A Facile Synthesis and Investigation of Na$_8$[ZrErNd(MoO$_4$)$_9$] Complex

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Article info	Abstract
	The continuous growth of rare earth elements (REE) value and the widespread use of molybdates in medicine and various industries and technologies determine the ever-increasing interest in this type of material. In this research, the interactions in the ZrOCl$_2$-Er$_2$Cl$_3$-NdCl$_3$-Na$_2$MoO$_4$-H$_2$O multicomponent system at a temperature of 20 °C were studied by the method of residual concentrations well known as Tananaev's or so-called apparent volume method. It was shown that a chemical reaction takes place in the system under study, resulting in the formation of a complex molecule that is insoluble in water. A detailed physicochemical study (X-ray diffraction, IR spectroscopy, thermal analysis) of the formed material was carried out. For the first time, it was possible to obtain rare earth element's molybdates in the form of Na$_8$[ZrErNd(MoO$_4$)$_9$]·3.86H$_2$O complex material by low cost and low-temperature method.

1. Introduction

The modernity of this research is conditioned by the growing value of rare earth elements (REE), zirconium compounds and the widespread use of molybdates in medicine and various industries and technologies.

Zirconium compounds attract huge attention conditioned with the development of new areas of science, modern technologies and medicine [1]. It is known that zirconium oxyhydrate hydrogels have antimicrobial activity against some pathogenic microorganisms, such as *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*. The detected bactericidal effect can be used to create new antimicrobial agents. Synthetic and semi-synthetic antibiotics currently used as bactericidal preparations have certain disadvantages, namely, a pronounced toxic effect on many human organs and systems [2].

Molybdenum is a biologically important element found in small amounts in various tissues of animals and plants. Note that molybdenum is a component of xanthoxidase, an enzyme that accelerates nitrogen, in particular purine metabolism in the body [3].

REE molybdates (Ln-molybdates) have high ionic and electronic conductivity, luminescent, ferroelectric and piezoelectric properties; their scope is constantly expanding. The importance of REE molybdates is also due to their utilization for solving environmental problems associated with radiometric studies of the environment [4–6].

REE do not belong to classical biomaterials; however, it is known that they are capable of exhibiting some biological activity [7]. Back in 1897, the antimicrobial effect of a number of REE salts was reported in the treatment of tuberculosis and leprosy. Since the 1920s it is known about the ability of REE salts to prevent blood clotting. As for other types of pharmacological action of REE compounds on the body, it is reported that a number of REE compounds reduce blood pressure, and lower serum cholesterol and glucose levels [8].

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Heterometallic complexes formed by Zr, Er, Nd are also of great interest in organometallic catalytic processes. Due to their potential novel properties and reactivity not available to homometallic species, heteromultimetallic complexes of these metals are of interest [9]. These might result from the interaction between the two different metals. Rare-earth metal transition metal hydride complexes have been studied for almost 30 years, but there are still only a few of them [10].

In our daily lives, intermetallic hydrides of rare-earth metals and transition metals are crucial. These substances are specifically used in batteries or as hydrogen storage materials. Such intermetallic compounds' molecular analogues might prove to be intriguing substitutes for both of these uses, among others [11].

Coordination compounds of lanthanides are highly monochromatic, which is of fundamental importance in the development of RGB systems, lasers, and special selective labels [12–14]. In medicine, solid-state neodymium (Nd: YAG) and erbium (Er: YAG) lasers are actively used [15].

The purpose of this work is for the first time to develop a provident, low-temperature and low-cost method for the synthesis of Na$_8$[ZrNdEr(MoO$_4$)$_9$] new complex material, as well as to study some of its physicochemical properties to find out its potential application sphere.

The residual concentrations method by I.V. Tananaev [16] was used to study the interaction in ZrOCl$_2$-ErCl$_3$-NdCl$_5$-Na$_2$MoO$_4$-H$_2$O multicomponent system. The essence of this method is to determine the composition of the precipitate obtained as a result of a chemical reaction [17–18]. It is sufficient to have data on the chemical analysis of the initial solutions and filtrates obtained after the equilibrium between the precipitate and the solution is established. This method is also known as "apparent volume method" in the literature.

Previously, we synthesized simple RE molybdates containing Er and Nd. A phenomenological study of these simple molybdates was carried out to reveal their thermoluminescent properties. It is assumed that the complex material synthesized within this research can be used in laser and medical technologies. Nd exhibits a small but significant TL response. There is an assumption that modified Nd compounds can be used for dosimetry of intense fluxes of ionizing radiation in the range of $10^5 \div 10^7$ rad. During the RTL study, Er showed an insignificant response, but it has not been fully studied [19].

2. Experimental part

Na$_2$MoO$_4$·2H$_2$O (≥99.5%, Merck, Germany), ZrOCl$_2$·8H$_2$O (98%, Merck, Germany), ErCl$_3$·6H$_2$O (99.995%, Merck, Germany), NdCl$_3$·H$_2$O (≥99.99%, Sigma Aldrich, USA) were used as raw materials. The concentrations of all initial solutions were 0.3 M. The concentration of (MoO$_4$)$^{2-}$ (Mo) in the initial and equilibrium solutions was determined using the complexometric titration method [20], and the concentration of Zr^{4+}, Er^{3+} and Nd^{3+} was determined by the gravimetric method [21].

The reaction between ZrOCl$_2$, ErCl$_3$, NdCl$_3$ and Na$_2$MoO$_4$ in an aqueous media was carried out as follows: a solution of sodium molybdate was filled in a beaker with a volume of 25 ml and solutions of ZrOCl$_2$, ErCl$_3$, NdCl$_3$ were added in such a way as to satisfy the molar ratios of 1:1:1:9 according to the calculation of the chemical reaction. The concentrations of Zr, Er, Nd in the initial aliquots were the same (in mole fractions).

The onset of equilibrium of the chemical reaction was established by the results of systematic observation of the sediment's height and periodic analysis of the control sample of the liquid phase based on the features of composition and the solution's pH relationship. After equilibrium was established, the solid phase was separated from the filtrate, thoroughly washed with deionized water several times and dried in an oven at a temperature of 90–100 °C.

The complete composition of the sediment was determined after the physicochemical study. X-ray diffraction analysis (XRD) of the obtained material was carried out by powder-XRD method on a Bruker D8 Advance diffractometer with CuKα radiation and Ni filter (Bruker, Germany). IR spectra were obtained on a Specord 75IR (Carl Zeiss, Germany) spectrophotometer in the frequency range of 400–4000 cm^{-1}. For IR analyses the samples were prepared in the form of tablets with KBr.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses were studied on a STA 449F1 Jupiter (Netzsch, Germany) simultaneous thermal analysis setup in an argon (Ar) atmosphere of grade 5.0 (99.999%). The instrument was calibrated in terms of temperature and sensitivity using metal standards. Permissible measurement

error: DSC baseline reproducibility ±1 μV; limit of permissible absolute error of temperature measurement: ±1.5 °C; limit of the permissible relative error in measuring the specific heat of phase transitions: ±3.0%. The reactive powder mixture (20–35 mg; the sensitivity of the scales is 50 ng) was placed into the platinum crucible with lids. The type of measurement was sample + correction. The empty crucible data obtained under identical conditions was used as a correction file. Before the experiment, a cycle of evacuation-filling with Ar of the internal volume of the balance and furnace was carried out. Then, after the pressure was balanced and stabilized, the measurements were carried out according to the following program: thermostatic at 30 °C (10 min) → heating to 1430 °C → cooling to 40 °C. The rate of heating-cooling to a given temperature was 20 °C min^{-1}. The carrier gas flow rate during the experiment was 50 ml min^{-1}.

3. Results and discussion

Equilibrium in the system under study is reached after 17 days. Then the solutions were kept for another 3 days to make the results reliable. According to the results, the amount of precipitate does not change (Table 1). The pH of equilibrium solutions was 3–4, the temperature - 20 °C, and the color of the precipitate was steel gray. The resulting precipitate was separated, washed and dried for further analysis.

Based on the data of chemical analysis of the initial and equilibrium solutions, the ratio of Zr:Er:Nd:MoO$_3$ in the precipitate was determined, which corresponds to the formula of Na$_8$[ZrErNd(MoO$_4$)$_9$] (Table 2).

According to the results of XRD analysis (Fig. 1), the blunt-edged peaks are characterized by relatively large half-widths, typical of nanomaterials with very small particle sizes.

The results of IR spectroscopic study of the obtained material are shown in Fig. 2. The absorption bands of water in the molecular form are observed in the IR spectrum. A rather broad band ν(H$_2$O) with a peak at ≈3438.87 cm^{-1} (typical for stretching vibrations of associated HOH hydroxyls) was registered, which was attributed to water of crystallization; bands at 1630.81 cm^{-1}, 1576.53 cm^{-1} corresponded to bending vibrations of δ(H$_2$O) [22].

The IR spectrum also shows absorption bands at 2923.76 cm^{-1} and 2847.56 cm^{-1} (the frequency of antisymmetric doubly degenerate stretching vibrations νSOH+νEOH [23]; the bands at 1115.45 cm^{-1} and 1140.67 cm^{-1} are attributed to vibrations of the hydronium ion ν$_α$(OH^{3+}) [19, 23]. Analysis
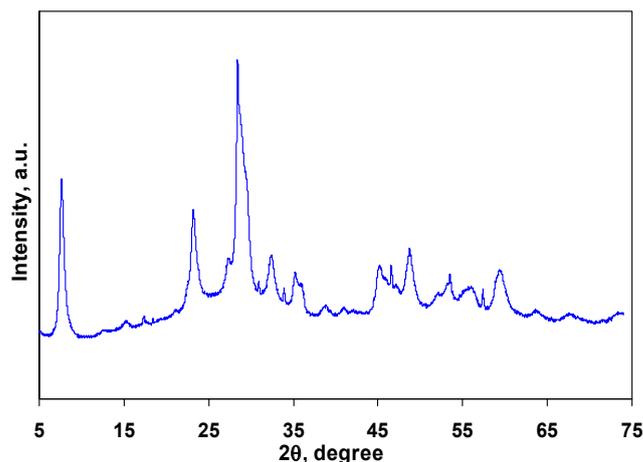
Fig. 1. X-ray diffraction pattern of the dried sediment.

Table 1
Apparent volume of precipitation, ml

Apparent volume of precipitation, ml	Period, days						
	7	9	12	15	17	19	20
	8.5	8.1	7.5	7.45	7.42	7.42	7.42
	8.4	7.95	7.6	7.47	7.42	7.42	7.42

Table 2
Chemical analysis data for the ZrOCl$_2$-ErCl$_3$-NdCl$_3$-Na$_2$MoO$_4$-H$_2$O system

MoO$_3$ in initial solution		MoO$_3$ in sediment		Zr^{4+}, mol·L^{-1}		Er^{3+}, mol·L^{-1}		Nd^{3+}, mol·L^{-1}	
g L^{-1}	mol L^{-1}	g L^{-1}	mol L^{-1}	solution	sediment	solution	sediment	solution	sediment
129.6	9	128.3	8.9	1	0.99	1	0.99	1	0.99
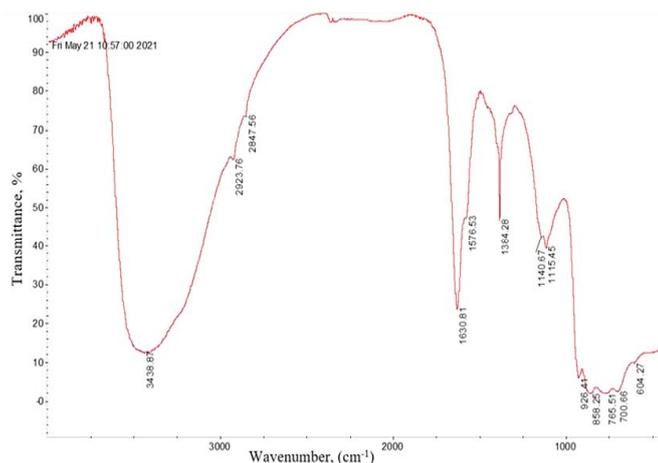
Fig. 2. IR spectrum of the dried sediment.

of the IR spectrum indicates that some of the water molecules are included in the structure of the synthesized compound and are not surface adsorbed. The IR spectrum also clearly shows absorption bands corresponding to internal vibrations of the $(MoO_4)^{2-}$ group. The absorption band at 941.46 cm^{-1} corresponds to the maximum high-frequency stretching vibration of the undistorted tetrahedral anion – $\nu_1(A_1)$ [MoO$_4$]$^{2-}$. There is also an absorption band at 858.25 cm^{-1}, which corresponds to degenerate vibrations $\nu_3(F)$ [MoO$_4$]$^{2-}$ (indicating partial removal of degeneracy as a result of intermolecular interactions). The absorption bands at 765.51 cm^{-1}, 700.66 cm^{-1}, and 604.27 cm^{-1} correspond to the three times degenerate antisymmetric stretching vibration [MoO$_4$]$^{2-}$-$\nu_3(F_2)$ (ν_{as}) [24–25].

The obtained sample was also subjected to thermal analysis (TG/DSC) in the temperature range of 20–1400 °C. As can be seen from Fig. 3, all transformations detected during the heating consist of two or three inseparable thermal effects. Transformations 1 and 2 are accompanied by weight loss. The temperature intervals for measuring the weight loss were chosen based on the data of the DTG curve.

According to the results obtained, the process of dehydration of the complex material begins already at low temperatures (100–329.8 °C, endothermic effect 1, peaks a, b, c; appropriate weight loss is 8.34%) and is most likely associated with the evaporation of humidity and adsorbed water. Effect a with a peak at 142 °C is formed in the range of 84.5–159.7 °C and has a value of -44.87 J g^{-1}. Effect b with a peak at 200.4 °C is registered in the range of 159.7–257.9 °C and has a value of -122.1 J g^{-1}. And finally, effect d with a peak at 281.0 °C is detected in the range 257.9–329.8 °C and is described with a value of 31.93 J g^{-1}.

In the temperature range of 533.4–633.4 °C an exothermic effect 2 is observed (peaks d, e, f) with a total weight loss of 3.68%, apparently corresponding to the removal of crystallization water. The effect d has a peak at 551.2 °C (533.4–570.4 °C temperature domain) and is described with a value of +24.75 J g^{-1}. The effect e with a peak at 582.4 °C and effect f with a peak at 614.5 °C are detected at temperature stages 570.4–599.3 °C and 599.3–633.4 °C with values of +20.66 J g^{-1} and +26.85 J g^{-1}, respectively.
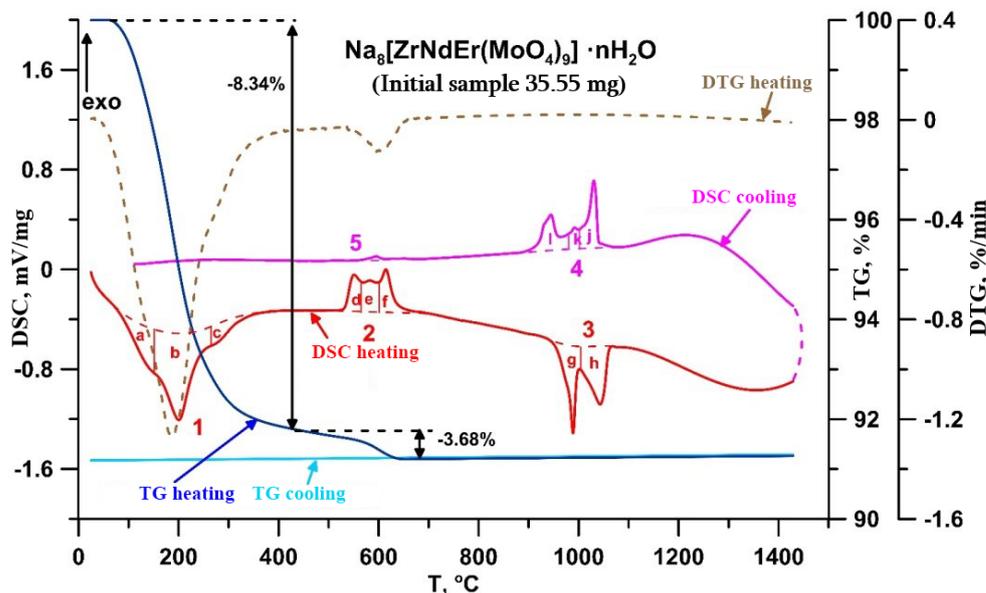
Fig. 3. Thermal analysis results of Na₈[ZrNdEr(MoO₄)₉] · nH₂O.
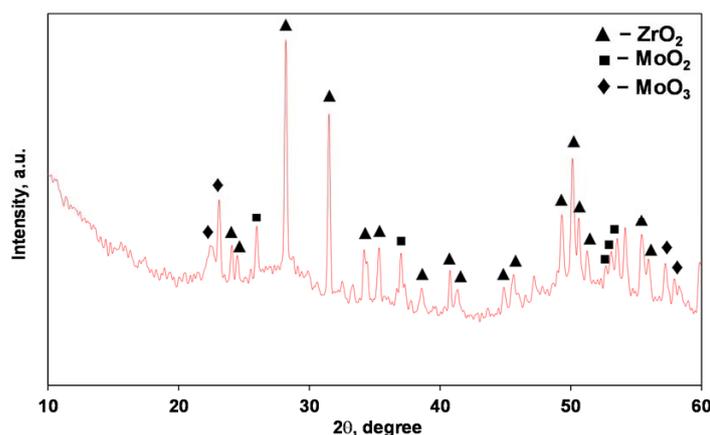
Fig. 4. XRD pattern of the sediment after thermal treatment.

Upon further heating above 900 °C, two endo-thermic effects 3 were registered (peaks g and h), which, upon cooling, are turning into three exo-thermic effects (j, k, and l). This stage is not accompanied by weight loss, apparently due to the structural changes (polymorphic transformation) in the sample. The effect g has a peak at 988.8 °C (975.0–1002.5 °C temperature domain) and is described with a value of 55.32 J g^{-1}. The effect h with a peak at 1043.1 °C is formed in the range of 1002.5–1060.1 °C (-62.78 J g^{-1}). Upon further cooling up to 610 °C, the sample is thermally stable.

According to the weight loss data of the sample, the amount of water of crystallization in the studied sample is 3.86 H_2O molecules per formula unit, i.e. the formula of the synthesized complex material should be written as $Na_8[ZrErNd(MoO_4)_9]\cdot3.86H_2O$.

The XRD pattern of residual crystals after cooling is given in Fig. 4. According to the results obtained, the presence of zirconium and molybdenum oxides (ZrO_2, MoO_2, MoO_3) was detected. It is supposed, that erbium and neodymium oxides are placed in the crystal lattice of molybdenum and zirconium oxides and most probably a solid solution was formed.

Thus, applying Tananaev's well-known method, it was possible for the first time to synthesize fine-grained complex material, which was investigated by certain physicomechanical methods to determine the composition of the substance, its stability in a certain temperature range, as well as the amount of crystallization water.

4. Conclusions

In this work, the multicomponent $ZrOCl_2$-ErCl$_3$-NdCl$_3$-Na$_2$MoO$_4$-H_2O system was studied by the method of residual concentrations (Tananaev method) at room temperature (20 °C). It has been established that a chemical reaction occurs in the system under study with the formation of a water-insoluble complex compound. TG/DSC and IR examinations reveal the composition of the material obtained with the formula of $Na_8[ZrErNd(MoO_4)9]\cdot3.86H_2O$. Thus, for the first time, a low-cost and low-temperature method was suggested for the synthesis of previously unknown complex REE molybdate.

Acknowledgements

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