

Phase equilibria in the $\text{Ti}_2\text{MoO}_4\text{-Ho}_2(\text{MoO}_4)_3\text{-Zr}(\text{MoO}_4)_2$ system and the crystal structure of $\text{Ho}_2\text{Zr}_2(\text{MoO}_4)_7$ and $\text{TiHoZr}_{0.5}(\text{MoO}_4)_3$

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Subsolidus phase relations in the $\text{Ti}_2\text{MoO}_4\text{-Ho}_2(\text{MoO}_4)_3\text{-Zr}(\text{MoO}_4)_2$ system have been studied by X-ray diffraction and differential thermal analysis methods. The system has been shown to contain molybdates with the compositions $\text{Ti}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2) and $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2 : 1 : 4). A new ternary molybdate $\text{TiHoZr}_{0.5}(\text{MoO}_4)_3$ was discovered by the method of spontaneous solution-melt crystallization through spontaneous nucleation, and its crystal structure has been determined to be: sp. gr. $R\bar{3}$, $a = b = 13.3665(2)$ Å, $c = 11.9844(4)$ Å, $V = 1854.31(7)$ Å³, $Z = 6$. The mixed three dimensional framework of the crystal structure is composed of Mo tetrahedra sharing O vertices with (Ho,Zr)O₆ octahedra. The thallium atoms occupy wide channels in the framework. Crystals of binary molybdate of $\text{Ho}_2\text{Zr}_2(\text{MoO}_4)_7$ composition were grown by solution-melt crystallization and their crystal structure were determined to be: sp. gr. $C2/c$, $a = 20.6668(4)$, $b = 9.8193(2)$, $c = 13.8187(3)$ Å, $b = 113.678(1)^\circ$, $V = 2568.20(9)$ Å³, $Z = 4$. The crystal structure is composed of three types of polyhedra: MoO₄ tetrahedra, ZrO₆ octahedra, and eight-vertex HoO₈.

Key words. Phase equilibria, synthesis, Thallium, Holmium, Zirconium, Molybdates, Crystal structure, Space group.

Introduction

Complex oxide compounds are of considerable interest for modern science and technology. The molybdates attract attention due to their catalytic and ion exchange properties and the diversity of their crystal structures. The MoO₆ octahedrons are usually highly distorted because of the relatively small effective radius of the Mo⁶⁺ ion in the oxygen environment, which is favorable for the formation of low-symmetry crystal structures. In studies of solid-state reactions in the $\text{M}_2\text{MoO}_4\text{-Ln}_2(\text{MoO}_4)_3\text{-Hf}(\text{MoO}_4)_2$ ($M = \text{K, Ti, Rb}$) systems, the following phases have been identified, synthesized, and characterized: $\text{M}_5\text{LnHf}(\text{MoO}_4)_6$ ($M = \text{K, Ln} = \text{Sm-Lu}$; $M = \text{Ti, Rb, Ln} = \text{Ce-Lu}$), $\text{M}_2\text{LnHf}_2(\text{MoO}_4)_{6.5}$ ($M = \text{Ti, Rb}$; $\text{Ln} = \text{Ce-Lu}$), and $\text{MLnHf}_{0.5}(\text{MoO}_4)_3$ ($M = \text{Ti, Ln} = \text{Ce-Nd}$) [1-8].

The present study is a continuation of our systematic research on phase equilibria in systems containing molybdates of mono-, tri-, and tetravalent metals. Which includes phase equilibria studies of the ternary salt system $\text{Ti}_2\text{MoO}_4\text{-Ho}_2(\text{MoO}_4)_3\text{-Zr}(\text{MoO}_4)_2$; developing a

method for the solid-state synthesis of ternary molybdates discovered in this system; and investigate their structural properties.

Experimental

Reagents

Standard ceramic method was used to synthesize samples from Ti_2O_3 (chemically pure grade), Ho_2O_3 (99.9%), HfO_2 (chemically pure grade), and MoO_3 (chemically pure grade).

Synthesis

To avoid MoO_3 loss by sublimation, sintering was undertaken in stages, starting at 400 °C. Ti_2MoO_4 was synthesized by annealing at 400-550 °C for 50 hrs. Holmium molybdate was prepared from the Ho_2O_3 (99.9%) and MoO_3 via step annealing at 400-850 °C for 100 hrs. Zirconium molybdate was prepared by step annealing of stoichiometric proportions of ZrO_2 and MoO_3 at temperatures between 400-700 °C for 100-150 hrs.

The phase formation in the $\text{Ti}_2\text{MoO}_4\text{-Ho}_2(\text{MoO}_4)_3\text{-Zr}(\text{MoO}_4)_2$ system were investigated by the cross-section method in the subsolidus region. The revealed quasibinary cross-sections were studied at 5-10 mol. % intervals. Samples for the investigation were prepared

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by the solid-state synthesis. The annealing was started at 450 °C and performed with steps of 50 °C and intermediate grinding at 20-30 hrs intervals.

Powder XRD and DSC

The establishment of the equilibrium was monitored by X-ray powder diffraction with Bruker Advance D8 automatic powder diffractometer (CuK α radiation, graphite monochromator, the maximum scan angle $2\theta = 90^\circ$, the scan step 0.01-0.02 $^\circ$, the exposure time was 1 sec per frame).

Differential scanning calorimetric (DSC) measurements were performed on a STA 449 F1 Jupiter thermoanalyzer (NETZSCH) over the temperature range of 30-900 °C in the argon flow. Pt crucibles were used as vessels. Pt-PtRh thermocouples were used for measurement. The precision of temperature measurement was $\pm 1^\circ\text{C}$. The heating and cooling rates were 10 °C/min.

Single crystal XRD

The unit cell parameters and intensities of reflections were measured at room temperature on a Bruker X8 Apex CCD automatic four-circle diffractometer equipped with an area detector according to the standard procedure (MoK α radiation, graphite monochromator).

Results and Discussion

Phase equilibria

Data on the bounding sides of the Ti_2MoO_4 - $\text{Ho}_2(\text{MoO}_4)_3$ - $\text{Zr}(\text{MoO}_4)_2$ system were taken from the literature. It is known, that the double molybdates $\text{TiHo}(\text{MoO}_4)_2$, $\text{Ti}_5\text{Ho}(\text{MoO}_4)_4$, and $\text{Ti}_8\text{Zr}(\text{MoO}_4)_6$, $\text{Ti}_2\text{Zr}(\text{MoO}_4)_3$ are formed in the Ti_2MoO_4 - $\text{Ho}_2(\text{MoO}_4)_3$ and Ti_2MoO_4 - $\text{Zr}(\text{MoO}_4)_2$ systems [9, 10]. In the $\text{Ho}_2(\text{MoO}_4)_3$ - $\text{Zr}(\text{MoO}_4)_2$ system, the existence of the double molybdates $\text{Ho}_2\text{Zr}_2(\text{MoO}_4)_7$ and $\text{Ho}_2\text{Zr}(\text{MoO}_4)_5$ were verified [11].

The results of the investigation of the system are presented in Fig. 1.

The following quasibinary cross-sections exist in the subsolidus region 500-550 °C:

$\text{Ti}_5\text{Ho}(\text{MoO}_4)_4$ - $\text{Ti}_8\text{Zr}(\text{MoO}_4)_6$;
 $\text{Ti}_8\text{Zr}(\text{MoO}_4)_6$ - $\text{TiHo}(\text{MoO}_4)_2$;
 $\text{TiHo}(\text{MoO}_4)_2$ - $\text{Ti}_5\text{HoZr}(\text{MoO}_4)_6$;
 $\text{Ti}_8\text{Zr}(\text{MoO}_4)_6$ - $\text{Ti}_5\text{HoZr}(\text{MoO}_4)_6$;
 $\text{Ti}_2\text{Zr}(\text{MoO}_4)_3$ - $\text{Ti}_5\text{HoZr}(\text{MoO}_4)_6$;
 $\text{TiHo}(\text{MoO}_4)_2$ - $\text{Ti}_2\text{Zr}(\text{MoO}_4)_3$;
 $\text{Ti}_2\text{Zr}(\text{MoO}_4)_3$ - $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$;
 $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ - $\text{Zr}(\text{MoO}_4)_2$;
 $\text{TiHo}(\text{MoO}_4)_2$ - $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$;
 $\text{TiHo}(\text{MoO}_4)_2$ - $\text{Ho}_2\text{Zr}_2(\text{MoO}_4)_7$;
 $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ - $\text{Ho}_2\text{Zr}_2(\text{MoO}_4)_7$;
 $\text{TiHo}(\text{MoO}_4)_2$ - $\text{Ho}_2\text{Zr}(\text{MoO}_4)_5$.

Molybdate $\text{Ti}_5\text{HoZr}(\text{MoO}_4)_6$ was synthesized by

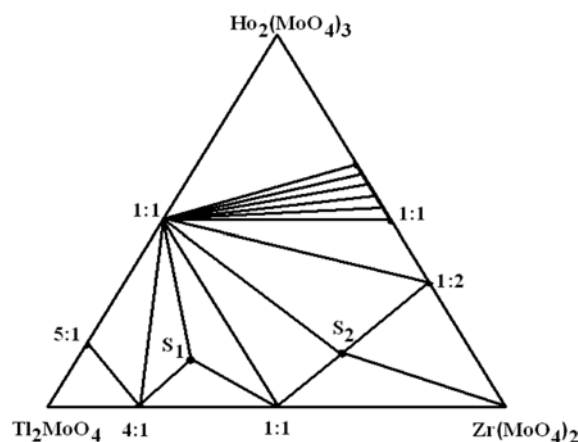


Fig. 1. Subsolidus structure of the phase diagram of the Ti_2MoO_4 - $\text{Ho}_2(\text{MoO}_4)_3$ - $\text{Zr}(\text{MoO}_4)_2$ system. Notations: S_1 - $\text{Ti}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2), S_2 - $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2:1:4).

annealing in the temperature range of 450-550 °C for 100 hrs (The first was calcined at 450 °C for 50 hrs, then temperature was increased to 500 °C and calcined for 30 hrs, after that temperature was increased to 550 °C and calcined for 20 hrs); $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ was synthesized at 500-600 °C for 100-150 hrs (Initially was calcined at 500 °C for 30-50 hrs, then at 550 °C for 40-50 hrs and finally at 600 °C for 30-50 hrs. By analogy with the systems Ti_2MoO_4 - $\text{Ln}_2(\text{MoO}_4)_3$ - $\text{Hf}(\text{MoO}_4)_2$ ($\text{Ln} = \text{Ce-Nd}$) in which compounds with compositions of $\text{TiLnHf}_{0.5}(\text{MoO}_4)_3$ (1 : 1 : 1) ($\text{Ln} = \text{Ce-Nd}$) formed [1-3], and the formation of $\text{TiHoZr}_{0.5}(\text{MoO}_4)_3$ (1 : 1 : 1) was suggested. The $\text{TiHoZr}_{0.5}(\text{MoO}_4)_3$ compound could not be synthesized by solid-phase reaction under our experimental conditions. In connection with this, the search for a new phase of 1 : 1 : 1 composition was carried out by solution-melt crystallization during spontaneous nucleation. Two experiments were carried out on crystallization. In these two experiments, a eutectic mixture of molybdenum oxide and thallium molybdate (38 mol % MoO_3 and 62 mol % Ti_2MoO_4) was used as a solvent. A mixture of Ti_2MoO_4 , $\text{Ho}_2(\text{MoO}_4)_3$, $\text{Zr}(\text{MoO}_4)_2$ at a molar ratio of 1 : 1 : 1 was used as a charge.

In the first experiment, the weight ratio of the charge: solvent - 1 : 2, and in the second - 1 : 3. The homogenization temperature of the first experiment was 800 °C for 2 hours, and the second one - 840 °C for 6 hours. The cooling rate of the melts in these two experiments was 10 deg / h. In the first experiment, $\text{TiHoZr}_{0.5}(\text{MoO}_4)_3$ crystals could not be synthesized, but instead $\text{Ho}_2\text{Zr}_2(\text{MoO}_4)_7$ crystals were detected. The second experiment was successful, the crystallization of $\text{TiHoZr}_{0.5}(\text{MoO}_4)_3$ was confirmed with XRD.

Crystal structure of $\text{Ho}_2\text{Zr}_2(\text{MoO}_4)_7$

The SHELXL-97 program package [12] was used for the full-matrix least-squares refinement of crystal structure in the anisotropic approximation. Table 1

Table 1. Crystallographic parameters, details of the X-ray diffraction experimental conditions and structure refinement for $Ho_2Zr_2(MoO_4)_7$ and $TlHoZr_{0.5}Mo_3O_{12}$.

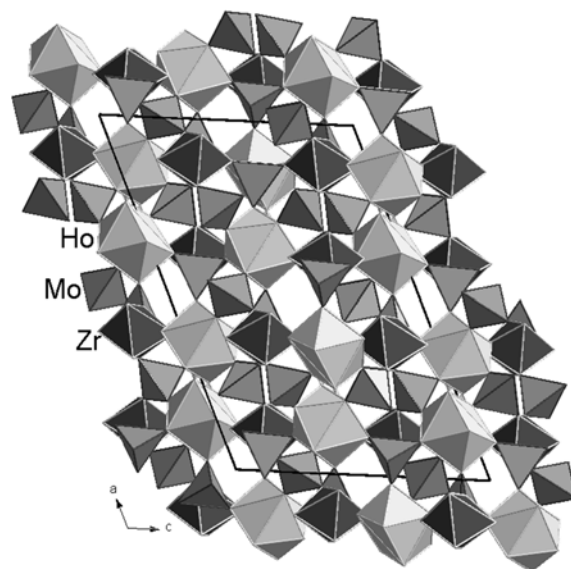
Compound	(1)	(2)
Formula unit	$Ho_2Zr_2Mo_7O_{28}$	$TlHoZr_{0.5}Mo_3O_{12}$
Formula weight	1631.88	894.73
Crystal system	monoclinic	trigonal
Space group	$C2/c$	$R\bar{3}$
Unit cell parameters	a (Å) = 20.6668(4) b (Å) = 9.8193(2) c (Å) = 13.8187(3) β (deg) = 113.678(1)	a (Å) = 13.3665(2) b (Å) = 13.3665(2) c (Å) = 11.9844(4)
V , Å ³	2568.20(9)	1854.31(7)
Z ; ρ_{calcd} , g/cm ³	4; 4.221	6; 4.807
μ (MoK α), mm ⁻¹	10.256	22.723
Crystal size / mm	0.30 × 0.16 × 0.08	0.10 × 0.10 × 0.03
θ - Scan range/deg	2.58–35.00	3.91–29.96
Number of measured reflections	18177	5700
Number of unique reflections	5651	1205
$R(\text{int})$	0.0236	0.0278
Number of reflections with $I > 2\sigma(I)$	5411	1040
Number of parameters in refinement	178	59
GOOF on F^2	1.130	1.198
R factor, $I > 2\sigma(I)$	0.0182	0.0935
R_1	0.0409	0.2953
wR_2		
R factor based on all I_{hkl}	0.0196	0.1023
R_1	0.0413	0.3065
wR_2		
Residual electron density/e Å ⁻³ , $\rho_{\text{max}}/\rho_{\text{min}}$	1.236/-1.032	7.405/-4.324

Table 2. Main interatomic distances (Å) in the $Ho_2Zr_2(MoO_4)_7$ structure.

Mo1 tetrahedron		Mo3 tetrahedron	
Bond	d , Å	Bond	d , Å
Mo1-O2	1.718(2)	Mo3-O11	1.727(2)
Mo1-O1	1.728(2)	Mo3-O9	1.742(2)
Mo1-O4	1.784(2)	Mo3-O12	1.748(2)
Mo1-O3	1.795(2)	Mo3-O10	1.825(2)
< Mo1-O >	1.756	< Mo3-O >	1.7605
Mo2 tetrahedron		Mo4 tetrahedron	
Mo2-O5	1.727(2)	Mo4-O14	1.723(2) × 2
Mo2-O8	1.737(2)	Mo4-O13	1.792(2) × 2
Mo2-O7	1.777(2)	< Mo4-O >	1.7575
Mo2-O6	1.799(2)	Ho1 antiprism	
< Mo2-O >	1.760	Ho1-O9	2.264(2)
Zr1 octahedra		Ho1-O1	2.328(2)
Zr1-O10	2.037(2)	Ho1-O12	2.332(2)
Zr1-O13	2.064(2)	Ho1-O11	2.337(2)
Zr1-O6	2.066(2)	Ho1-O8	2.349(2)
Zr1-O3	2.097(2)	Ho1-O14	2.372(2)
Zr1-O4	2.100(2)	Ho1-O2	2.395(2)
Zr1-O7	2.107(2)	Ho1-O5	2.408(2)
< Zr1-O >	2.0785(2)	< Ho1-O >	2.348(2)

presents crystallographic characteristics, details of the X-ray diffraction experiment and structure refinement.

The space group of each crystal was chosen on the

**Fig. 2.** Fragment of the crystal structure of $Ho_2Zr_2(MoO_4)_7$ projected onto the (010) plane.

basis of an analysis of extinctions in an array of intensities, compared to the calculated intensities. Selected interatomic distances are listed in Table 2.

Detailed crystal data can be obtained from the ICSD inorganic structure database (depository number CSD-421 208).

The crystal structure of $Ho_2Zr_2(MoO_4)_7$ is composed

by three types of polyhedra: MoO₄ tetrahedra, ZrO₆ octahedra, and eight-vertex HoO₈. Four distinct species of Molybdenum in tetrahedral oxygen environments were identified and the average Mo-O distances are nearly equal (1.718(2)-1.825(2) Å) and close to standard distances [13]. The projection of the crystal structure perpendicular to the [010] direction is shown in Fig. 2.

The zirconium atoms have an octahedral environment with typical Zr-O distances of 2.037(2)-2.107(2) Å, and the holmium atoms have a slightly distorted tetragonal antiprismatic oxygen environments with typical Ho-O distances of 2.264(2)-2.408(2) Å. The average deviation of atomic positions in the quadrilateral faces of the prism formed by the O1O5O8O12 and O2O9O11O14 atoms is 0.043 and 0.338 Å, respectively. It has an inflection along the edge O9O14 with the formation of a dihedral angle of 144.8°. The ZrO₆ octahedrons are linked via their common vertices with the bridging Mo1O₄, Mo3O₄, and Mo4O₄ tetrahedra, forming a 3D open-work; in the latter, one can isolate mixed double-row polyhedral chains extending along c axis. The Ho³⁺ ions lie in the voids of the framework and reinforce the structure.

The Zr-O and Ho-O distances found in this study agree well with the corresponding bond lengths in Dy₂Hf₂(MoO₄)₇ [14] (with consideration of the differences in the ionic radii of the corresponding elements [15]) binary molybdate.

Crystal structure of TiHoZr_{0.5}(MoO₄)₃

The crystal symmetry and the unit cell parameters of the triple thallium-holmium-zirconium molybdate indicated that these crystals belongs to the new structural type of compounds of the composition 1 : 1 : 1, which includes CsAlZr_{0.5}(MoO₄)₃ and CsFeZr_{0.5}(MoO₄)₃ [16, 17].

The independent determination of the crystal structure in the centrosymmetric space group $R\bar{3}$ with the use of the SHELX-97 program package [12] confirmed this suggestion.

A refinement of the structure according to the model [16, 17] was carried out in the centrosymmetric group $R\bar{3}$ by the full-matrix least squares by F² in the anisotropic approximation using SHELX-97 software. The unit cell parameters and intensities of reflections for TiHoZr_{0.5}(MoO₄)₃ were measured at room temperature. The crystallographic characteristics, the X-ray data collection conditions and structure refinement statistics are given in Table 1. The coordinates and displacement parameters of the basis atoms are presented in Table 3 and selected interatomic distances are listed in Table 4.

The structure solution and refinement were performed taking into account the statistical distribution of Ho and Zr atoms in the nine-fold M1 site (in the center of symmetry). Taking account of this fact, the final refinement of coordinates and isotropic displacement of basis atoms was performed. The occupancy factor of M1 = 2/3Ho + 1/3Zr was taken in accordance with the given

Table 3. Coordinates of the basis atoms ($\times 10^4$) and equivalent isotropic displacement ($\text{\AA}^2 \times 10^3$, $U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33})$) in the crystal structure of TiHoZr_{0.5}(MoO₄)₃.

Atom	x	y	z	U _{eq}
Tl1	3333	6667	5019(2)	99(1)
Tl2	3333	6667	1667	160(30)
Mo1	0269(2)	5133(3)	3197(1)	38(1)
M1*	1667	8333	3333	43(1)
O1	-0062(19)	4991(19)	1800(18)	75(8)
O2	1050(60)	6570(30)	3420(19)	140(20)
O3	1070(40)	4500(40)	3653(18)	95(12)
O4	-0970(30)	4250(20)	3910(40)	106(12)

* – The occupancy of the site M1 = 2/3Ho + 1/3Zr.

Table 4. Main interatomic distances (Å) and bond angles in the TiHoZr_{0.5}(MoO₄)₃ structure.

Mo1 tetrahedron		Tl1 polyhedron	
Bond	d / Å	Bond	d / Å
Mo1-O4	1.70(3)	Tl1-O4	3.05(3) × 3
Mo1-O3	1.75(3)	Tl1-O2	3.55(6) × 3
Mo1-O1	1.72(2)	Tl1-O3	3.38(4) × 3
Mo1-O2	1.69(3)	Tl1-O1	3.79(4) × 3
< Mo1-O >	1.715	Tl1-O4'	3.84(4) × 3
Angle	ωw / deg	Tl2 polyhedron	
O4-Mo1-O1	107.8(17)	Tl2-O2	3.65(6) × 6
O3-Mo1-O1	116.0(14)	Tl2-O3	3.80(6) × 6
O4-Mo1-O2	123(2)	Tl2-O1	3.93(6) × 6
O3-Mo1-O2	108.7(19)	M1 = (Fe,Hf) octahedron	
O1-Mo1-O2	105.0(11)	M1-O2	2.07(3) × 2
O4-Mo1-O3	97.0(19)	M1-O1	2.16(2) × 2
< O-Mo1-O >	109.6	M1-O3	2.12(3) × 2
		< M-O >	2.117
Shortest intercationic distances			
Mo1-Mo1'	4.182(2)	Mo1-M1	3.714(1)
Mo1-Tl1	4.166(2)	Mo1-M1	3.719(1)
Mo1-Tl1'	4.546(2)	Mo1-M1	3.844(1)
Mo1-Tl2	3.994(2)	M1-Tl1	4.355(1)
Tl1-Tl1'	3.949(2)	M1-M1'	5.554(2)
Tl1-Tl2	4.018(2)	Tl2-M1	4.345(1)

chemical formula of this molybdate, TiHoZr_{0.5}(MoO₄)₃.

It should be noted that the statistical occupancy of one crystallographic site by tri- and tetravalent cations is not only typical of this structural type but is also one of the structural distinguishing features of a group of compounds of the composition 5 : 1 : 2 [18].

However, with the significant difference in the ionic radii of Ho³⁺ and Zr⁴⁺ [15], their statistical arrangement in one polyhedron is difficult, which was expressed in the increased isotropic displacement of the oxygen atoms. It is possible that the represented unit cell is a subcell of a true enlarged cell that is not fixed from the experimental X-ray data obtained. In addition, the appearance of an additional peak -Tl2- can be explained by the distribution of 6 thallium atoms in a

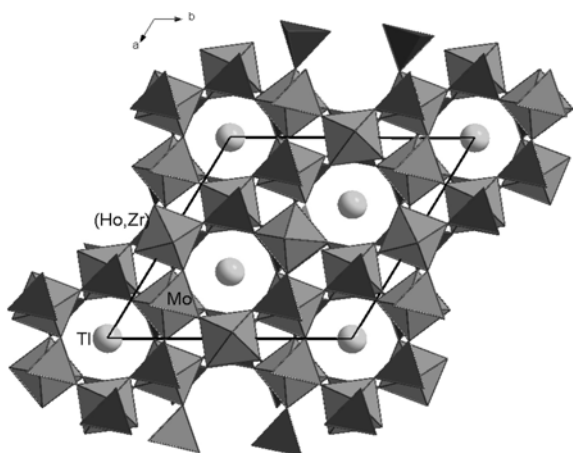


Fig. 3. Mixed framework consisting of MoO_4 tetrahedra and $(\text{Ho,Zr})\text{O}_6$ octahedra in the crystal structure of $\text{TiHoZr}_{0.5}(\text{MoO}_4)_3$ (the projection of the layer onto the (001) plane; the Ti atoms are represented by spheres).

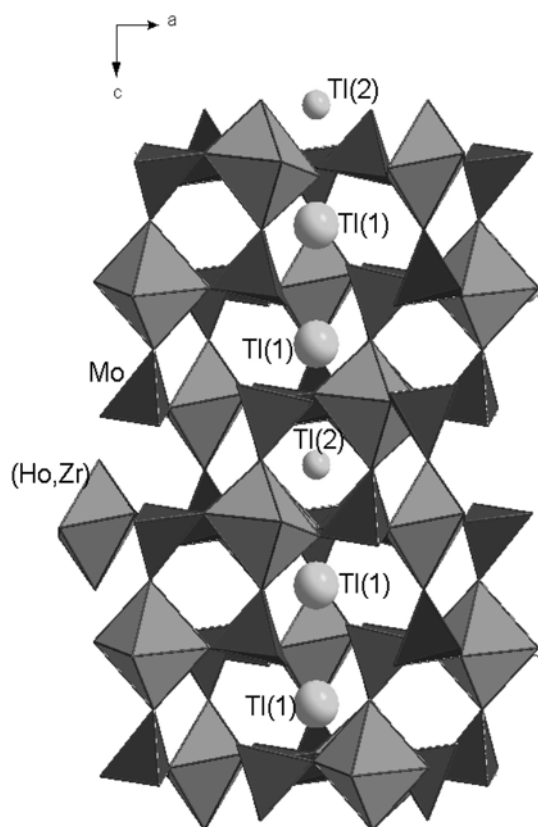


Fig. 4. Fragment of the crystal structure of $\text{Ho}_2\text{Zr}_2(\text{MoO}_4)_7$ projected onto the (010) plane.

cell in two positions. Allowance for the possible twinning of the crystal did not significantly improve the obtained structural data.

In the crystal structure of the molybdate under consideration, there are the following three types of polyhedra: MoO_4 tetrahedra; $(\text{Ho,Zr})\text{O}_6$ octahedra; Ti polyhedra.

The slightly distorted MoO_4 tetrahedron is characterized by the Mo-O distances varying in the range of 1.69(3)-

1.75(3) Å. The variation in the Mo-O distances is associated with the different coordination modes of O atoms by other cations, and their average distance is close to the standard value.

The Ho and Zr atoms, which are statistically distributed in the M1 site, are in an octahedral oxygen environment, and the M1-O distances are slightly different (2.07(3)–2.16(2) Å). These distances are comparable with those in the structures of $\text{Zr}(\text{MoO}_4)_2$ [13], $\text{Rb}_5\text{ErHf}(\text{MoO}_4)_6$ [6], and $\text{K}_5\text{LuHf}(\text{MoO}_4)_6$ [7].

The low-charged alkali cations Ti occupy large polyhedra. The low-charged thallium cations are located inside large 12-vertex polyhedra with groups of three Ti-O distances being equal to 3.05(3), 3.38(4), 3.55(6), and 3.79(4) Å. The Ti-O distances are comparable in the structure of $\text{Ti}_2\text{Mg}_2(\text{MoO}_4)_3$ [19]. A small part of thallium ions -Ti2- are located inside the “loose” polyhedra with Ti2-O distances equal to 3.65(6), 3.80(6), 3.93(6) Å (Table 3).

As a result, the crystal structure of this molybdate is a three-dimensional mixed framework (Fig. 3) composed of successively alternating MoO_4 tetrahedra and $(\text{Ho,Zr})\text{O}_6$ octahedra connected to one-another by sharing O vertices.

The key feature of the structure is the presence of wide channels, along axis 3, accommodating thallium cations (Fig. 4).

The Ti-Ti distances in the channels are 3.949(2) Å and 4.018(2) Å. Two Ti polyhedra located at shorter distance are separated from each other by a thin “empty” layer shaped like a flattened octahedron of O4 atoms with a height of ≈ 1.38 Å. The polyhedra Ti1 and Ti2 have a common slightly corrugated plane of O2 and O3 atoms with a deviation of the constituent atoms from the mean square plane by ~ 0.14 Å.

Thermal properties

Thermal properties of $\text{Ti}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2) and $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2 : 1 : 4) were investigated by differential scanning calorimetry (DSC). The experiments were carried out at a temperature range from 25 °C to 800 °C and at a heating rate of 10 K/min under a flux of 20 ml / min of argon. The temperature dependences of the DSC signals for the $\text{Ti}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2) and $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2 : 1 : 4) compounds are shown in Fig. 5.

Three endothermic signals at 448 °C, 546 °C and 579 °C were detected on heating for the $\text{Ti}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2), as shown in Fig. 5(a). Two endothermic signals at 547 °C and 756 °C were detected for $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2:1:4) (Fig. 5(b)). The endothermic peaks at 579 °C and 756 °C correspond to the melting points. To determine the nature of the endoeffects at 448 °C and 547 °C samples were measured in the “heating-cooling” mode (without melting). Upon cooling, the curve for $\text{Ti}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2) shows an exothermic effect at 399 °C (398 °C), and for the $\text{Ti}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2:1:4)

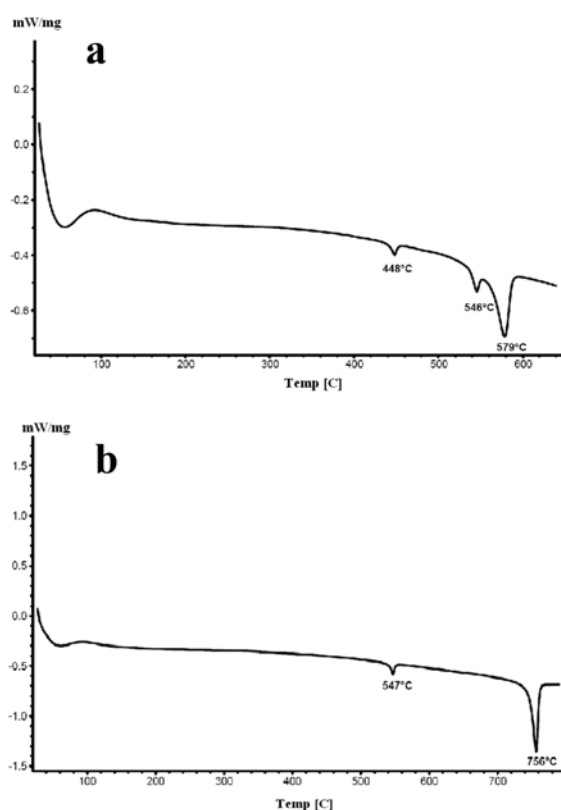


Fig. 5. Thermal analysis of the $\text{Tl}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2) (a) and $\text{Tl}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2 : 1 : 4) (b) compounds.

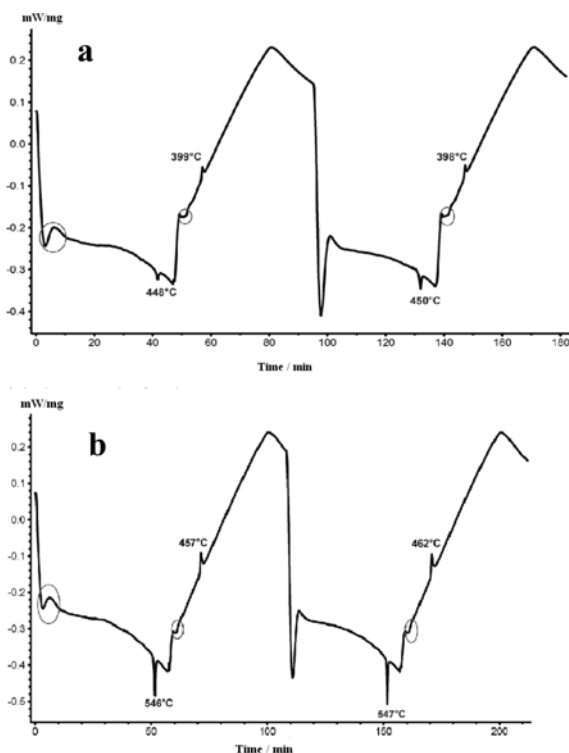


Fig. 6. Differential scanning calorimetry (DSC) heating and cooling curves for $\text{Tl}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2) (a) and $\text{Tl}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2 : 1 : 4) (b) (with an oval red, the endoeffects associated with the effect of the instrument are highlighted).

compound shows an exothermic effect at 457 °C (462 °C). The resulting temperature hysteresis reaches ~ 50 °C (for the $\text{Tl}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2), as shown in Fig. 6(a) and ~85 °C (for the $\text{Tl}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2 : 1 : 4) (Fig. 6(b)).

Thus, this indicates the existence of a phase transition (type I) in $\text{Tl}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2) and $\text{Tl}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2 : 1 : 4).

Conclusions

In summary, the phase equilibria in the $\text{Tl}_2\text{MoO}_4\text{-Ho}_2(\text{MoO}_4)_3\text{-Zr}(\text{MoO}_4)_2$ system were studied for the first time. New compounds $\text{Tl}_5\text{HoZr}(\text{MoO}_4)_6$ (5 : 1 : 2) and $\text{Tl}_2\text{HoZr}_2(\text{MoO}_4)_{6.5}$ (2 : 1 : 4) were found to be formed in this system. It was revealed by the method of intersecting sections. The triple molybdate of $\text{TlHoZr}_{0.5}(\text{MoO}_4)_3$ was prepared by a solution-melt crystallization, and its structure has been determined. $\text{TlHoZr}_{0.5}(\text{MoO}_4)_3$ was not obtained by the solid-phase method. Filling of channels with thallium cations in this type of framework structures may provide the conditions for efficient ion transport. Further studies in this area are in progress. Crystals of binary holmium and zirconium molybdate of $\text{Ho}_2\text{Zr}_2(\text{MoO}_4)_7$ composition were grown by solution-melt crystallization under spontaneous nucleation conditions.

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