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Thallium ionic conductivity of new thallium indium hafnium molybdate ceramics

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Abstract

In the process of studying the system Tl_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$, a new thallium indium hafnium molybdate was found. The crystal structure of the molybdate $Tl_5InHf(MoO_4)_6$ was determined in the centrosymmetric space group $R3c$ ($a = 10.63893$ (5) Å, $c = 38.1447(3)$ Å; $V = 3739.04$ (4) Å^3, $Z = 6$). The structure is a three-dimensional framework consisting of alternating $(Hf,In)O_6$-octahedra connected by MoO_4-tetrahedra. Each octahedron has common vertices with tetrahedra. The atoms arranged in this way form channels extended along with the a and b axes, in which thallium atoms are located. The conductivity behavior of $Tl_5InHf(MoO_4)_6$ ceramics was studied in the temperature range from 300 to 870 K. The conductivity of the heavy cations of thallium is activated with increasing temperature.

Keywords Synthesis · Thallium · Molybdates · Phase diagram · DSC · Conducting material

Introduction

Currently, there is great interest in inorganic compounds (in particular, molybdenum-containing [1]) which exhibit the properties of catalysts [2–4], ferroelectric, piezoelectric, photoluminescent [5], laser [6, 7], and magnetic and have high ionic conductivity [8–18]. The molybdates are the proposed candidates for the creation of phosphors, white LEDs, and active lasers [19–25].

In recent decades, ternary molybdates with the general chemical formula $A_xB_yCz(MoO_4)n$, containing various combinations of A, B, and C cations, have been actively studied. For these compounds, the most characteristic structures are NASICON [26] and alluaudite [27]. Due to their structural features, they have high ionic conductivity ($\sigma = 10^{-3}$–10^{-2} S cm^{-1}). For example, $Na_{1-x}A_{1-x}R_{1+x}(MoO_4)_3$ ($A =$ Mg, Mn, Co, Ni, Zn, Cd; $R =$ Al, Fe, Cr, Sc, In) and $Ag_{1-x}Mg_{1-x}R_{1+x}(MoO_4)_3$ (where $R =$ Al or Sc and $0 \leq x \leq 0.5$) crystallize in the NASICON-type structure (space group $R3c$) (sodium (Na) Super Ionic CONductor) [28–30]. A specific feature of phases with a NASICON structure is a rhombohedral framework $\{[R_2(MoO_4)]_3^{n-}\}_{3\infty}$ consisting of RO_6 octahedra and MoO_4 tetrahedra. $A(R)$ atoms are at threefold axes and MoO_4 groups are at twofold axes. The vacant parts of octahedral and tetrahedral voids merge into a three-dimensional network of channels, which are filled with alkali metal cations. This contributes to high ionic conductivity $\sigma = 10^{-3}$–10^{-2} S cm^{-1} at about $T = 750$–800 K. $K_{0.13}Na_{3.87}Mg(MoO_4)_3$ (space group $C2/c$, $\sigma = 3.8 \times 10^{-2}$ S cm^{-1} at 853 K) crystallizes in the alluaudite-type [31]. The structure is formed by infinite chains composed of edge sharing $(Mg/Na)_2O_{10}$ dimmers, which are linked together via bridging MoO_4 tetrahedra, yielding to a three-dimensional framework enclosing two distinct types of hexagonal tunnels in which Na^+ and K^+ cations reside. $Na_{25}Cs_8R_5(MoO_4)_{24}$ ($R =$ In, Sc, Fe) form a distinctive family of pseudo-orthorhombic alluaudite-related structures with the parent space group $Pbca$ [17]. Its structural features are alluaudite-like polyhedral layers composed of pairs of edge-shared $(R,Na)O_6$ and NaO_6 octahedra connected by bridging MoO_4 tetrahedra. The layers are joined together by means of interlayer MoO_4 tetrahedra, thus forming open 3D

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frameworks with cavities filled with Cs^+ and Na^+ ions. The manner of stacking layers is somewhat different from the alluaudite type. The conductivity for $Na_{25}Cs_8R_5(MoO_4)_{24}$ (R = In, Sc, Fe) is $\sigma = 10^{-3}$–10^{-2} S cm^{-1} at about $T = 700$ K. The $M_5RA(MoO_4)_6$ compounds (where M = K, Rb, Cs, R = lanthanide trivalent ion, Al^{3+}, Cr^{3+}, Fe^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, Bi^{3+}, $A = Zr^{4+}$ or Hf^{4+}) [15, 32–48] form family with the space group $R3c$. The crystal structure of $M_5RA(MoO_4)_6$ compounds is a three-dimensional mixed-metal framework, which is built by a regular alternation of Mo tetrahedra and two sorts of $(R,A)O_6$ octahedra, which are linked to one another via O-corner sharing. Large interstices accommodate two sorts of alkaline atoms. These M^+ polyhedra fill in variously oriented large-cross-section channels. From this, conditions for rapid ion transport can appear in this type of framework structure provided that channels are populated by appropriate cations with appropriate ionic radii. Studies of the conductivity of these compounds showed that it has an order of 10^{-3} S cm^{-1}.

Since the compounds $M_5RA(MoO_4)_6$ (where M = K, Rb, Cs, R = lanthanide trivalent ion, Al^{3+}, Cr^{3+}, Fe^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, Bi^{3+}, $A = Zr^{4+}$ or Hf^{4+}) [15, 32–48] were obtained only with alkali metals, the idea arose to replace the alkali metal with thallium. Thallium is a rather uncommon element. The presence of a lone pair of electrons in the monovalent thallium cation can contribute to the distortion of the coordination environment, which in turn may improve the conductive properties of $M_5RA(MoO_4)_6$ compounds. As a trivalent metal, we decided to use indium. For us, the study of this class of compounds is of not only practical but also theoretical interest.

Experimental

Preparation of samples

The complex molybdate compositions were prepared by the solid-state reaction method. Tl_2CO_3 (chemically pure, Red Chemist, Russia), In_2O_3 (chemically pure, Ural Plant of Chemical Reagents, Russia), HfO_2 (chemically pure, IGIC RAS, Russia), and MoO_3 (chemically pure, Red Chemist, Russia) were used as starting reagents. A stoichiometric mixture of In_2O_3 and MoO_3 was used for the synthesis of $In_2(MoO_4)_3$ at 673–1023 K for 50 h. To avoid losses of MoO_3 through sublimation, the annealing was started at 673 K. Thallium molybdate, Tl_2MoO_4, was obtained by the following reaction: $Tl_2CO_3 + MoO_3 = Tl_2MoO_4 + CO_2$ at 673–823 K for 100 h. When working with thallium compounds, we followed the recommended precautions. This is, of course, a white coat, hand protection, and simple gauze mask respiratory. Hafnium molybdate, $Hf(MoO_4)_2$, was synthesized by stepwise annealing of stoichiometric mixtures of HfO_2 and MoO_3 at 673–1023 K for 100 h. The starting

compounds were well mixed and ground in agate mortar with a pestle. To accelerate the interaction, the reaction mixtures were gradually annealed at the temperatures specified in the interval and ground after every 24 h of annealing.

The phase formation in the Tl_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ system was investigated by the cross-section method in the subsolidus region. We took from the literature information about what compounds are formed in binary systems, which are sides of the studied triangle [49–52]. So, on the side of Tl_2MoO_4–$In_2(MoO_4)_3$ [49, 50], the authors found two compounds of the compositions $TlIn(MoO_4)_2$ (1:1) and $Tl_5In(MoO_4)_4$ (5:1). Two composition $Tl_8Hf(MoO_4)_6$ (4:1) and $Tl_2Hf(MoO_4)_3$ (1:1) were found in the Tl_2MoO_4–$Hf(MoO_4)_2$ system [51]. But inside the $In_2(MoO_4)_3$–$Hf(MoO_4)_2$ system, new compounds could not be detected [52]. In order to determine which segments are quasi binary and to reveal the formation of new triple molybdates, we selected about twenty samples. The composition of the samples was determined using the concentration triangle. As a result, we got the following kind of triple Tl_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ system (Fig. 1). Seven segment $Tl_5In(MoO_4)_4$–$Tl_8Hf(MoO_4)_6$, $TlIn(MoO_4)_2$–$Tl_8Hf(MoO_4)_6$, $TlIn(MoO_4)_2$–$Tl_2Hf(MoO_4)_3$, $TlIn(MoO_4)_2$–$Hf(MoO_4)_2$, $TlIn(MoO_4)_2$–$Tl_5InHf(MoO_4)_6$, $Tl_5InHf(MoO_4)_6$–$Tl_8Hf(MoO_4)_6$, and $Tl_5InHf(MoO_4)_6$–$Tl_2Hf(MoO_4)_3$ divide the Tl_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ system into seven subsystems.

$Tl_5InHf(MoO_4)_6$ was synthesized from simple molybdates of thallium, indium, and hafnium at a molar ratio of the corresponding starting components of 5:1:2. Annealing was carried out in the temperature range of 723–853 K for 80 h. $Tl_5InHf(MoO_4)_6$ is a white powder. The synthesis of triple molybdate was carried out according to the following reaction:

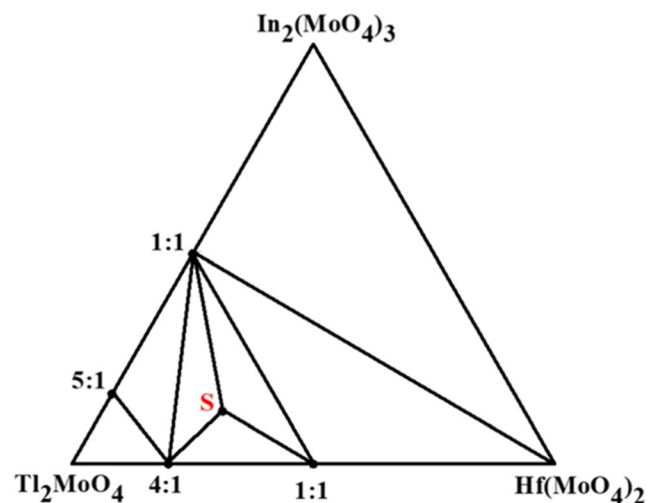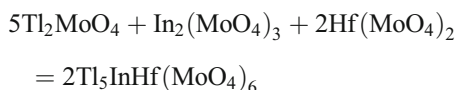Fig. 1 Phase equilibria of the Tl_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ system in the subsolidus region 803–853 K, where S is $Tl_5InHf(MoO_4)_6$

Table 1 Main parameters of processing and refinement of the $Tl_5InHf(MoO_4)_6$ sample

Compound	$Tl_5InHf(MoO_4)_6$
Sp.Gr.	$R\bar{3}c$
a, Å	10.63893 (5)
c, Å	38.1447 (3)
V, Å^3	3739.04 (4)
Z	6
2θ-interval, °	5–140
R_{wp} (%)	4.59
R_p (%)	4.70
R_{exp} (%)	3.04
χ^2	1.51
R_B (%)	3.10

$$5Tl_2MoO_4 + In_2(MoO_4)_3 + 2Hf(MoO_4)_2$$
$$= 2Tl_5InHf(MoO_4)_6$$

Molybdate is insoluble in water and organic solvents but dissolves when heated in HCl, H_2SO_4, and HNO_3.

Characterization methods

PXRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer (Bruker, Berlin, Germany) with Cu-Kα radiation ($\lambda = 1.5418$ A°) at room temperature. The scanning range is between 5 and 100° with a scanning width of 0.02 and a rate of 0.1 s^{-1}.

The variable counting time (VCT) scheme was used to collect the diffraction data of $Tl_5InHf(MoO_4)_6$ for Rietveld analysis. The measurement time was systematically increased towards higher 2θ angles, leading to drastically improved data quality [53, 54]. To collect the X-ray data using VCT scheme, five ranges were generated on the diffraction pattern: 5–32.0° (exposure per point: 0.5 s; step: 0.0069°), 32.0–59.0° (exposure per point: 1 s; step: 0.0069°), 59.0–86.0° (exposure per point: 2 s; step: 0.0069°), 86.0–113.0° (exposure per point: 4 s; step: 0.0069°), and 113.0–140° (exposure per point: 8 s; step: 0.0069°). Total experimental time was equal to ~ 19 h. The esd's $\sigma(I_i)$ of all points on patterns were calculated using intensities I_i: $\sigma(I_i) = I_i^{1/2}$. The intensities and obtained esd's were further normalized, taking into account actual value of exposition time, and saved in xye-type file. So transformed powder pattern has usual view in whole 2θ range 5–140°, but all high-angle points have small esd's.

Differential scanning calorimetry (DSC) was carried out on a NETZSCH STA 449 F1 TG/DSC/DTA (Jupiter) thermal analyzer. The sample charge was 18 mg, and the rate of temperature rise was 10 K/min in the Ar atmosphere. Sample was placed into platinum crucible with lid. The relative error of weight change determination was $\Delta = 1\%$, and that of heat effects was $\Delta = 2$–
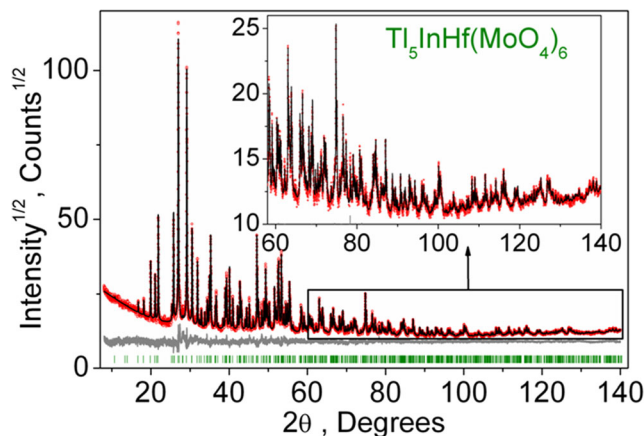

Fig. 2 Difference Rietveld plot of $Tl_5InHf(MoO_4)_6$

5%. The differential thermal analysis (DTA) curves were calculated using a specially developed program from Netzsch.

The electrical conductivity was measured using a two-contact impedance spectroscopy method with heating and cooling in the frequency range of $1–10^6$ Hz (impedance meter "Z-1500 J"). Ceramic disks for dielectric investigations were prepared by pressing the powders at 100 bar, and sintering at 773 K for 2 h. The disks were 10 mm in diameter and 1.5–2-mm thick. For making electrodes, large surfaces of the disks were covered with colloid platinum, followed by annealing at about 773 K for 1 h.

The ionic conductivity σ was calculated using the formula

$$\sigma = \frac{4T}{\pi D^2 R} \tag{1}$$

where T is the thickness of the ceramic in cm, D is diameter in cm, and R is ohmic resistance in Ω.

The geometric-to-X-ray density ratio was used as the criterion for evaluation of the density of the resulting ceramics. The geometric density was calculated by dividing the weight of the sintered sample by its volume estimated from geometric dimensions. The size of the preliminarily polished sample was measured with an accuracy of ± 0.01 mm. The theoretical density was calculated by the equation,

$$\rho_{x-ray} = 1.66MZ/V \tag{2}$$

where M is the molecular weight of the formula unit of a substance, Z is the number of formula units, and V is the unit cell volume.

Results and discussion

Crystal structure

It was found that the $Tl_5InHf(MoO_4)_6$ is isostructural to the $K_5InHf(MoO_4)_6$ compound, the structure of which was

Table 2 Fractional atomic coordinates and isotropic displacement parameters (Å^2) of Tl$_5$InHf(MoO$_4$)$_6$

Atom	x	y	z	B_{iso}	Occ.
Mo	0.35048 (15)	0.05613 (14)	0.03328 (3)	1.54 (7)	1
Hf1	0	0	0	1.42 (9)	0.325 (12)
In1	0	0	0	1.42 (9)	0.675 (12)
Hf2	0	0	0.25	1.20 (8)	0.675 (12)
In2	0	0	0.25	1.20 (8)	0.325 (12)
Tl1	0	0	0.35503 (3)	3.28 (7)	1
Tl2	0.38767 (12)	0	0.25	4.14 (8)	1
O1	0.1699 (10)	0.0340 (11)	0.0320 (3)	1.95 (12)	1
O2	0.4828 (9)	0.2334 (10)	0.0493 (2)	1.95 (12)	1
O3	0.3549 (11)	−0.0789 (10)	0.0494 (3)	1.95 (12)	1
O4	0.4011 (10)	0.0507 (10)	−0.0061 (2)	1.95 (12)	1

established in [46]. Therefore, the atomic coordinates of the latter were taken as a starting model for the Rietveld refinement using the TOPAS 4.2 program [55]. The ratio of Hf/In in two sites were refined taking into account that sum of occupancies are equal to 1 in each site. In order to reduce number of refined parameters, only one thermal parameter was refined for all O atoms. Refinement was stable and gave low R-factors (Table 1, Fig. 2).

Coordinates of atoms and main bond lengths are in Table 2 and Table 3 respectively. The comparison of the Tl$_5$InHf(MoO$_4$)$_6$ unit cell parameters obtained by us (Table 1) with the data from [46] ($a = 10.564(1)$ Å, $c = 37.632(4)$ Å, $V = 3637.0(6)$ Å^3) shows their good agreement. The Mo–O bond lengths are in the range of 1.58(1)–1.82 (1) Å, the (Hf/In)–O lengths in the range of 2.06 (1)–2.14(1) Å, and the Tl–O lengths are in the range of 2.81(1)–3.04 (1) Å. The sum of the valence forces are equal: BVS(Mo) = 7(1); BVS(In1/Hf1) = 4.0 (3); BVS (In2/Hf2) = 3.2(3); BVS (Tl1) = 0.9(1); BVS(Tl2) = 0.6 (1). The crystallographic data are deposited in Cambridge Crystallographic Data Centre (CSD # 1995678). The data can be downloaded from the site (www.ccdc.cam.ac.uk/data_request/cif).

The crystal structure of Tl$_5$InHf(MoO$_4$)$_6$ is shown in Fig. 3. The structure is a three-dimensional framework consisting of alternating (Hf,In)O$_6$-octahedra connected by MoO$_4$-tetrahedra. Each octahedron has common vertices with tetrahedra. The atoms arranged in this way form channels extended along with the a and b axes, in which thallium atoms are located.

Thermal and electrical properties

Figure 4 shows the results of combined TG/DSC analysis of Tl$_5$InHf(MoO$_4$)$_6$ from 380 K temperature to 960 K. DSC heating curve of Tl$_5$InHf(MoO$_4$)$_6$ clearly shows the endothermic effects corresponding to the first-order phase transition at ($T = 837$ K, $\Delta H = -2.27$ J/g) and incongruently melting of the

Table 3 Main bond lengths (Å) of Tl$_5$InHf(MoO$_4$)$_6$

Mo–O1	1.816 (5)	Tl1–O3^{ii}	2.806 (9)
Mo–O2	1.805 (9)	Tl1–O4^{i}	2.980 (8)
Mo–O3	1.585 (9)	Tl2–O2^{i}	3.134 (6)
Mo–O4	1.607 (8)	Tl2–O3^{iii}	3.103 (8)
(Hf1/In1)–O1	2.057 (10)	Tl2–O4^{ii}	3.037 (8)
(Hf2/In2)–O2^{i}	2.136 (9)		

Symmetry codes: (i) $-x + 2/3, -y + 1/3, -z + 1/3$; (ii) $-x + y + 2/3, -x + 1/3, z + 1/3$; (iii) $y + 2/3, -x + y + 1/3, -z + 1/3$
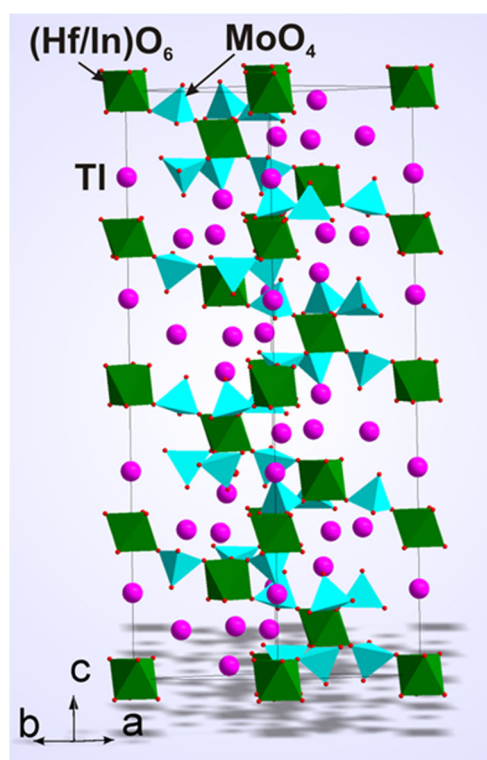
Fig. 3 Projection of the Tl$_5$InHf(MoO$_4$)$_6$ structure on (001) plane

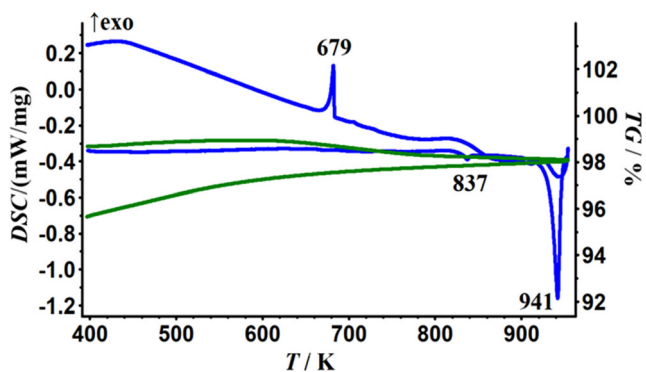**Fig. 4** DSC curve of the $Tl_5InHf(MoO_4)_6$

molybdate at ($T = 941$ K, $\Delta H = -47.89$ J/g). Similar transitions were detected in $K_5InHf(MoO_4)_6$ isostructural compound [47]. When cooling on the DSC curve, we see exoeffects, related to the crystallization of the compounds into which the molybdate $Tl_5InHf(MoO_4)_6$ is decomposed. During the heating (green curve above) and cooling (green curve below), the TG is very clear and there is no loss in weight. This indicates the complete absence of volatile impurities.

Figure 5 shows the temperature dependences of the conductivity on the versus reciprocal temperature obtained by heating and cooling ceramics at different frequencies (from 100 Hz to 100 kHz). The density of ceramics was 79%. In the region of 800 K, an anomaly of conductivity is observed due to a phase transition. The temperature hysteresis, which is characteristic of, which is accompanied by an increase in conductivity, is clearly visible. The transition temperature corresponds to the differential thermal analysis (Fig. 4).

Figure 6 shows the complex impedance (imaginary -Z'' versus real Z') plots at different temperatures ranging from 473 to 853 K under air for the $Tl_5InHf(MoO_4)_6$ sample. The diagrams at temperatures up to 573 K show the patterns of a deformed semicircular arc and a low-frequency
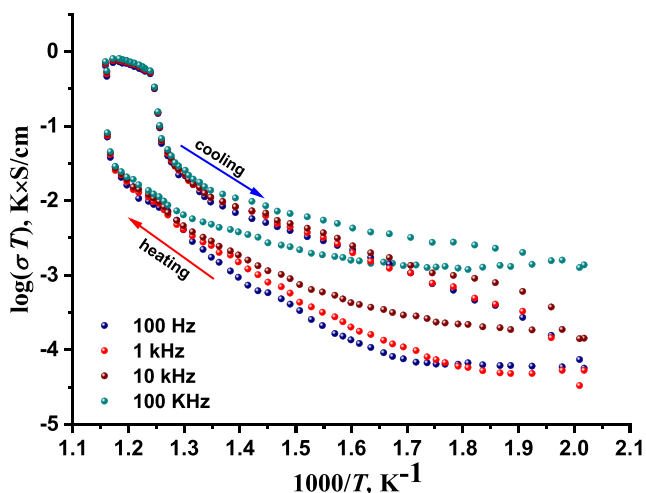

Fig. 5 Variation of conductivity σT (K S cm^{-1}) as a function of $1000/T$ (K^{-1}) for $Tl_5InHf(MoO_4)_6$ sample at 100-Hz to 100-kHz frequencies (heating and cooling)

tail. The appearance of the tail at lower frequency may be owing to the polarized phenomena associated with the thallium-ion conduction across the electrolyte/electrode boundary. Graphs obtained in the form of deformed semicircular arcs show the presence of two overlapping semicircles with reaching zero on Z'-axis and Z''-axis in the high-frequency region (Fig. 6). For a high-frequency semicircle, the capacitance values are of the order of 10^{-10} F, which can be considered as the average value of capacitance for bulk and grain-boundary conductivity (10^{-12} and 10^{-8} F). That is, the semicircle is associated both with contributions of the bulk and grain boundary. The resistance of the grain boundaries decreases with increasing temperature and, accordingly, the conductivity increases. This behavior is characteristic of solid electrolytes.

As can be seen from Fig. 7, the dependence of the electrical conductivity of $Tl_5InHf(MoO_4)_6$ ceramics with an increase in frequency does not substantially change up to a certain value, starting from which it grows exponentially, which, apparently, corresponds to the intergrain contribution to the total conductivity. The total conductivity of the samples increases with increasing temperature, and the boundary frequency shifts to the high-frequency region. The increase in conductivity in the entire studied temperature range at low frequencies is due to an increase in the concentration of the main charge carriers.

In accordance with the type of hodographs of impedance was select an equivalent circuit using the method of impedance spectroscopy. The shift of the semicircle centers on the hodograph below the abscissa indicates that the system cannot be described by a combination of pure resistances and capacities, but it is necessary to replace all capacities with modified frequency-dependent elements (constant phase element—CPE). In Fig. 8 shows an equivalent circuit that describes well the processes taking place in the system. The impedance of ceramics is contributed by the bulk of ceramic grains, grain boundaries, and electrode-electrolyte interface. The impedance of the electrochemical cell $Pt|Tl_5InHf(MoO_4)_6|Pt$ s the sum of the grain bulk resistance R_b with constant phase element CPE_b connected in parallel, the grain boundary resistance R_{gb} with constant phase element CPE_{gb} connected in parallel, and the electrode impedance Z_{el}.

From the analysis of complex impedance was obtained temperature dependence of the DC conductivity of $Tl_5InHf(MoO_4)_6$ molybdate. In Fig. 9, for clarity, the dependence is presented in Arrhenius coordinates.

The graph observes two linear sections with slopes. Dependency is well described Arrhenius–Frenkel law, i.e., processes are thermal activation.

The activation energy was calculated using the following formula
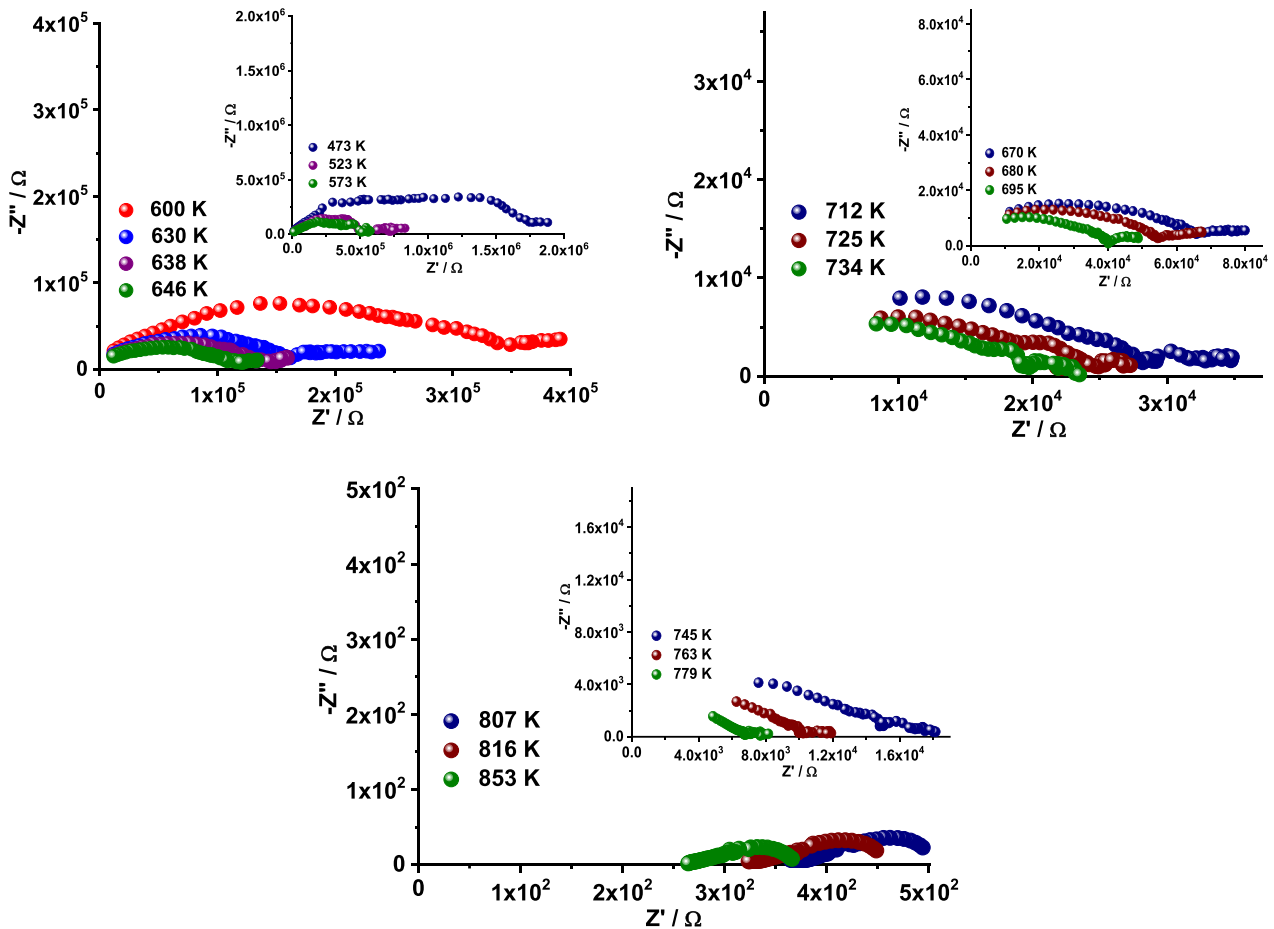
$$\sigma dc = \sigma 0 \exp(-Ea/k_bT) \tag{3}$$
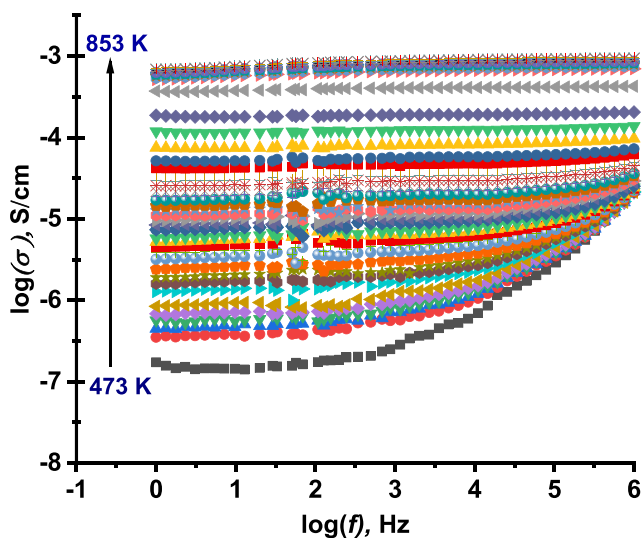
Fig. 6 Impedance spectra of $Tl_5InHf(MoO_4)_6$

In this relation, E_a is the activation energy, k_b is the Boltzmann constant, and σ_0 is a constant.

Above the phase transition, the total ionic conductivity of the obtained compound reaches 9.8×10^{-4} S cm^{-1} (853 K) and the activation energy is 0.85 eV. This value is compatible with the cationic conductivity mechanism. Based on the structure of the compound presented in this article, the ionic conductivity observed in $Tl_5InHf(MoO_4)_6$ is most probably due to monovalent Tl^+ cation anisotropic mobility. The alkali metal
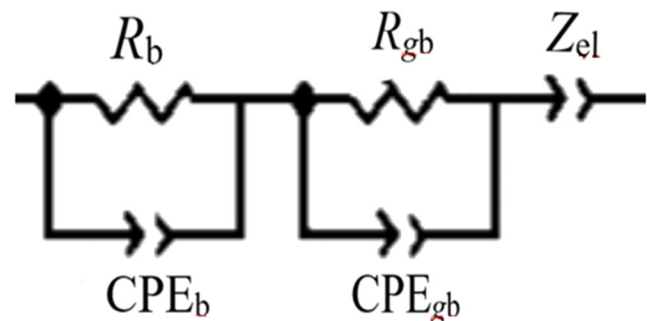

Fig. 7 Dependence of the conductivity of $Tl_5InHf(MoO_4)_6$ on frequency and temperature

Fig. 8 Equivalent circuit used for calculating the impedance spectra of $Tl_5InHf(MoO_4)_6$
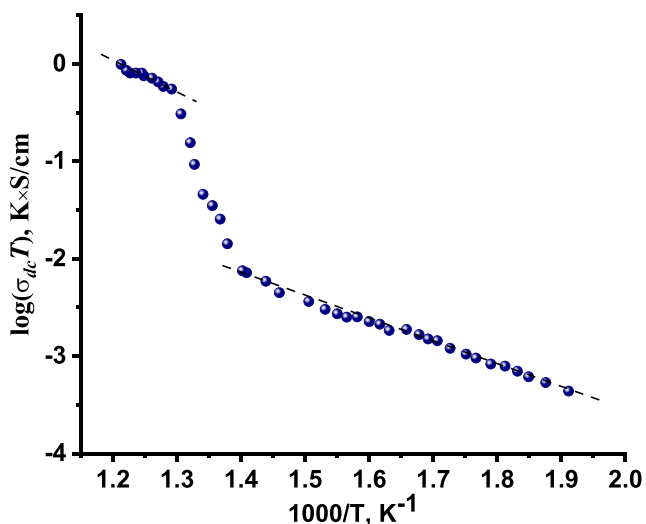
Fig. 9 Plot of $\log(\sigma_{dc}T)$ versus $1000/T$ for $Tl_5InHf(MoO_4)_6$ compound

substitution in the group of $M_5RA(MoO_4)_6$ (where M = K, Rb, Cs, R = lanthanide trivalent ion, Al^{3+}, Cr^{3+}, Fe^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, Bi^{3+}, A = Zr^{4+} or Hf^{4+}) compounds for thallium did not lead to an increase in conductivity. Conductivity of $Tl_5InHf(MoO_4)_6$ commensurate with the conductivity of $Cs_5AlZr(MoO_4)_6$ (σ_{total} = 0.8×10^{-4} S cm^{-1} at 673 K), $Cs_5BiZr(MoO_4)_6$ (σ_{total} = 0.7×10^{-4} S cm^{-1} at 673 K), $Cs_5FeZr(MoO_4)_6$ (σ_{total} = 1.2×10^{-4} S cm^{-1} at 673 K), $Cs_5AlZr(MoO_4)_6$ (σ_{total} = 0.8×10^{-4} S cm^{-1} at 673 K) [56], $Rb_5CeHf(MoO_4)_6$ (σ_{total} = 1.7×10^{-3} S cm^{-1} at 723 K), $Rb_5YbHf(MoO_4)_6$ (σ_{total} = 1.7×10^{-3} S cm^{-1} at 723 K) [48], $K_5RHf(MoO_4)_6$ (R = In, Sc) (σ_{total} = 1.1×10^{-3} S cm^{-1} at 900 K) [33, 47], and $K_5RZr(MoO_4)_6$ (R = Al, Cr, Fe, In, Sc) (σ_{total} ~ 10^{-3} S cm^{-1} at 723–873 K) [15] compounds. It should be noted that the conductivity is close to those of the NASICON-type conductors and comparable or even better than that of ionic conductors, such as molybdates with lyonsite-type structure. For comparison, the conductivity for $LiNbFe(PO_4)_3$ (σ_{total} = 6.6×10^{-6} S cm^{-1}), $LiNbFe(PO_4)_3$ (σ_{total} = 6.6×10^{-6} S cm^{-1}), and $LiZr_2(PO_4)_3$ (σ_{total} = 5×10^{-4} S cm^{-1}) at 573 K [57–60]. In the system $Li_{2+x}Mg_{2(1-x)}Fe_x(MoO_4)_3$ with lyonsite-type structure, conductivity ranges at 573 K from 1.1×10^{-7} for $Li_2Mg_2(MoO_4)_3$ to 6.6×10^{-7} S cm^{-1} for $Li_3Fe(MoO_4)_3$ [10].

Conclusions

The phase relations of the ternary system Tl_2MoO_4–$In_2(MoO_4)_3$–$Hf(MoO_4)_2$ were studied and a new molybdate $Tl_5InHf(MoO_4)_6$ was discovered. The study of a new thallium indium hafnium molybdate using PXRD showed that the compound has trigonal space group $R3c$: a = 10.63893 (5) Å, c = 38.1447(3) Å; V = 3739.04 (4) $Å^3$, Z = 6. It was established in the work that the structure is a framework

consisting of alternating mixed $(Hf,In)O_6$ octahedra connected by MoO_4 tetrahedra. Each octahedron has common vertices with tetrahedrons. The atoms arranged in this way form channels extended along with the a and b axes, in which thallium atoms are located. The electrical properties of $Tl_5InHf(MoO_4)_6$ sample with relative density of 79% were studied using complex impedance spectroscopy. The Arrhenius plots of $Tl_5InHf(MoO_4)_6$ show a jump in conductivity. Above 853 K, the electrical conductivity reaches ~ 10^{-3} S·cm^{-1}. The transition temperature correlates with thermal analysis. It should be noted that the conductivity of the compound $K_5RHf(MoO_4)_6$ (R = In, Sc) [33, 47] almost did not change its value when potassium was replaced by thallium. $Tl_5InHf(MoO_4)_6$ can be considered as a promising solid electrolyte due to high electrical conductivity.

References

1. Lv DD, Zhang DF, Pu XP, Gao MC, Ma HY, Li HY, Zhang TT (2015) Combustion synthesis of $Li_8Bi_2(MoO_4)_7$ and photocatalytic properties. Mater Lett 144:150–152. https://doi.org/10.1016/j.matlet.2015.01.062
2. Tsyrenova GD, Solodovnikov SF, Khaikina EG, Khobrakova ET, Bazarova ZG, Solodovnikova ZA (2004) Phase formation in the systems Ag_2MoO_4-MO-MoO_3(M = Ca, Sr, Ba, Pb, Cd, Ni, Co, Mn) and crystal structures of $Ag_2M_2(MoO_4)_3$(M = Co, Mn). J Solid State Chem 177:2158–2167. https://doi.org/10.1016/j.jssc.2004.01.002
3. Nasri R, Larbi T, Amlouk M, Zid MF (2018) Investigation of the physical properties of $K_2Co_2(MoO_4)_3$ for photocatalytic application. J Mater Sci Mater Electron 29:18372–18379. https://doi.org/10.1007/s10854-018-9951-x
4. Lu Y, Li Y, Huang Y, Chen C, Cai P, Seo HJ (2015) A visible-light-driven photocatalyst of NASICON $Li_2Ni_2(MoO_4)_3$ nanoparticles. J Am Ceram Soc 98:2165–2169. https://doi.org/10.1111/jace.13612
5. Loiko P, Vilejshikova EV, Volokitina AA, Trifonov VA, Serres JM, Mateos X, Kuleshov NV, Yumashev KV, Baranov AV, Pavlyuk AA (2017) Growth, structure, Raman spectra and luminescence of orthorombic $Li_2Mg_2(MoO_4)_3$ crystals doped with Eu^{3+} and Ce^{3+} ions. J Lumin 188:154–161. https://doi.org/10.1016/j.jlumin.2017.04.021
6. Lu D, Gong X, Chen Y, Huang J, Lin Y, Luo Z, Huang Y (2018) Synthesis and photoluminescence characteristics of the $LiGd_3(MoO_4)_5$: Eu^{3+} red phosphor with high color purity and brightness. Opt Mater Express 8:259–269. https://doi.org/10.1364/OME.8.000259
7. Wang GQ, Li LY, Feng YN, Yu H, Zheng XH (2018) Tb^{3+} and Yb^{3+}-doped novel $KBaLu(MoO_4)_3$ crystals with disordered chained structure showing down- and upconversion luminescence. CrystEngComm 20:3657–3665. https://doi.org/10.1039/C8CE00461G
8. Ines E, Zid MF, Driss A (2013) Synthesis, crystal structure and electrical properties of the molybdenum oxide $Na_{1.92}Mg_{2.04}Mo_3O_{12}$. J Crystallogr 2013:1–6. https://doi.org/10.1155/2013/146567

9. Nasri R, Marzouki R, Georges S, Obbade S, Zid MF (2018) Synthesis, sintering, electrical properties and sodium migration pathways of new lyonsite $Na_2Co_2(MoO_4)_3$. Turk J Chem 42:1–31. https://doi.org/10.3906/kim-1801-89

10. Sebastian L, Piffard Y, Shukla AK, Taulelle F, Gopalakrishnan J (2003) Synthesis, structure and lithium-ion conductivity of $Li_{2−2x}Mg_{2+x}(MoO_4)_3$ and $Li_3M(MoO_4)_3$ (M = Cr, Fe). J Mater Chem 13:1797–1802. https://doi.org/10.1039/B301189E

11. Prabaharan SRS, Fauzi A, Michael MS, Begam KM (2004) New NASICON-type $Li_2Ni_2(MoO_4)_3$ as a positive electrode material for rechargeable lithium batteries. Solid State Ionics 17:157–165. https://doi.org/10.1016/j.ssi.2004.05.001

12. Begam K, Selladurai S (2004) Synthesis and redox behavior of a new polyanion compound, $Li_2Co_2(MoO_4)_3$, as 4 V class positive electrode material for lithium batteries. Ionics 10:77–83. https://doi.org/10.1007/BF02410310

13. Zapart MB, Zapart W, Maczka M (2016) Complex ferroelastic domain patterns of $K_{1−x}Rb_xSc(MoO_4)_2$ crystals. Ferroelectrics 1:34–41. https://doi.org/10.1080/00150193.2016.1160729

14. Zapart W, Zapart MB (2013) Phase transitions in ferroelastic $RbIn(MoO_4)_2$ at 163 and 143 K. Ferroelectrics 1:116–120. https://doi.org/10.1080/00150193.2013.839289

15. Bazarova JG, Logvinova AV, Bazarov BG, Tushinova YL, Dorzhieva SG, Temuujin J (2018) Synthesis of new triple molybdates $K_5RZr(MoO_4)_6$ (R = Al, Cr, Fe, In, Sc) in the K_2MoO_4–$R_2(MoO_4)_3$–$Zr(MoO_4)_2$ systems, their structure and electrical properties. J Alloys Compd 741:834–839. https://doi.org/10.1016/j.jallcom.2018.01.208

16. Yudin VN, Zolotova ES, Solodovnikov SF, Solodovnikova ZA, Korolkov IY, Stefanovich SY, Kuchumo BM (2019) Synthesis, structure, and conductivity of alluaudite-related phases in the Na_2MoO_4–Cs_2MoO_4–$CoMoO_4$ system. Eur J Inorg Chem:277–286. https://doi.org/10.1002/ejic.201801307

17. Savina AA, Solodovnikov SF, Belov DA, Solodovnikova ZA, Stefanovich SY, Lazoryakd BI, Khaikina EG (2017) New alluaudite-related triple molybdates $Na_{25}Cs_8R_5(MoO_4)_{24}$ (R = Sc, In): synthesis, crystal structures and properties. New J Chem 41:5450–5457. https://doi.org/10.1039/C7NJ00202E

18. Kotova IY, Solodovnikov SF, Solodovnikova ZA, Belov DA, Stefanovich SY, Savina AA, Khaikina EG (2016) New series of triple molybdates $AgA_3R(MoO_4)_5$ (A = Mg, R = Cr, Fe; A = Mn, R = Al, Cr, Fe, Sc, In) with framework structures and mobile silver ion sublattices. J Solid State Chem 238:121–128. https://doi.org/10.1016/j.jssc.2016.03.003

19. Xue J, Li H, Noh HM, Choi BC, Park SH, Jeong JH, Kim JH (2018) Molybdenum substitution induced luminescence enhancement in $Gd_2W_{1−x}Mo_xO_6$:Eu^{3+} phosphors for near ultraviolet based solid-state lighting. J Lumin 202:97–106. https://doi.org/10.1016/j.jlumin.2018.05.033

20. Solodovnikov SF, Khaikina EG, Solodovnikova ZA, Kadyrova YM, Khal'baeva KM, Zolotova ES (2007) New families of lithium-containing triple molybdates and the stabilizing role of lithium in their structure formation. Dokl Chem 416:207–212. https://doi.org/10.1134/S0012500807090029

21. Khaikina EG, Bazarova ZG, Solodovnikov SF, Klevtsova RF (2011) Troynye molibdaty kak osnova novykh perspektivnykh slozhnooksidnykh materialov. Eng Ecol 1:48–49

22. Morozov VA, Lazoryak BI, Smirnov VA, Mikhailin VV, Basovich OM, Khaikina EG (2001) Crystal structures and luminescence properties of ternary molybdates $LiMNd_2(MoO_4)_4$ (M = K, Rb, Tl). Russ J Inorg Chem 46:873–879

23. Zhou L, Du P (2019) Solegel synthesis of $CaLa_2(MoO_4)_4$:$2xSm^{3+}$ microparticles: a red-emitting phosphor with splendid thermal stability for near-ultravioletbased white light-emitting diodes. Appl Phys A Mater Sci Process 125:282–285

24. Lim CS, Aleksandrovsky AS, Molokeev MS, Oreshonkov AS, Ikonnikov DA, Atuchin VV (2016) Triple molybdate scheelite-type upconversionphosphor $NaCaLa(MoO_4)_3$:Er^{3+}/Yb^{3+}: structural and spectroscopic properties. Dalton Trans 45:15541–15551. https://doi.org/10.1039/c6dt02378a

25. Lim CS, Aleksandrovsky AS, Molokeev MS, Oreshonkov AS, Atuchin VV (2017) Microwave synthesis and spectroscopic properties of ternary scheelite-type molybdate phosphors $NaSrLa(MoO_4)O_3$:Er^{3+}, Yb^{3+}. J Alloys Compd 713:156–163

26. Hong HJ (1976) Crystal-structures and crystal-chemistry in system $Na_{1+x}Zr_2Si_xP_{3−x}O_{12}$. Mater Res Bull 11:173–182. https://doi.org/10.1016/0025-5408(76)90073-8

27. Velikodny YuA (1975) Double molybdates and tungstates of alkali metals with indium and scandium Dissertation, Moscow

28. Lazoryak BI, Efremov VA (1987) Phases of $Na_{2x}Zn_2Sc_{2(1−x)}$-II$(MoO_4)_3$, $Na_{2x}Cd_2Sc_{2(1−x)}$-II$(MoO_4)_3$, $Na_{2x}Mg_2Sc_{2(1−x)}$-II$(MoO_4)_3$ changed composition. Zh Neorg Khim 32:652–656

29. Kozhevnikova NM, Mokhosoev MV (1992) Triple molybdates. Zh Neorg Khim 37:2395–2401

30. Kotova IY, Belov DA, Stefanovich SY (2011) $Ag_{1−x}Mg_{1−x}R_{1+x}(MoO_4)_3$ Ag^+-conducting NASICON-like phases, where R = Al or Sc and $0 \leq x \leq 0.5$. Russ J Inorg Chem 56:1259–1263. https://doi.org/10.1134/S0036023611080122

31. Ines E, Samuel G, Youssef BS, Abderrahmen G, Zid MF, Boughazala H (2015) Synthesis, crystal structure, sintering and electrical properties of a new alluaudite-like triple molybdate $K_{0.13}Na_{3.87}MgMo_3O_{12}$. RSC Adv 5:38918–38925. https://doi.org/10.1039/c5ra02276b

32. Bazarova JG, Tushinova YL, Bazarov BG, Oyun BE, Angarhayev JD (2018) Phase equilibrium in the systems Cs_2MoO_4–$R_2(MoO_4)_3$–$Hf(MoO_4)_2$ (R = Al, Cr, Fe, Bi, La–Lu). Izvestiya Vuzov-Prikladnaya Khimiya i Biotekhnologiya 8:19–28. https://doi.org/10.21285/2227-2925-2018-8-2-19-28

33. Grossman VG, Bazarova JG, Molokeev MS, Bazarov BG (2020) New triple molybdate $K_5ScHf(MoO_4)_6$: synthesis, properties, structure and phase equilibria in the M_2MoO_4–$Sc_2(MoO_4)_3$–$Hf(MoO_4)_2$ (M = Li, K) systems. J Solid State Chem 283:121143. https://doi.org/10.1016/j.jssc.2019.121143

34. Dorzhieva SG, Bazarov BG, Bazarova JG (2019) New molybdates in the Rb_2MoO_4–(M_2MoO_4)–M-IZr$(MoO_4)_2$ (M-I = Na, K) systems as promising ion-conducting materials. Letters on Materials 9:17–21. https://doi.org/10.22226/2410-3535-2019-1-17-21

35. Logvinova AV, Bazarov BG, Tushinova YL, Bazarova JG (2017) Phase relations in the K_2MoO_4–$Ln_2(MoO_4)_3$–$Zr(MoO_4)_2$ (Ln = La–Lu, Y) systems. Inorg Mater 53:1286–1292. https://doi.org/10.1134/S0020168517120081

36. Grossman VG, Bazarov BG, Bazarova TT, Glinskaya LA, Bazarova JG, Temuujin J (2017) Phase equilibria in the Tl_2MoO_4–$Ho_2(MoO_4)_3$–$Zr(MoO_4)_2$ system and the crystal structure of $Ho_2Zr_3(MoO_4)_7$ and $TlHoZr_{0.5}(MoO_4)_3$. J Ceram Process Res 18:875–881

37. Gongorova LI, Bazarov BG, Chimitova OD, Anshits AG, Vereschagina TA, Klevtsova RF, Glinskaya LA, Bazarova ZG (2012) Crystal structure of a new ternary molybdate $Rb_5CeZr(MoO_4)_6$. J Struct Chem 53:329–333. https://doi.org/10.1134/S0022476612020175

38. Chimitova OD, Bazarov BG, Klevtsova RF, Anshits AG, Fedorov KN, Dubentsov AV, Vereshchagina TA, Tushinova YL, Glinskaya LA, Bazarova ZG, Gongorova LI (2010) Crystal structure of triple molybdate in the Rb_2MoO_4–$Nd_2(MoO_4)_3$–$Zr(MoO_4)_2$ system. J Struct Chem 51:173–176. https://doi.org/10.1007/s10947-010-0025-z

39. Namsaraeva TV, Bazarov BG, Klevtsova RF, Glinskaya LA, Fedorov KN, Bazarova ZG (2010) Subsolidus phase equilibrium in Cs_2MoO_4–$Al_2(MoO_4)_3$–$Zr(MoO_4)_2$ system and crystal structure

of new ternary molybdate Cs(AlZr$_{0.5}$)(MoO$_4$)$_3$. Russ J Inorg Chem 55:209–214. https://doi.org/10.1134/S0036023610020129

40. Bazarov BG, Namsaraeva TV, Klevtsova RF, Anshits AG, Vereshchagina TA, Kurbatov RV, Glinskaya LA, Fedorov KN, Bazarova ZG (2008) Phase equilibrium in the Cs$_2$MoO$_4$–Bi$_2$(MoO$_4$)$_3$–Zn(MoO$_4$)$_2$ system and the crystal structure of new triple molybdate Cs$_5$BiZr(MoO$_4$)$_6$. Russ J Inorg Chem 53:1484–1488. https://doi.org/10.1134/S0036023608090222

41. Bazarov BG, Chimitova OD, Bazarova TT, Arkkhincheeva SI, Bazarova ZG (2008) Phase relations in the systems M_2MoO$_4$–Cr$_2$(MoO$_4$)$_3$–Zr(MoO$_4$)$_2$ (M = Li, Na, or Rb). Russ J Inorg Chem 53:959–961. https://doi.org/10.1134/S0036023608060247

42. Bazarov BG, Chimitova OD, Klevtsova RF, Tushinova YL, Glinskaya LA, Bazarova ZG (2008) Crystal structure of a new ternary molybdate in the Rb$_2$MoO$_4$–Eu$_2$(MoO$_4$)$_3$–Hf(MoO$_4$)$_2$ system. J Struct Chem 49:53–57. https://doi.org/10.1007/s10947-008-0008-5

43. Chimitova OD, Bazarov BG, Klevtsova RF, Fedorov KN, Glinskaya LA, Kuznetsov MV, Bazarova ZG (2007) Synthesis, crystal structure, and electrical properties of the new ternary molybdate Rb$_5$NdHf(MoO$_4$)$_6$. Russ Chem Bull 56:2135–2139. https://doi.org/10.1007/s11172-007-0337-0

44. Romanova EY, Bazarov BG, Klevtsova RF, Glinskaya LA, Tushinova YL, Fedorov KN, Bazarova ZG (2007) Phase formation in the K$_2$MoO$_4$–Lu$_2$(MoO$_4$)$_3$–Hf(MoO$_4$)$_2$ system and the structural study of triple molybdate K$_5$LuHf(MoO$_4$)$_6$. Russ J Inorg Chem 52:749–752. https://doi.org/10.1134/S0036023607050154

45. Bazarov BG, Klevtsova RF, Chimitova OD, Glinskaya LA, Fedorov KN, Tushinova YL, Bazarova ZG (2006) Phase formation in the Rb$_2$MoO$_4$–Er$_2$(MoO$_4$)$_3$–Hf(MoO$_4$)$_2$ system and the crystal structure of new triple molybdate Rb$_5$ErHf(MoO$_4$)$_6$. Russ J Inorg Chem 51:800–804. https://doi.org/10.1134/S0036023606050196

46. Bazarov BG, Klevtsova RF, Bazarova TT, Glinskaya LA, Fedorov KN, Bazarova ZG (2005) Synthesis and crystal structure of triple molybdate K$_5$InHf(MoO$_4$)$_6$. Russ J Inorg Chem 50:1146–1149

47. Grossman VG, Bazarov BG, Bazarova JG (2019) K$_5$InHf(MoO$_4$)$_6$: a solid state conductor. IOP Conf Ser: Earth Environ Sci 320: 012050

48. Chimitova OD, Bazarov BG, Fedorov KN, Bazarova ZG (2008) Electrical properties of triple molybdates Rb$_5$LnHf(MoO$_4$)$_6$. Russ J Appl Chem 81:2043–2044

49. Sul'timova LB, Burdakova IB, Khaikina EG, Bazarova ZG (2000) Tl$_2$MoO$_4$–R_2(MoO$_4$)$_3$ (R = In, Sc) systems. Russ J Inorg Chem 45: 1900–1904

50. Pleskov MY, Morozov VA, Lazoryak BI, Zhizhin MG, Burdakova IB, Khal'baeva KM, Tsyrenova GD, Khaikina EG (2005) Structures of double molybdates TlR(MoO$_4$)$_2$ (R = In, Sc, Fe, Cr, Al). Russ J Inorg Chem 50:604–614

51. Bazarov BG, Klevtsova RF, Bazarova TT, Glinskaya LA, Fedorov KN, Bazarova ZG, Chimitova OD (2006) Systems Tl$_2$MoO$_4$–E(MoO$_4$)$_2$, where E = Zr or Hf, and the crystal structure of Tl$_8$Hf(MoO$_4$)$_6$. Russ J Inorg Chem 51:794–799. https://doi.org/10.1134/S0036023606050184

52. Tushinova YuL, Bazarova JG, Arkhincheeva SI (2002) Phase equilibria in systems R_2(MoO$_4$)$_3$–Zr(MoO$_4$)$_2$, Vsesos. scientific reading from int. participation, dedicated. 70th birthday of member USSR Academy of Sciences M.V. Mokhosoeva. Publishing House of the BSC SB RAS. 90–91

53. Madsen I, Hill RJ (1992) Variable step-counting times for Rietveld analysis or getting the most out of your experiment time. Adv X-ray Anal 35:39–47

54. Madsen IC, Hill RJ (1994) Collection and analysis of powder diffraction data with near-constant counting statistics. J Appl Crystallogr 27:385–392

55. Bruker AXS (2008) TOPAS V4: general profile and structure analysis software for powder diffraction data. – user's manual. Bruker AXS. Karlsruhe. Germany

56. Namsaraeva TV (2010) Phase equilibrium, crystalline structures and properties of new double and triple molybdates in systems Cs$_2$MoO$_4$–R_2(MoO$_4$)$_3$– Zr(MoO)$_2$ (R = Al, Cr, Fe, In, Sc, Bi), D. Sc. Dissertation, Irkutsk State University

57. Boilot JP, Colin G, Colomban P (1988) Relation structure fast ion conduction in the NASICON solid-solution. J Solid State Chem 73: 160–171. https://doi.org/10.1016/0022-4596(88)90065-5

58. Delmas C, Viola JC, Olazcuaga R, Le Flem G, Hagenmuller P, Cherkaoui F, Brochu R (1981) Ionic-conductivity measurements in the solution Na$_{1+X}$Zr$_{2-X}L_X$(PO$_4$)$_3$. Mater Res Bull 16:83–90. https://doi.org/10.1016/0025-5408(81)90182-3

59. Sudreau F, Petit D, Boilot JP (1989) Dimorphism, phase-transitions, and transport-properties in LiZr$_2$(PO$_4$)$_3$. J Solid State Chem 83:78–90. https://doi.org/10.1016/0022-4596(89)90056-X

60. Thangadurai V, Shukla AK, Gopalakrishnan J (1999) New lithium-ion conductors based on the NASICON structure. J Mater Chem 9: 739–741. https://doi.org/10.1039/a807007e