The base of the crystal structure is a skeletal mixed plane of  $(\text{Hf}, \text{Li})\text{O}_6$  octahedrons and  $\text{MoO}_4$  tetrahedrons. The atoms of rubidium are located in large voids of this plane. All the reflections of the  $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  compound on an X-ray pattern were satisfactorily indexed based on the assumption of the isostructurality of  $\text{Rb}_5\text{Li}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  [24]. The results of the specification using the Le-Baile method are presented in Table 1, and calculated and experimental X-ray diffraction patterns with difference curves are shown in Figure 3. According to the results of differential scanning calorimetry, the compound melted at  $597^\circ\text{C}$ .

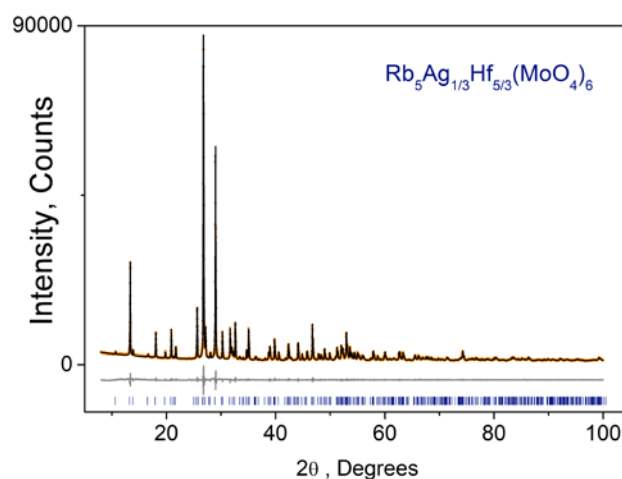
**Table 1.** Crystallographic characteristics and parameters of unit cell specification of the  $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$  compound using Le-Baile method

Compound	$\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$
Space group	$R\bar{3}c$
$a$ , Å	10.7117 (1)
$c$ , Å	38.5464 (5)
$V$ , Å <sup>3</sup>	3830.27 (9)
$2\theta$ -interval, °	8–100
$R_{wp}$ , %	4.10
$R_p$ , %	3.26
$R_{exp}$ , %	2.15
$\chi^2$	1.90
$R_B$ , %	0.46

Therefore, a new compound was added to the series of the compounds with the  $\text{Me}_5(\text{Li}_{1/3}\text{Hf}_{5/3})(\text{MoO}_4)_6$  (Me = K, Rb, Tl) composition [16]. All



**Fig. 2.** DSC curve for the  $\text{Rb}_5\text{AgHf}_2(\text{MoO}_4)_6$  sample



**Fig. 3.** Experimental (circles), calculated (line), difference, and dashed X-ray diffraction patterns of  $\text{Rb}_5\text{Ag}_{1/3}\text{Hf}_{5/3}(\text{MoO}_4)_6$

these triple molybdates have already been included in a rather large group of isostructural compounds whose structure was first solved for the  $\text{K}_5(\text{Mg}_{0.5}\text{Zr}_{1.5})(\text{MoO}_4)_6$  compound [25]. All the above-mentioned compounds have cage structures built from isolated  $\text{MO}_6$  octahedrons and  $\text{XO}_4$  tetrahedrons which differ in the nature of the mutual arrangement of the polyhedrons. As a result, various numbers of cavities of different shapes and isomorphous substitutions were formed.

#### 4. Conclusion

Thus, the phase equilibria in the subsolidus region of the  $\text{Ag}_2\text{MoO}_4$ – $\text{Rb}_2\text{MoO}_4$ – $\text{Hf}(\text{MoO}_4)_2$  system were studied for the first time, the formation of new triple molybdates was identified, and the system was triangulated.

## Author contributions

All authors made an equivalent contribution to the preparation of the publication.

## Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

## References

1. Kozhevnikova N. M., Mokhosoev M. V. *Trojnye molibdaty* [Triple molybdates]. Ulan-Udje: Izdatel'stvo Burjatskogo gosuniversiteta Publ.; 2000. 298 p. (In Russ.)
2. Khaikina G. E., Solodovnikov S. F., Basovich O. M., Solodovnikova Z. A., Kadyrova Y. M., Savina A. A., Zolotova E. S., Yudin V. N., Spiridonova T. S. Triple molybdates one-, one- and three(two)valence metals. *Chimica Techno Acta*. 2015;(2)4: 356–372. <https://doi.org/10.15826/chimtech.2015.2.4.032>
3. Dridi W., Zid M. F. Crystal Structure of New One-Dimensional Triple Molybdate  $\text{Na}_2\text{K}_2\text{Cu}(\text{MoO}_4)_3$ . *Journal of Structural Chemistry*. 2018;59: 1128–1132. <https://doi.org/10.1134/S0022476618050153>
4. Bazarova J. G., Chimitova O. D., Grossman V. G., Bazarov B. G., Tushinova Yu. L. Regularities of trigonal triple molybdates formation  $\text{M}_2\text{LnHf}(\text{MoO}_4)_6$  in the systems  $\text{M}_2\text{MoO}_4$ – $\text{Ln}_2(\text{MoO}_4)_3$ – $\text{Hf}(\text{MoO}_4)_2$  (M=K, Tl, Rb; Ln=La–Lu). *Uspehi sovremennogo estestvoznaniya*. 2016;10: 14–19. Available at: <https://www.elibrary.ru/item.asp?id=27179218> (In Russ., abstract in Eng)
5. Spiridonova T. S., Savina A. A., Kadyrova Yu. M., Belykh E. P., Khaikina E. G. New compounds  $\text{Li}_3\text{Ba}_2\text{Bi}_3(\text{XO}_4)_8$  (X = Mo, W): synthesis and properties. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2021;23(1): 73–80. <https://doi.org/10.17308/kcmf.2021.23/3306>
6. Gulyaeva O. A., Solodovnikova Z. A., Solodovnikov S. F., Yudin V. N., Zolotova E. S., Komarov V. Yu. Subsolidus phase relations and structures of solid solutions in the systems  $\text{K}_2\text{MoO}_4$ – $\text{Na}_2\text{MoO}_4$ – $\text{MMoO}_4$  (M = Mn, Zn). *Journal of Solid State Chemistry*. 2019;272: 148–156. <https://doi.org/10.1016/j.jssc.2019.02.010>
7. Vats B. G., Shafeeq M., Kesari S. Triple molybdates and tungstates scheelite structures: Effect of cations on structure, band-gap and photoluminescence properties. *Journal of Alloys and Compounds*. 2021;865: 158818. <https://doi.org/10.1016/j.jallcom.2021.158818>
8. Kozhevnikova N. M., Batueva S. Y. Erbium-doped upconversion phosphor in the  $\text{Li}_2\text{MoO}_4$ – $\text{BaMoO}_4$ – $\text{Y}_2(\text{MoO}_4)_3$  system. *Inorganic Materials*. 2020;56(3): 286–291. <https://doi.org/10.1134/S0020168520030085>
9. Logvinova A. V., Bazarov B. G., Bazarova J. G. Obtaining iron (III) – containing triple molybdate  $\text{K}_5\text{FeZr}(\text{MoO}_4)_6$  by sol-gel technology. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2020;22(3): 353–359. <https://doi.org/10.17308/kcmf.2020.22/2966>
10. Spiridonova T. S., Savina A. A., Kadyrova Y. M., Khaikina E. G., Solodovnikov S. F., Solodovnikova Z. A., Yudin V. N., Stefanovich S. Y. New triple molybdate  $\text{Rb}_2\text{AgIn}(\text{MoO}_4)_3$ : synthesis, framework crystal structure and ion-transport behaviour. *Acta Crystallographica. Section C, Structural Chemistry*. 2018;74(12): 1603–1609. <https://doi.org/10.1107/s2053229618014717>
11. Kotova I. Yu., Solodovnikov S. F., Solodovnikova Z. A., Belov D. A., Stefanovich S. Yu., Savina A. A., Khaikina E. G. New series of triple molybdates  $\text{AgA}_3\text{R}(\text{MoO}_4)_5$  (A=Mg, R=Cr, Fe; A=Mn, R=Al, Cr, Fe, Sc, In) with framework structures and mobile silver ion sublattices. *Journal of Solid State Chemistry*. 2016;238: 121–128. <https://doi.org/10.1016/j.jssc.2016.03.003>
12. Bazarova J. G., Tushinova Yu. L., Grossman V. G., Bazarova Ts. T., Bazarov B. G., Kurbatov R. V. Phase relations in the  $\text{Me}_2\text{MoO}_4$ – $\text{In}_2(\text{MoO}_4)_3$ – $\text{Hf}(\text{MoO}_4)_2$ , where Me=Li, K, Tl, Rb, Cs. *Chimica Techno Acta*. 2018;5(3): 126–131. <https://doi.org/10.15826/chimtech.2018.5.3.01>
13. Grossman V. G., Bazarova J. G., Bazarov B. G., Molokeyev M. S. New triple molybdate  $\text{K}_5\text{ScHf}(\text{MoO}_4)_6$ : synthesis, properties, structure and phase equilibria in the  $\text{M}_2\text{MoO}_4$ – $\text{Sc}_2(\text{MoO}_4)_3$ – $\text{Hf}(\text{MoO}_4)_2$  (M = Li, K) systems. *Journal of Solid State Chemistry*. 2020;283: 121143. <https://doi.org/10.1016/j.jssc.2019.12.1143>
14. Tsyrenova G. D., Solodovnikov S. F., Popova N. N., Solodovnikova Z. A., Pavlova E. T., Naumov D. Yu., Lazoryak B. I. Phase equilibria in the  $\text{Cs}_2\text{MoO}_4$ – $\text{ZnMoO}_4$ – $\text{Zr}(\text{MoO}_4)_2$  system, Crystal structures and properties of new triple molybdates  $\text{Cs}_2\text{ZnZr}(\text{MoO}_4)_4$  and  $\text{Cs}_2\text{ZnZr}_2(\text{MoO}_4)_6$ . *Journal of Physics and Chemistry of Solids*. 2015;81: 93–99. <https://doi.org/10.1016/j.jpcs.2015.01.015>
15. Dorzhieva S. G., Bazarov B. G., Bazarova J. G. New molybdates in the  $\text{Rb}_2\text{MoO}_4$ – $\text{M}^I_2\text{MoO}_4$ – $\text{Zr}(\text{MoO}_4)_2$  ( $\text{M}^I$  – Na, K) systems as promising ion-conducting materials. *Letters on Materials*. 2019;9(1): 17–21. <https://doi.org/10.22226/2410-3535-2019-1-17-21>
16. Balsanova L. V. *Troinye molibdaty litiya, odnovalentnykh metallov i gafniya* [Ternary molybdates of lithium, monovalent metals and hafnium], Cand. chem. sci. diss. Abstr. Irkutsk: Izdatel'stvo Buryatskogo gosuniversiteta; 2004. 23 p. Available at: <https://viewer.rusneb.ru/ru/rsl01002728973?page=1&rotate=0&theme=white> (In Russ.)
17. Zaharov A. M. *Diagrammy sostojaniya dvojnih i trojnih sistem* [State diagrams of double and triple systems]. Moscow: Metallurgija Publ.; 1978. 296 p. (In Russ.)

18. Bruker AXS TOPAS V4: General profile and structure analysis software for powder diffraction data. *User's Manual*. Bruker AXS, Karlsruhe, Germany. 2008.

19. Kadyrova Yu. M., Solodovnikov S. F., Solodovnikova Z. A., Basovich O. M., Spiridonova T. S., Khajkina E. G. New silver-rubidium double molybdate. *Vestnik Burjatskogo gosudarstvennogo universiteta*. 2015;(3): 21–25. Available at: <https://www.elibrary.ru/item.asp?id=23233676> (In Russ., abstract in Eng.)

20. Spiridonova T. S., Solodovnikov S. F., Kadyrova Yu. M., Solodovnikova Z. A., Savina A. A., Khaikina E. G. Double molybdates of silver and monovalent metals. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2021;23(3): 421–431. <https://doi.org/10.17308/kcmf.2021.23/3527>

21. Bazarov B. G., Chimitova O. D., Klevtsova R. F., Tushinova Yu. L., Glinskaya L. A., Bazarova Zh. G. Crystal structure of a new ternary molybdate in the  $\text{Rb}_2\text{MoO}_4$ – $\text{Eu}_2(\text{MoO}_4)_3$ – $\text{Hf}(\text{MoO}_4)_2$  system. *Journal of Structural Chemistry*. 2008;49: 53–57. <https://doi.org/10.1007/s10947-008-0008-5>

22. Zolotova E. S., Sergey F. Solodovnikov S. F., Solodovnikova Z. A., Vasilii N. Yudin V. N., Uvarov N. F., Sukhikh A. S. Selection of alkali polymolybdates as fluxes for crystallization of double molybdates of alkali metals, zirconium or hafnium, revisited crystal structures of  $\text{K}_2\text{Mo}_2\text{O}_7$ ,  $\text{K}_2\text{Mo}_3\text{O}_{10}$ ,  $\text{Rb}_2\text{Mo}_3\text{O}_{10}$  and ionic conductivity of  $\text{A}_2\text{Mo}_2\text{O}_7$  and  $\text{A}_2\text{Mo}_3\text{O}_{10}$  ( $\text{A} = \text{K}, \text{Rb}, \text{Cs}$ ). *Journal of Physics and Chemistry of Solids*. 2021;154: 110054. <https://doi.org/10.1016/j.jpcs.2021.110054>

23. Bazarova J. G., Tushinova Y. L., Bazarov B. G. Phase equilibria in systems  $\text{Ag}_2\text{MoO}_4$ – $\text{Ln}_2(\text{MoO}_4)_3$ – $\text{Hf}(\text{MoO}_4)_2$ ,  $\text{Ln} = \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}$ . *BSU bulletin. Chemistry. Physics*. 2018;(4): 8–12. <https://doi.org/10.18101/2306-2363-2018-4-8-12> (In Russ., abstract in Eng.)

24. Solodovnikov S. F., Zolotova E. S., Balsanova L. V., Bazarov B. G., Bazarova Zh. G. Phase formation in the  $\text{Rb}_2\text{MoO}_4$ – $\text{Li}_2\text{MoO}_4$ – $\text{Hf}(\text{MoO}_4)_2$  system and the crystal structure of  $\text{Rb}_5(\text{Li}_{1/3}\text{Hf}_{5/3})(\text{MoO}_4)_6$ . *Russian Journal of Inorganic Chemistry*. 2003;48(7): 1084–1088. Available at: <https://www.elibrary.ru/item.asp?id=13434803>

25. Klevtsova R. F., Bazarova Zh. G., Glinskaya L. A., Alekseev V. I., Arkhincheeva S. I., Bazarov B. G., Klevtsov P. V., Fedorov K. N. Sintez troinykh molibdatov kaliya, magniya, tsirkoniya i kristallicheskaya struktura [Synthesis of ternary molybdates of potassium, magnesium, zirconium and crystal structure  $\text{K}_5(\text{Mg}_{0.5}\text{Zr}_{1.5})(\text{MoO}_4)_6$ ]. *Journal of Structural Chemistry*. 1994;35(3): 286. Available at: <https://jsc.niic.nsc.ru/article/16603> / <https://jsc.niic.nsc.ru/article/16603/> (In Russ.)

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