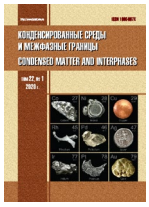

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Obtaining Iron (III) – Containing Triple Molybdate $K_5FeZr(MoO_4)_6$ by Sol-Gel Technology

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Abstract

Oxide compounds, as the basis of promising materials, are used in various fields of modern technologies due to their electrical and optical properties. Some of them, possessing a combination of ferroelectric, scintillation, electrical, and optical properties, are being studied as promising materials for electronics. In this case, their dispersion plays an important role.

Traditionally, the synthesis of oxide compounds is carried out by ceramic technology. More promising for the synthesis of fine powders are the methods of "soft" chemistry, among which we have identified and applied the sol-gel method. In this method, "mixing" occurs at the molecular level, which contributes to an increase in the reaction rates and a decrease in the synthesis temperature. The method involves the use of inorganic salts as precursors in combination with complexing agents (citric acid). The use of such precursors allows one to achieve high uniformity at relatively low temperatures. A feature of this approach is the use of fewer organic compounds: an aqueous solution of citric acid is used as a chelating agent. The aim of this work was to obtain triple molybdate by sol-gel technology (SGT) based on the example of iron-containing potassium zirconium molybdate.

The iron-containing triple potassium zirconium molybdate was obtained using the of citrate sol-gel technology and solid-phase synthesis (SPS) methods. The triple molybdate obtained by two methods was characterized by X-ray phase analysis, DSC, and impedance spectroscopy.

The developed sol-gel synthesis technique allowed lowering the synthesis temperature, to obtain triple molybdate with high values of homogeneity, dispersion, and electrical conductivity. This technique can be used to obtain double and triple zirconium (hafnium) molybdates containing a trivalent cation.

Keywords: iron-containing, triple molybdate, zirconium, potassium series, sol-gel synthesis.

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1. Introduction

Molybdates of different valence elements are of interest due to their ion-conducting [1–7] and luminescent properties [8–15]. The methods developed to date for obtaining new promising molybdates are very diverse [16-18]. The most common method for the preparation of triple molybdates is solid-phase synthesis, which is characterized by the simplicity of the experiment. The main disadvantage of this method is the high temperature and duration of the synthesis. An alternative methods are the so-called "soft chemistry" or solution methods: sol-gel, precipitation from aqueous solutions, etc. Solution methods allow obtaining nanoscale objects and significantly reduce both the temperature and the duration of synthesis.

Now, special attention is paid to finely dispersed and nanodispersed materials. The reduction of the particle size of the compounds allows to obtain materials with unique properties (optical, ion-conducting, etc.).

The aim of this work was to obtain triple molybdate by solid-phase synthesis (SPS) and sol-gel technology (SGT) using the example of iron-containing potassium zirconium molybdate.

2. Experimental

For the synthesis of triple molybdate $K_5FeZr(MoO_4)_6$ we have developed a sol-gel method based on a citrate gel. Potassium nitrate KNO_3, iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$ (CP) , zirconyl nitrate $ZrO(NO_3)_2 \cdot 2H_2O$ and ammonium paramolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were used as starting materials, citric acid was used as a complexing agent. The sol-gel synthesis scheme is shown in Fig. 1. Stoichiometric amounts of the source components were dissolved in distilled water.

Prepared solutions of potassium and iron nitrates, zirconium and ammonium paramolybdate were added to the citric acid solution with the formation of metal-citrate complex. The resulting solution was evaporated at a temperature of 70–80 °C until the solution passed into a sol and then into a gel. The resulting gel, which was a translucent mass, was first dried in the oven at a temperature of ~100–150 °C until the water was completely removed, and then it was dried in the furnace at a temperature of 200 °C for the conversion into a xerogel. Xerogel was an amorphous mass that was easily ground into powder in a mortar. Molybdate powders $K_5FeZr(MoO_4)_6$ (no.1) were obtained after annealing in the furnace at a temperature of 500–550 ° C.

Along with the synthesis of $K_5FeZr(MoO_4)_6$ using sol-gel technology, this molybdate was obtained using ceramic technology.

For solid-phase synthesis, commercial reagents K_2MoO_4 (CP), $Fe(NO_3)_3 \cdot 9H_2O$ (CP), MoO_3 (P.A.) and $ZrO(NO_3)_2 \cdot 2H_2O$ (P.A.) were used the starting materials. Molybdate $Fe_2(MoO_4)_3$ was obtained by solid-phase synthesis from molybdenum trioxide and iron nitrate by annealing at 400–800 °C for

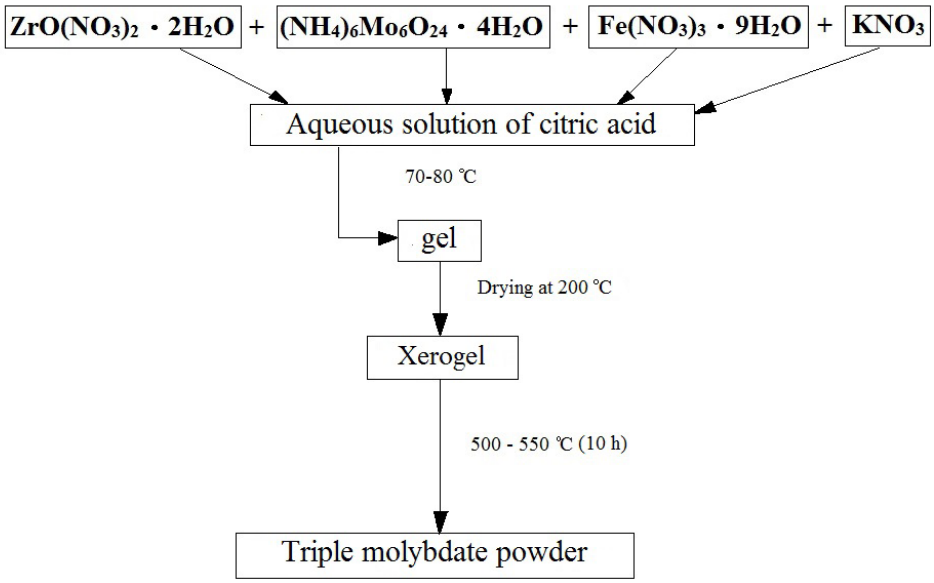

Fig. 1. Sol-gel synthesis scheme

150 h and intermediate homogenization of the samples. Synthesis of $Zr(MoO_4)_2$ was carried out according to the solid-phase method by stepwise annealing of a stoichiometric mixture of zirconyl nitrate and molybdenum trioxide in the temperature range of 450–750 °C for 100–150 h. Triple molybdate $K_5FeZr(MoO_4)_6$ (sample no. 2) was obtained using ceramic technology by annealing stoichiometric amounts of reaction mixtures K_2Moo_4, $Fe_2(MoO_4)_3$ and $Zr(MoO_4)_2$ in the temperature range 400–550 °C with a stepwise increase in temperature with a step of 50 °C and homogenization before each change in the heat treatment mode.

The powders of samples 1 and 2 obtained after annealing were studied by X-ray diffraction analysis (XRD) on a D8 Advance diffractometer (Bruker) using Cu*K*α radiation.

The diffractogram of the synthesized molybdate sample no. 2 (solid-phase synthesis) coincides with the diffractogram of the powder of sample no. 1 (sol-gel method).

Thermal analysis was performed on a NETZSCH STA 449 F1 Jupiter device. The recording was carried out in an argon atmosphere in platinum crucibles.

Electron microscopic studies of the samples were performed using a scanning electron microscope "Hitachi-3400N". The accelerating voltage was 20 keV, the operating distance was 10 mm.

3. Results and discussion

The diffractogram (no. 2) obtained during X-ray phase analysis $K_5FeZr(MoO_4)_6$ is shown in Fig. 2.

According to XRD data, synthesized molybdate $K_5FeZr(MoO_4)_6$ (sample no. 2) was isostructural to triple molybdate $Rb_5FeHf(MoO_4)_6$ [19] and crystallizes in the hexagonal system $P6_3$, Z = 2. The identification of parameters of the unit cells of the obtained phases was performed using single crystal data of the isostructural compound. The calculation was carried out according to the uniquely indexed lines of powder XRD patterns of triple molybdate using the TOPAS 4.2 software package. The parameters of unit cells are presented in the Table.

The thermal characteristics of the obtained compounds were studied by differential scanning calorimetry (DSC) in the temperature range 25–750 °C using NETZSCH STA 449 F1 Jupiter device. On the DSC curves of molybdate (sample no. 2) (Fig. 3), two endothermic effects were recorded. The first endothermic effect should be attributed to the presence of a polymorphic transition in the sample. The second endothermic effect on the DSC curves corresponded to the melting point. The compound melted incongruently. The same effects were recorded for molybdate (sample no. 1).

The morphology of the products was studied using scanning electron microscopy, which allowed estimating the particle size.

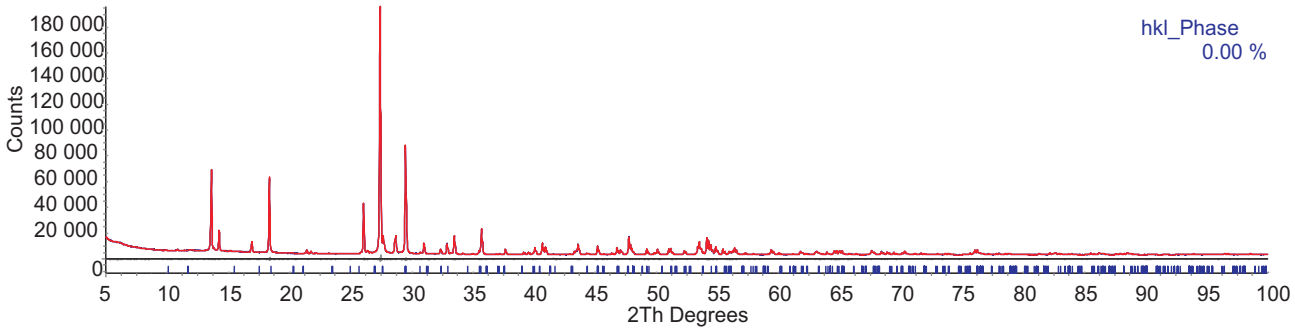

Fig. 2. The results of processing X-ray diffraction pattern of sample no. 2 of the composition $K_5FeZr(MoO_4)_6$ using the TOPAS 4.2 software package: blue line – experimental data; red line – calculated profile; strokes correspond to interplanar distances; the curve below is the difference between the experimental and calculated values

Table. Crystallographic and thermal characteristics of $K_5FeZr(MoO_4)_6$ (sample no. 2)

Compound	Unit Cell Parameters			T phase change	T melting
	a, Å	*c*, Å	*V*, Å^3		
$K_5FeZr(MoO_4)_6$	10.088(1)	15.089(1)	1330.0(3)	554	668

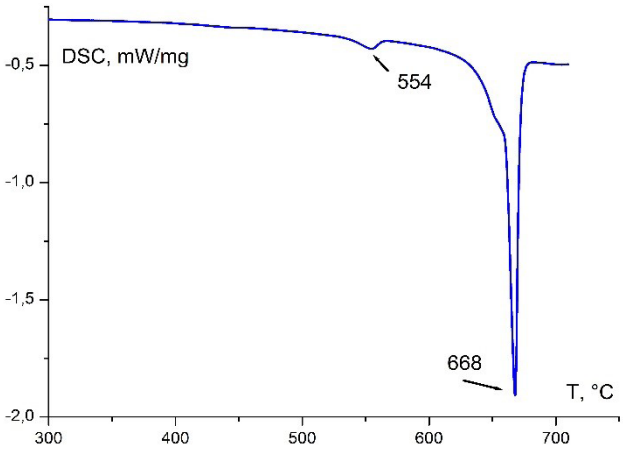

Fig. 3. DSC curve for $K_5FeZr(MoO_4)_6$ sample (no. 2)

Electron microscopic examination of samples $K_5FeZr(MoO_4)_6$ obtained by solid-phase synthesis showed that the compounds are spherical particles with sizes from ~ 1 to ~ 6 μm. Samples of $K_5FeZr(MoO_4)_6$ obtained by sol-gel technology, consist of spherical particles with sizes from ~ 0.2. up to ~ 4 mm as can be seen on microphotographs (Fig. 4).

Temperature and frequency conductivity dependencies of $K_5FeZr(MoO_4)_6$ (sample no. 1) was investigated in the temperature range 473–863 K using a "Z-1500J" impedance meter in heating and cooling modes (2 K/min) at a frequency in the range of 1 Hz – 1 MHz.

Molybdate $K_5FeZr(MoO_4)_6$ was obtained by two methods in the form of a powder was compressed under pressure into tablets in the form of disks with the diameter of 10 mm and thickness of 1–2 mm. These tablets were annealed at 550–600 °C for 10 h. Electrodes were applied to the surface of the disks by firing with platinum paste before measurements. The temperature dependence of the conductivity $K_5FeZr(MoO_4)_6$ (sample no. 1) in Arrhenius coordinates is shown in Fig. 5. When the sample is heated, an abrupt increase in conductivity occurred in the phase transition region (880–900 K), reaching a value of $10^{-2.5}$ S/cm, which is an order of magnitude higher than the conductivity of $K_5FeZr(MoO_4)_6$ (sample no. 2), obtained by solid-phase synthesis (Fig. 6).

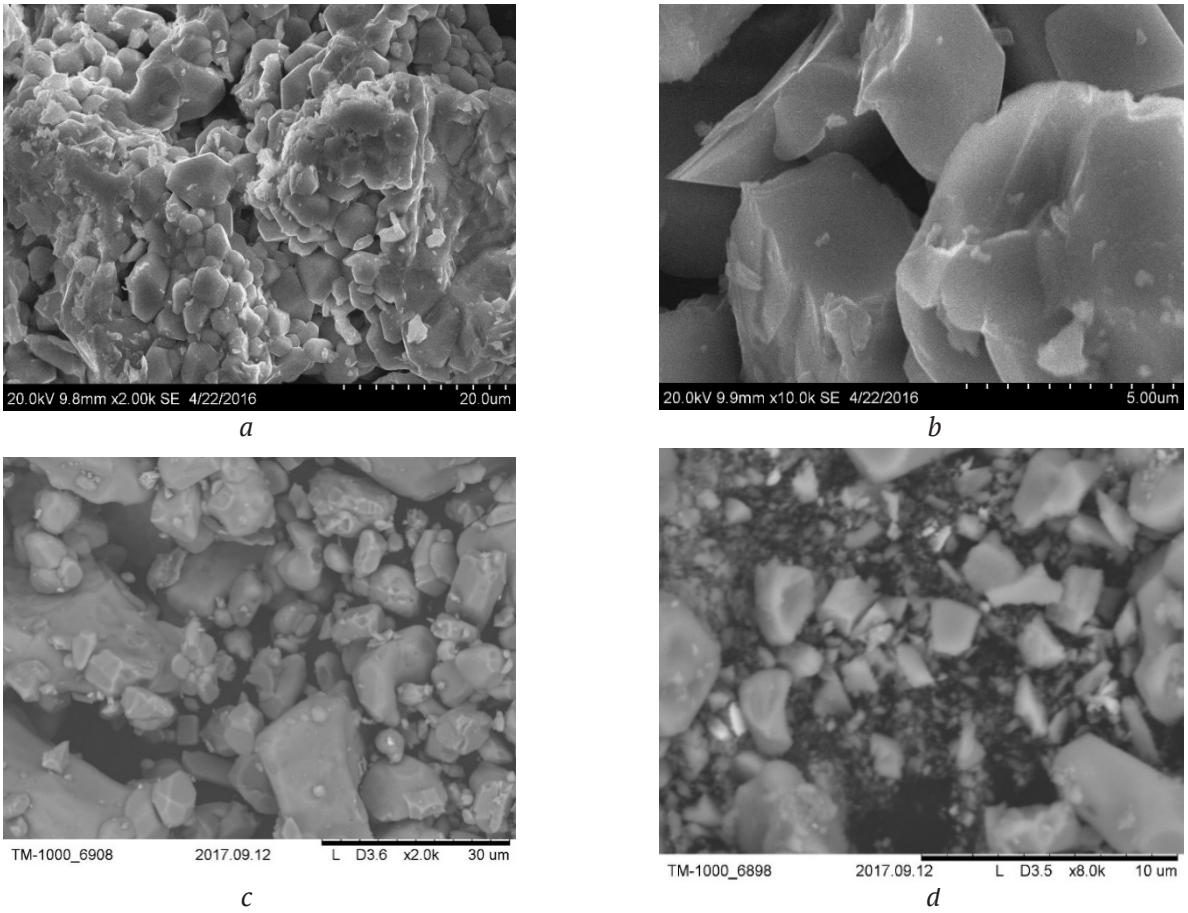

Fig. 4. Microphotographs of $K_5FeZr(MoO_4)_6$ samples obtained solid-phase synthesis (a, b) and sol-gel technology (c, d)

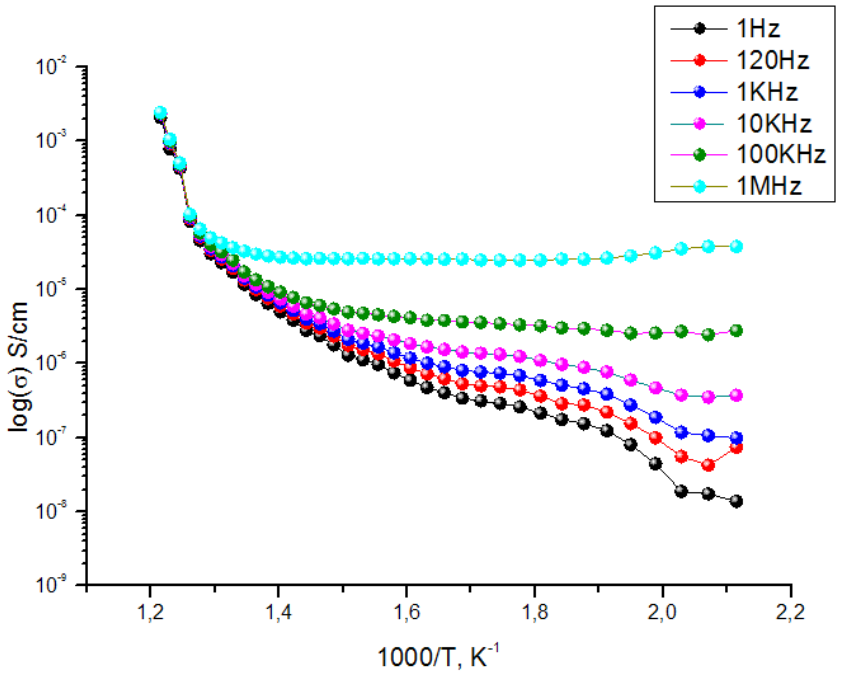

Fig. 5. Temperature dependence of conductivity $K_5FeZr(MoO_4)_6$ (sample no. 1) obtained by sol-gel technology

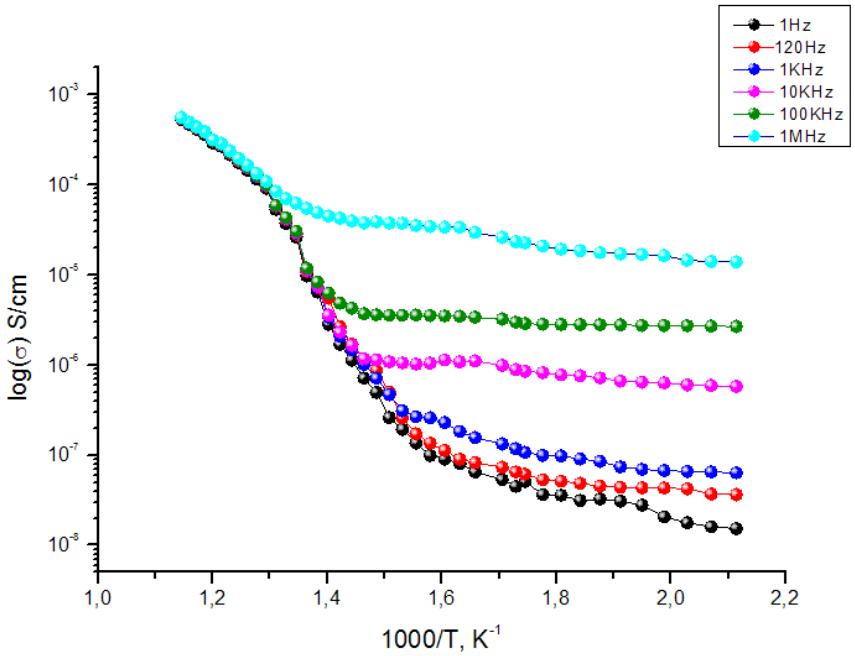

Fig. 6. A fragment of the temperature-frequency dependence of the conductivity $K_5FeZr(MoO_4)_6$ (sample no. 2) obtained by solid-phase synthesis

4. Conclusions

A sol-gel method for the synthesis of triple molybdates $M_5RZr(MoO_4)_6$ (R = trivalent metals) based on the for example of $K_5FeZr(MoO_4)_6$ was developed. Iron-containing triple molybdate was obtained by two methods: ceramic and sol-gel technology.

Studies of the obtained molybdates by X-ray diffraction analysis, DSC, electron microscopy, and impedance spectroscopy showed that the compounds crystallize in the hexagonal syngony, in the space group $P6_3$, Z = 2, undergoing a phase transition at 554 °C and melt incongruently at 668 °C. The molybdate obtained by the sol-gel

technology consists of particles with sizes from ~ 0.2 to ~ 4 μm. The developed technique for the synthesis of sol-gel technology, in comparison with ceramic technology, allows not only to reduce the synthesis temperature, but also to obtain compounds in a nanodispersed state with high electrical conductivity. The electrical conductivity of this molybdate is an order of magnitude higher than the conductivity of molybdate obtained by ceramic technology.

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Conflict of interest

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

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