

Complex Oxide Compounds of Polyvalent Metals: Synthesis, Structure and Properties

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Abstract

Complex oxide compounds with two or three combinations of single-double and single-double-quadruple charged cations were obtained by means of solid-phase synthesis. Electrophysical properties of the obtained compounds were studied using ceramic pellets according to the West and Tallane technique. Non-linear optical phase analysis revealed phase transitions in the molybdates and tungstates of single-double and single-quadruple valence metals. It was shown that triple molybdates can be referred to solid electrolytes judging from their ion conductivity.

INTRODUCTION

Complex oxide compounds and materials based on them attract the attention of the researchers because of non-linear optical and electrical properties, in particular piezoelectric and electrophysical behaviour.

Among oxide materials of interest are molybdenum- and tungsten-containing compounds in which these elements are combined with other single- and polyvalence metals. Literature presents a large amount of data demonstrating the perspectives of molybdates and tungstates as luminophores, segnetoelectrics, catalysts and solid electrolytes.

The search for and the creation of novel materials is an urgent and complicated scientific and technological problem involving several stages. Physicochemical aspect is of primary importance for all these stages. In order to govern the process of materials formation, one should be aware of: (i) the data on phase equilibrium in multicomponent systems that were studied for the purpose of searching for new compounds and solvents to grow single crystals; (ii) the data on structure and on the analysis of structural features of these compounds;

(iii) preparation of ceramic and single crystal materials; (iv) assumed fields of their application.

Fundamental investigation of the connection between the composition, structure and properties is very important for applied studies including search for novel materials that can be used as luminophores, chemical sensors, catalysts, piezo- and segnetoelectrics, solid electrolytes, *etc.*

Systematic studies of phase formation in the systems containing molybdenum and tungsten have been carried out at the Laboratory of Oxide Systems of the Buryat Scientific Centre of the Siberian Branch of the RAS for more than 20 years. The methods for the preparation of double molybdates and tungstates as poly- and single crystals have been worked out; the structure, as well as thermal, crystallographic, electrophysical and other characteristics of these compounds have been determined.

The effect of various factors (cation size, the degree of bond ionicity, electronegativity) on the interaction in double and triple oxide systems were analysed, as well as the structure and properties of the formed phases. The composition – structure – properties connection was established, and structural charts (maps)

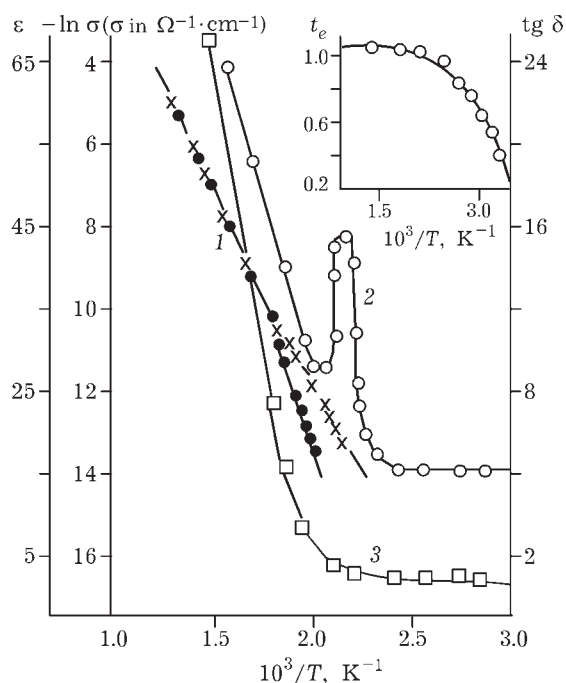


Fig. 1. Temperature dependence of σ (1), ϵ (2) and $\text{tg } \delta$ (3) for TlLiWO_4 . The insertion shows electron transport numbers.

were built that allowed to divide the compounds into groups according to the structural types. The series of segnetoelectric, segneto-elastic, piezoelectric materials based on double molybdates and tungstates were created on the basis of the revealed connections between the composition, structure and properties. The assumed application fields were outlined [1, 2].

In this work we present the results obtained in the studies into electrophysical properties of the representatives of groups of compounds obtained by us for the first time when conducting systematic studies of complex oxide systems [3].

EXPERIMENTAL

The subjects of our investigation were ceramic samples isolated as intermediate phases when studying triple oxide and salt systems [1–3]. The samples were prepared according to

a standard solid-phase synthesis technique, and annealed at 500–600 °C with intermediate attrition. All the samples were single-phase according to the data of X-ray phase analysis. Ceramic samples were prepared as discs with the diameter of 20 mm and 2 mm thick ($P = 200$ mPa). The density of discs after annealing was 94–96 %. Temperature dependencies of the electrical conductivity, dielectric permittivity and the tangent of the angle of dielectric losses of these samples were studied. The measurement of electrical conductivity of the triple molybdate samples was described in [2].

Some compounds taken as fine crystals were studied by means of the generation of the second optical harmonics (SOH). This technique was described in detail in [4, 5].

RESULTS AND DISCUSSION

Figure 1 shows temperature dependence of the total conductivity (σ), permittivity (ϵ), the tangent of the angle of dielectric losses ($\text{tg } \delta$) and electron transport numbers (t_e) for TlLiWO_4 . With increasing temperature, ϵ and $\text{tg } \delta$ increase and exhibit anomalies within the range of 200–210 °C.

The results of SOH measurements (Table 1) suggest that the structure of TlLiWO_4 is not central symmetrical. In particular, TlLiWO_4 and $\text{Tl}_2\text{Pb}(\text{MoO}_4)_2$ exhibit high I_{2w}/I_w (SiO_2) equal to 200 and 70, respectively, and show polar properties. In TlLiWO_4 , phase transition exists from the polar state into non-polar one. Under the temperature change rate involved in the study (5–7 °C/min), the transition is not completely reversible but is characterized by a substantial temperature hysteresis (Fig. 2). At heating and cooling the transition points are 230 and 180 °C, respectively. The character of SOH intensity changes with temperature for TlLiWO_4 corresponds to the change of symme-

TABLE 1
Properties of the studied complex oxide compounds

Compound	Syngony, space group	I_{2w}/I_w (SiO_2) and P_s	Phase transition point, °C
TlLiWO_4	Monoclinic	200	200
$\text{Tl}_2\text{W}_4\text{O}_{13}$	Rhombic	10	200
$\text{Tl}_2\text{Pb}(\text{MoO}_4)_2$	Trigonal, $R3$	70	330
$\text{Tl}_4\text{Zn}(\text{MoO}_4)_3$	Rhombic, $Pnnc$	Segnetoelastic	200
$\text{Rb}_2\text{HfW}_5\text{O}_{18}$	HTB	9.5, 8.3	680

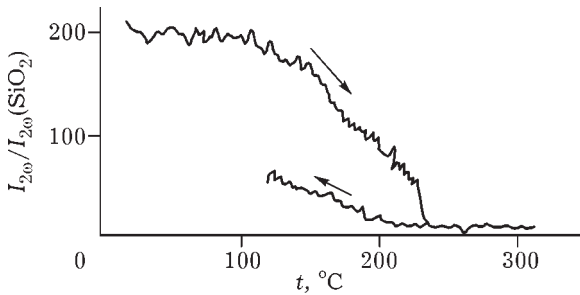


Fig. 2. SOH dependence on temperature for TlLiWO₄.

try $\bar{4}3m$ (high-temperature phase) \leftrightarrow $3m$ (low-temperature phase). In Tl₂Pb(MoO₄)₂ (Fig. 3) a reversible segnetoelectric transition was discovered near 330 °C. Thallium-lead molybdate can be referred to palmieryte segnetoelectrics.

The crystals Tl₄Zn(MoO₄)₃ grown according to the solution-melt technique under spontaneous nucleation were studied. Crystals are transparent, shaped as plates with the size up to 3 mm, crystallized in the rhombic syngony, space group *Pnnc*, unit cell parameters $a = 10.78(1)$, $b = 21.93(2)$, $c = 6.09(7)$ Å.

Temperature dependence of the intensity of the second optical harmonics shows phase transition between non-centrosymmetrical and centrosymmetrical states near 200 °C. Monotonous behaviour of the curve of temperature dependence of $I_{2\omega}/I_{2\omega}(SiO_2)$ and the absence of heat effect in the DTA curve obtained for Tl₄Zn(MoO₄)₃ point to the fact that the phase transition in these crystals is of the second type.

At temperatures below 200 °C, Tl₄Zn(MoO₄)₃ crystals are in a polydomain state. The domain structure can be observed with a polarization microscope as the sequence of light and dark bands. The domain structure of the crystals of this compound exhibits three orientation states. Above the phase transition point the domains are absent.

The permittivity and the tangent of the angle of dielectric losses for the Tl₄Zn(MoO₄)₃ crystals increase sharply in the vicinity of 200 °C (Fig. 4). The occurrence of a second-type phase transition from the polar phase to non-polar one in the Tl₄Zn(MoO₄)₃ crystal which is accompanied by the change in permittivity and dielectric losses, as well as the existence of domain structure in the polar phase allow us to refer this compound to segnetoelectrics-segnetoelastics.

According to experimental data, thallium (I)-containing oxides are characterized by substan-

tial increase of the conductivity (from $(1.1-4.3) \cdot 10^{-10}$ to $(3.0-5.3) \cdot 10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$) within the given temperature range. These is one fracture within the range of 200–250 °C which points to the presence of two types of conductivity, *i. e.* extrinsic at low temperatures

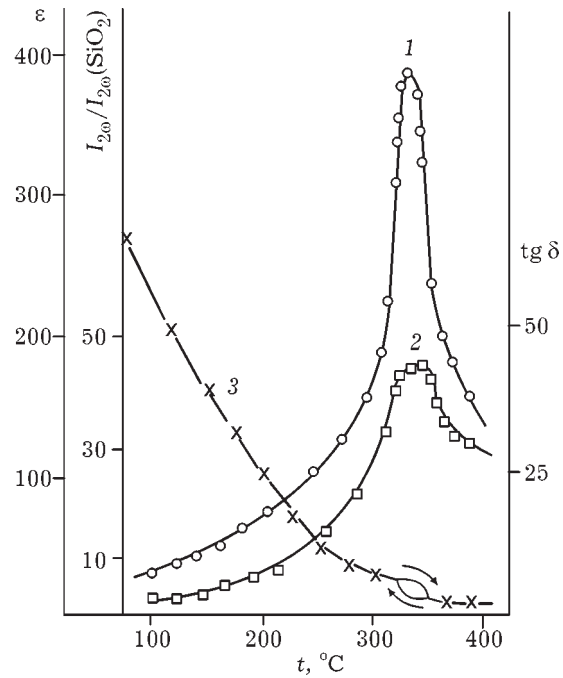


Fig. 3. Temperature dependence of ϵ (1), $\text{tg } \delta$ (2) and SOH (3) for Tl₂Pb(MoO₄)₂.

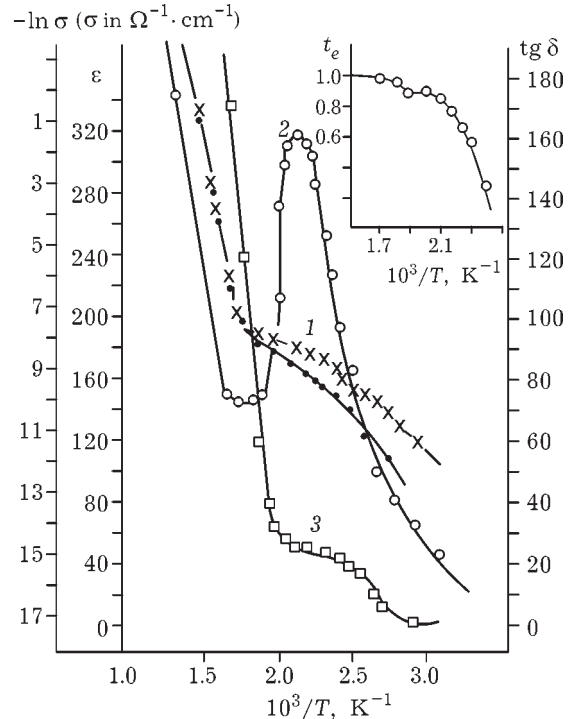


Fig. 4. Temperature dependence of σ (1), ϵ (2) and $\text{tg } \delta$ (3) for Tl₂Zn(MoO₄)₃. The insertion shows temperature dependence of transport numbers.

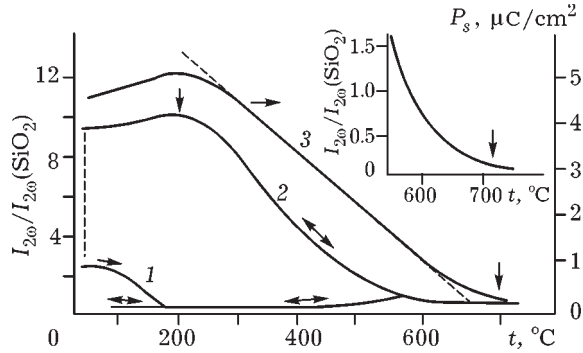


Fig. 5. Temperature dependencies of SOH and polarization for $\text{Rb}_2\text{HfW}_5\text{O}_{18}$ cooled from 800°C : 1 – heating (one month after cooling), 2 – cooling, 3 – polarization (calculation). The insertion shows curve 2 at another scale.

and intrinsic at higher temperatures. The analysis of electron (t_e) and ion (t_i) transport numbers suggests that ionic conductivity is predominant in the samples at low temperatures.

When temperature increases, the contribution from electron constituent increases; above 150°C it becomes prevailing which leads to the increase of total conductivity. Activation energy (E_a) of intrinsic conductivity varies within $2.8\text{--}3.0\text{ eV}$. At room temperature, the permittivity and tangent of the angle of dielectric losses are $15\text{--}20$ and $0.05\text{--}0.1$, respectively; while temperature increases they reach higher values.

The new compounds $\text{Me}_2\text{MW}_5\text{O}_{18}$ ($\text{Me} = \text{K}, \text{Rb}, \text{Cs}; \text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) [6] synthesized by us enter the series of hexagonal tungsten bronze (HTB). The studies by means of the generation of the second optical harmonics allowed to reveal segnetoelectric phase transitions in the new compounds within the temperature range of $600\text{--}750^\circ\text{C}$.

TABLE 2

Electrical properties of triple molybdates

Compound	$R_{\text{Me}^+}/R_{\text{Me}^{2+}}, \text{\AA}^*$	$\sigma \cdot 10^3, \Omega^{-1} \cdot \text{m}^{-1} (400^\circ\text{C})$	E_a, eV
$\text{K}_5\text{Mg}_{0.5}\text{Zr}_{1.5}(\text{MoO}_4)_6$	1.38/0.72 (Mg)	1.00	0.63
$\text{K}_5\text{Zn}_{0.5}\text{Zr}_{1.5}(\text{MoO}_4)_6$	1.38/0.75 (Zn)	1.84	0.56
$\text{K}_5\text{Mn}_{0.5}\text{Zr}_{1.5}(\text{MoO}_4)_6$	1.37/0.82 (Mn)	1.23	0.62
$\text{K}_5\text{Cd}_{0.5}\text{Zr}_{1.5}(\text{MoO}_4)_6$	1.38/0.95 (Cd)	2.03	0.54
$\text{Tl}_5\text{Mg}_{0.5}\text{Zr}_{1.5}(\text{MoO}_4)_6$	1.50/0.72	0.74	0.47
$\text{Tl}_5\text{Zn}_{0.5}\text{Zr}_{1.5}(\text{MoO}_4)_6$	1.50/0.75	1.03	0.48
$\text{Tl}_5\text{Cd}_{0.5}\text{Zr}_{1.5}(\text{MoO}_4)_6$	1.50/0.95	1.45	0.49
$\text{KMg}_{0.5}\text{Zr}_{0.5}(\text{MoO}_4)_6$		2.13	0.51
$\text{KZn}_{0.5}\text{Zr}_{0.5}(\text{MoO}_4)_6$		2.38	0.55
$\text{KMn}_{0.5}\text{Zr}_{0.5}(\text{MoO}_4)_6$		0.79	0.64
$\text{Tl}_5\text{Mg}_{0.5}\text{Zr}_{0.5}(\text{MoO}_4)_6$		1.17	0.48
$\text{Tl}_5\text{Zn}_{0.5}\text{Zr}_{0.5}(\text{MoO}_4)_6$		1.23	0.49
$\text{Tl}_5\text{Cd}_{0.5}\text{Zr}_{0.5}(\text{MoO}_4)_6$		2.18	0.50

*Ion radii are given according to Shannon and Pruitte.

Spontaneous polarization is maximum for HTB segnetoelectrics with $\text{Me} = \text{K}$ and Rb that possess asymmetrical paraphase (see Table 1). The dependencies $I_{2w}(T)$ for $\text{Me}_2\text{MW}_5\text{O}_{18}$ are similar for different M (Fig. 5). The phase transition $\alpha \leftrightarrow \beta$ in $\text{Rb}_2\text{HfW}_5\text{O}_{18}$ is of the first type close to the second one.

A systematic investigation of multicomponent systems led us to the preparation of new molybdates with three different cations. Single crystals of the representatives of different structural types were grown and their structures were deciphered [2]. The triple molybdates studied exhibit mixed ion conductivity with the predominance of ionic constituent at high temperatures (Table 2). Ion radii of the structure-forming bivalent cations with the coordination number 6 changed from 0.72 (Mg) to 0.95 (Cd) \AA .

Electrical properties of triple molybdates are connected with their structural features. The structures of $5:1:3$ and $1:1:1$ compounds exhibit infinite channels with large cross sections. Very mobile potassium atoms are located in these channels. In this case, high cation mobility is likely to be due to the possibility of potassium transport along the channel system. The difference in ion mobility was smoothed over since the measurements were carried out with ceramic samples in which the anisotropy of conductivity is not exhibited. The decrease of ion conductivity in the investigated compounds when passing from $\text{Cd} \rightarrow \text{Zn} \rightarrow \text{Mg}$ can be explained by the decrease of the size of struc-

ture-forming cation which hinders the movement in the channels; when passing from K to Tl, this can also be explained by the fact that it is difficult for Tl to move in the channels of the structure. Low activation energy of conductance (E_a) and rather high ion conductivity allow us to consider triple molybdates as solid electrolytes. The compounds containing *d*-elements with variable valence state (for example, Mn) fall out of the regularity revealed. Triple molybdates containing Mn should have ion conductivity between that of Zn and Cd, but in reality the electron constituent increases with temperature due to Mn valence changes.

It should be stressed that thallium-containing compounds 1 : 1 : 1 are not isostructural to potassium molybdates of the same composition and exhibit the conductivity different from that of potassium (see Table 2). The compounds $TlA_{0.5}Zr_{0.5}(MoO_4)_2$ ($A = Mg, Zn, Cd$) are related to the structural type of $KZn(MoO_4)_2$ where A and Zr atoms occupy statistically the positions that are characterized by octahedral coordination, Tl atoms occupy the positions of potassium atoms and Mo atoms find themselves in the same tetrahedral positions [7].

The compounds obtained can be used as electrode materials with mixed electron-ion conductivity since they exhibit a complex of useful properties (strength and high ion conductivity).

CONCLUSION

The studies of temperature dependence of SOH revealed the occurrence of segnetoelectric phase transitions in double molybdates of thallium (I) and bivalent metals (Pb, Zn) possessing non-central symmetric structures, as well as in

the tungstates of single- and quadruple-valent elements with the structure of the HTB type. The studied electrophysical properties of new triple molybdates of single-, double- and quadruple-valent elements (low conductivity activation energies and rather high ion conductivity) allow to consider them as solid electrolytes.

The changes of phase composition in the systems $Me_2MoO_4 - AMoO_4 - Zr(MoO_4)_2$ provide the possibility to vary the contributions from the electron and ion conductivities, depending on the goal to be followed. Electrophysical properties of double and triple molybdates are the evidence that they are promising as segnetoelectrics, solid electrolytes and other materials.

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