Full Articles

Synthesis, crystal structure, and electrical properties of the new ternary molybdate $Rb_5NdHf(MoO_4)_6$

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The subsolidus phase relations in the ternary salt system Rb_2MoO_4—$Nd_2(MoO_4)_3$—$Hf(MoO_4)_2$ were studied by X-ray powder diffraction. The ternary molybdates $Rb_5NdHf(MoO_4)_6$ (**1**) and $Rb_2NdHf_2(MoO_4)_{6.5}$ are formed in this system. Compound **1** without impurities was synthesized by the solid-phase method by varying the temperature in the range of 400—600 °C and the annealing time from 70 to 110 h. Single crystals of compound **1** were grown by the flux method. The structure of compound **1** was established and the electrical properties of ceramic samples of this compound were investigated. This ternary molybdate has mixed electronic-ionic conductivity with the ionic component predominating at 200—500 °C.

Key words: rubidium, neodymium, hafnium, ternary molybdates, phase equilibria, crystal structure, trigonal system, electronic-ionic conductivity.

A large assortment of devices, in particular, ferroelectric and piezoelectric transducers, sensors, and solid electrolyte fuel cells, can be designed based on complex oxide dielectrics with a large ionic bond contribution.[1] Among these materials, systems containing trivalent metal molybdates $M^{3+}{}_2(MoO_4)_3$ with $Sc_2(WO_4)_3$-type structures (space group *Pnca*) are of considerable interest. The $Sc_2(WO_4)_3$ compound has a complex structure built of two types of vertex-shared $W(1)O_4$ and $W(2)O_4$ tetrahedra and ScO_6 octahedra. The channels in the structure are favorable for the migration of mobile M^{3+} cations. The conductivity of molybdates with a $Sc_2(WO_4)_3$

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structure is several times higher than that of tungstates $M_2(WO_4)_3$ (M = Al, In, Sc, or Ln).[2,3]

Ternary salt systems containing mono-, tri-, and tetravalent metal molybdates are promising as new materials having valuable properties.

In the present study, we investigated the phase formation in the Rb_2MoO_4—$Nd_2(MoO_4)_3$—$Hf(MoO_4)_2$ system and determined the single-crystal structure of the new ternary molybdate $Rb_5NdHf(MoO_4)_6$ (**1**).

Results and Discussion

The formation of the $Rb_5Nd(MoO_4)_4$ and $RbNd(MoO_4)_2$ compounds in the Rb_2MoO_4—$Nd_2(MoO_4)_3$ system was confirmed in the studies.[4,5] Earlier,[6] double molybdates $Rb_8Hf(MoO_4)_6$ and $Rb_2Hf(MoO_4)_3$ have been synthesized in the Rb_2MoO_4—$Hf(MoO_4)_2$ system. Recently, we have revealed the double molybdate $Nd_2Hf_3(MoO_4)_9$ in the $Nd_2(MoO_4)_3$—$Hf(MoO_4)_2$ system.[7]

The results of investigation of the subsolidus phase relations in the Rb_2MoO_4—$Nd_2(MoO_4)_3$—$Hf(MoO_4)_2$ system are presented in Fig. 1. At 450—600 °C, new ternary molybdates with the compositions of 5 : 1 : 2 and 2 : 1 : 4 were formed in this system. We grew single crystals of molybdate with the composition of 5 : 1 : 2 (**1**) and established the crystal structure of this compound. In this structure, the Mo atom is tetrahedrally coordinated by oxygen atoms with the Mo—O distances in the range of 1.727(3)—1.828(2) Å. The differences in these distances are associated with the difference in the coordination of the O atoms to the Rb, Nd, and Hf cations and are comparable with those in other similar structures with analogous compositions.

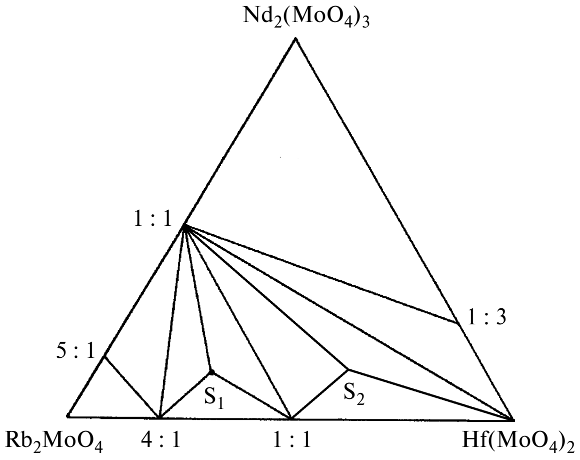

Fig. 1. Subsolidus phase diagram of the Rb_2MoO_4—$Nd_2(MoO_4)_3$—$Hf(MoO_4)_2$ system (5 : 1 : 2, 450—600 °C) (S_1, $Rb_5NdHf(MoO_4)_6$ (5 : 1 : 2); S_2, $Rb_2NdHf_2(MoO_4)_{6.5}$ (2 : 1 : 4)).

One of the structural features of the group of compounds with the composition 5 : 1 : 2 containing tri- and tetravalent cations, as well as of compounds with the composition 5 : 1 : 3 [8,9] containing di- and tetravalent cations, is that the A^{3+} (or A^{2+}) and Hf^{4+} (Zr^{4+}) cations are randomly distributed between two crystallographic positions. The refinement of the occupancies of these two positions in the structures showed that the large cations predominantly occupy the positions having an octahedral environment of its second coordination sphere by Mo atoms (M(1)—Mo(1), 3.754 Å).

The refinement of the occupancies of these positions in the structure under study led us to conclude that the M(1) atoms occupy a special position on the axis of inversion $\bar{3}$, and the M(2) atoms are located at the intersection of the twofold and threefold axes (ratios between Nd and Hf atoms in these positions are given in Table 1). The metal atoms in both positions are coordinated by oxygen atoms and have six equal distances (M(1)—O and M(2)—O distances are 2.252(3) and 2.074(2) Å, respectively). These distances are in satisfactory agreement with the average Nd—O and Hf—O distances in the $K_3NdSi_2O_7$ and $K_8Hf(MoO_4)_6$ structures.[10,11]

Two types of rubidium cations occupy large polyhedra. The Rb(1) atoms are located on a threefold axis in nine-vertex polyhedra with the Rb—O distances of 2.908(3), 2.963(3), and 3.279(3) Å (three each). The coordination polyhedron of the Rb(2) atom located on a twofold axis is formed by three pairs of more closely spaced O atoms (Rb—O, 2.937(3)—3.164(3) Å) and three pairs of more distant O atoms (Rb—O, 3.348(3)—3.469(4) Å). These atoms, all together, form a twelve-vertex polyhedron, which can be described as a distorted cuboctahedron.

The crystal structure of molybdate **1** (Fig. 2) can be described as a three-dimensional mixed framework con-

Table 1. Coordinates of the basis atoms ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3/\text{Å}^2$) in the crystal structure of **1**

Atom	*x*	*y*	*z*	U_{eq}[a]
M(1)[b]	0	0	0	9(1)
M(2)[c]	0	0	2500	8(1)
Mo(1)	3519(1)	576(1)	334(1)	13(1)
Rb(1)	0	0	3534(1)	31(1)
Rb(2)	3887(1)	0	2500	35(1)
O(1)	1777(3)	367(3)	365(1)	37(1)
O(2)	4858(3)	2333(3)	523(1)	22(1)
O(3)	3588(3)	−802(3)	538(1)	30(1)
O(4)	3924(4)	620(4)	−93(1)	39(1)

[a] $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.
[b] M(1) = 0.904(1)Nd + 0.096(1)Hf.
[c] M(2) = 0.096(1)Nd + 0.904(1)Hf.

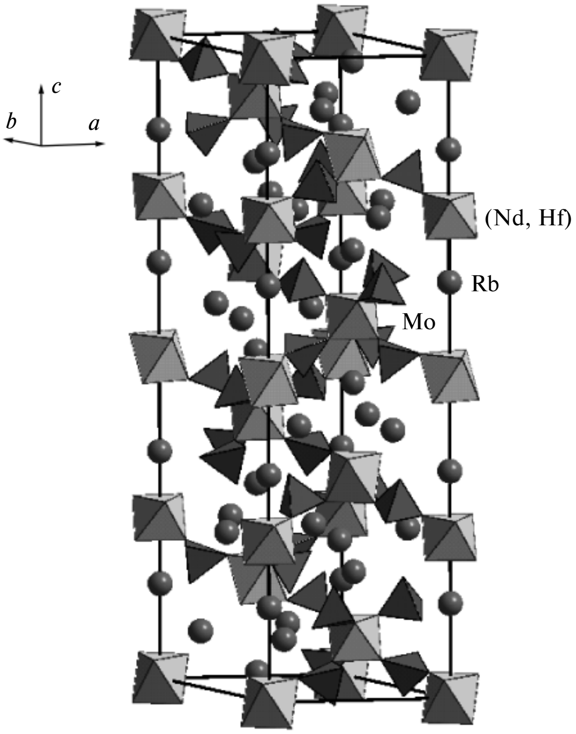

Fig. 2. Mixed framework consisting of MoO_4 tetrahedra and two types of $(Nd,Hf)O_6$ octahedra in the crystal structure of $Rb_5NdHf(MoO_4)_6$.

sisting of the successively alternating Mo tetrahedra and NdO_6 and HfO_6 octahedra sharing O vertices. The large cavities in the framework are occupied by two types of rubidium cations.

The conductivity of compound **1** was studied in the temperature range of 200—500 °C. The linear inverse temperature dependence of the total conductivity of rubidium neodymium hafnium molybdate in the $\log\sigma—T^{-1}$ coordinates is shown in Fig. 3. The activation energy E_a was determined from the slope of the linear plot.

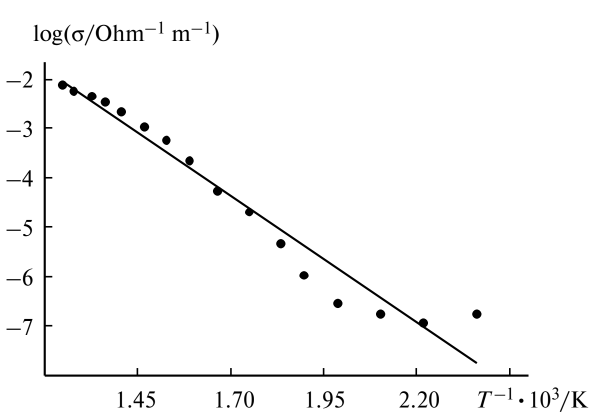

Fig. 3. Inverse temperature dependence of the ionic conductivity (σ) for $Rb_5NdHf(MoO_4)_6$ (**1**) in the $\log\sigma—T^{-1}$ coordinates.

An analysis of the temperature dependence of the electron transfer numbers (t_e) shows that ceramic samples of ternary molybdate have mixed electronic-ionic conductivity with the ionic component predominating at 300—500 °C.

Taking into account the low activation energy (E_a = 0.50 eV) and the rather high specific conductivity ($\sigma = 1.06 \cdot 10^{-3}$ Ohm^{-1} m^{-1}) of ternary molybdate **1**, this compound can be assigned to solid electrolytes.

Experimental

Commercial molybdenum trioxide (reagent grade), rubidium carbonate (special purity grade), hafnium oxide (special purity grade), and neodymium oxide (99.9%) were used as the starting compounds. Molybdates were prepared by solid-state reactions. To avoid losses of MoO_3 through sublimation, the annealing was started at 400 °C. The annealing temperature for rubidium and hafnium molybdates was 700 °C; for neodymium molybdate, 800 °C. The annealing time was 100 h.

Table 2. Crystallographic characteristics and the X-ray diffraction data collection and refinement statistics for compound **1**

Parameter	Characteristics
Empirical formula	$NdHfMo_6O_{24}Rb_5$
Molecular weight	1709.72
T/K	293(2)
Diffractometer	X8-APEX
Wavelength/Å	0.71073
Monochromator	Graphite
Scanning technique with a step of 0.5°	φ-Scan mode
Crystal system	Trigonal
Space group	$R\bar{3}c$
a/Å	10.7550(2)
b/Å	10.7550(2)
c/Å	38.8427(13)
V/Å^3	3891.0(2)
Z	6
d_{calc}/g cm^{-3}	4.378
μ/cm^{-1}	181.62
F(000)	4566
θ-Scan range/deg	2.43—32.57
Number of measured/ independent reflections	11941/1583
R_{int}	0.0191
Number of reflections with $I > 2\sigma(I)$	1502
Number of parameters in refinement	61
GOOF on F^2	1.059
R factor based on reflections with $I > 2\sigma(I)$	
R_1	0.0219
wR_1	0.0546
R factor based on all I_{hkl}	
R_1	0.0236
wR_2	0.0554
Extinction coefficient	0.000000(12)

The phase formation in the Rb_2MoO_4—$Nd_2(MoO_4)_3$—$Hf(MoO_4)_2$ system was studied by the cross-section method. The revealed quasibinary cross-sections were studied with a step of 5—10 mol.%. The establishment of the equilibrium was monitored by X-ray powder diffraction (Advance D8 Bruker AXS instrument equipped with a graphite monochromator).

Crystals of ternary molybdate **1** were grown by the flux method with spontaneous nucleation. Rubidium dimolybdate was used as the solvent. A mixture of the reagents and the solvent in a molar ratio of 2 : 1 was homogenized at 650 °C and then cooled to 510 °C at a rate of 1.5 °C h^{-1}.

Table 3. Shortest cation—cation distances (*r*), selected interatomic distances (*d*), and bond angles (ω) in the crystal structure of **1**

Parameter	Value
Distance	*r*/Å
Mo(1)—Mo(1´)	3.923
Mo(1)—Mo(1″)	4.389
Mo(1)—Rb(1)	3.802
Mo(1)—Rb(1´)	4.172
Mo(1)—Rb(2)	3.912
Mo(1)—Rb(2´)	3.946
Mo(1)—M(1)	3.754
Mo(1)—M(2)	3.711
M(2)—Rb(1)	4.017
M(2)—Rb(2)	4.180
Rb(1)—Rb(2)	4.136
Mo(1) Tetrahedron	
Bond	*d*/Å
Mo(1)—O(4)	1.727(3)
Mo(1)—O(3)	1.733(3)
Mo(1)—O(1)	1.774(3)
Mo(1)—O(2)	1.828(2)
<Mo(1)—O>	1.765
Angle	ω/deg
O(4)—Mo(1)—O(3)	109.2(2)
O(4)—Mo(1)—O(1)	107.3(2)
O(3)—Mo(1)—O(1)	110.2(2)
O(4)—Mo(1)—O(2)	108.1(1)
O(3)—Mo(1)—O(2)	111.1(1)
O(1)—Mo(1)—O(2)	111.0(1)
<O—Mo(1)—O>	109.45
M Octahedra	
Bond	*d*/Å
M(1)—O(1)	2.252(3) (×6)
M(2)—O(2)	2.074(2) (×6)
Rb(1)—O(3)*	2.908(3) (×3)
Rb(1)—O(4)*	2.963(3) (×3)
Rb(1)—O(2)*	3.279(3) (×3)
Rb(2)—O(4)**	2.937(3) (×2)
Rb(2)—O(3)**	3.090(3) (×2)
Rb(2)—O(2)**	3.164(3) (×2)
Rb(2)—O(3´)**	3.348(3) (×2)
Rb(2)—O(1)**	3.386(3) (×2)
Rb(2)—O(1´)**	3.469(4) (×2)

* The Rb(1) nine-vertex polyhedron.

** The Rb(2) cuboctahedron.

The single-crystal structure of **1** was studied by X-ray diffraction on an automated X8-APEX diffractometer (Mo-Kα radiation, F_{hkl} = 1502, R = 0.0219). The data collection and refinement statistics and selected crystallographic characteristics are given in Table 2. The centrosymmetric space group $R\bar{3}c$ was chosen based on the analysis of systematic absences supported by calculations. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method using the SHELXL-97 program package.[12] The structure solution revealed that the neodymium and hafnium atoms are distributed between different crystallographic sites. This fact was taken into account in the final refinement of the atomic coordinates and displacement parameters. The positional and equivalent isotropic thermal parameters of the basis atoms are given in Table 1. Selected interatomic distances are listed in Table 3.

The electrical properties were measured from pellets with a thickness of ~1 mm and a diameter of ~10 mm, which were prepared by pressing powder samples followed by annealing of the corresponding compound at $2/3T_m$. A platinum paste was used for electrical contacts. The paste was spread onto the surface of the pellets, and the pellets were annealed at 550 °C.

The temperature dependences of the conductivity (σ), the dielectric permeability (ε), and the dielectric loss tangent (tgδ) were studied on an experimental apparatus using Vest—Tallan's method; σ, ε, and tgδ were measured at an alternating current with the use of a E8-4 alternating current bridge equipped with a R-5025 capacitance box, which made it possible to extend the range of measurements of tgδ in samples. The direct current was measured with a E6-13A teraohmeter at the fixed voltages of 30 and 60 mV. The parameter t_e was determined as the ratio of the electronic conductivity measured at a direct current to the total conductivity measured at an alternating current

$$t_e = \sigma_{=}/\sigma_{\sim} = \rho_{\sim}/\rho_{=},$$

where $\rho_{\sim}$ and $\rho_{=}$ are the specific conductivities measured at alternating and direct currents, respectively.

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