Physicochemical Analysis of Inorganic Systems

PHASE TRANSFORMATIONS IN THE $KNd(SO_4)_2{\cdot}H_2O–SrSO_4{\cdot}0.5H_2O$ SYSTEM WHEN HEATED TO A TEMPERATURE OF 1000°C

© 2025 N. N. Bushuev*, G. K. Tatosyan

Mendeleev Russian University of Chemical Technology, Moscow, 125047 Russia

**e-mail: nbushuev@muctr.ru*

Received June 29, 2024

Revised October 10, 2024

Accepted October 17, 2024

X-ray phase and thermogravimetric analysis methods, the existence of three crystalline hydrate modifications of the composition $KNd(SO_4)_2{\cdot}H_2O$ has been established, and the parameters of their unit cells have been determined. Dehydration during the heating of $KNd(SO_4)_2{\cdot}H_2O$ at a temperature of 250°C leads to the formation of a partially dehydrated modification with an approximate composition of $KNd(SO_4)_2{\cdot}0.2H_2O$. Further heating to 400°C results in complete dehydration with the formation of an anhydrous monoclinic modification of $KNd(SO_4)_2$. The high-temperature triclinic modification of $KNd(SO_4)_2$ exists in the temperature range of 635 – 900°C and decomposes when heated above 900°C. The trigonal modification of $KNd(SO_4)_2{\cdot}H_2O$ forms solid solutions with the crystal matrix of $SrSO_4{\cdot}0.5H_2O$. The anhydrous modifications of $KNd(SO_4)_2$ do not form solid solutions with the anhydrous orthorhombic modification of $SrSO_4$.

Keywords: strontium sulfate, potassium and neodymium double sulfate, solid solutions, crystallization

DOI: 10.31857/S0044457X250112e5

INTRODUCTION

Rare earth elements (**REE**) La, Ce, Nd are contained in phosphogypsum waste from the production of extraction phosphoric acid in amounts of 1.5-2 wt.%. The search for mineral sources of REE, including those based on industrial waste from the production of extraction phosphoric acid, is an urgent task. Phosphogypsum waste also contains up to 2 wt.% Sr. These impurities negatively affect the binding properties of construction materials based on gypsum ($CaSO_4{\cdot}2H_2O$) and hemihydrate ($CaSO_4{\cdot}0.5H_2O$) products. The influence of REE and Sr on the joint crystallization of sulfate modifications with calcium sulfate is poorly understood and is of scientific and practical interest. The concurrent extraction of REE and Sr during the formation of phosphogypsum waste and its utilization is also of great importance.

Rare earth elements are widely used in the technology of manufacturing electronic materials, lasers, quantum generators, and magnetic materials [1-8]. Of particular interest is Nd, contained in phosphogypsum waste at a level of 0.5-0.8 wt. %. In work [9], the binary system $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$ was studied, in which the existence of a wide homogeneity region was found in the concentration range of 100-20 mol. % based on isostructural trigonal (pseudohexagonal) modifications of $KNd(SO_4)_2 \cdot H_2O$ and $SrSO_4 \cdot 0.5H_2O$. The stabilizing influence of K, Nd, and Sr on the thermodynamic stability of these solid solutions has been established. It is known that $SrSO_4 \cdot 0.5H_2O$ [10, 11] exists only for 120 minutes, followed by complete dehydration of this crystalline hydrate to the known stable orthorhombic modification of $SrSO_4$. The stabilization of solid crystalline hydrate solutions is explained by heterovalent substitution of two Sr^{2+} ions with K^+ and Nd^{3+} ions. The substitution of the divalent Sr^{2+} ion with the trivalent Nd^{3+} ion in the SrO_9 polyhedron leads to strengthening of the bond with the crystalline hydrate water molecule included in the coordination sphere of this polyhedron due to increased electrostatic interaction. The synthesis and mechanism of stabilization of the crystalline hydrate modification of $SrSO_4 \cdot 0.5H_2O$ are described in work [12] using the example of heterovalent substitution of Sr^{2+} ions with K^+ and La^{3+} ions, which indicates that $SrSO_4 \cdot 0.5H_2O$ is a good absorbent of rare earth elements in the presence of K^+ ions. An equally important task is to study the possibility of reverse desorption of REE and K from Sr in the form of corresponding sulfates or oxides during thermal treatment of solid solutions $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$.

The purpose of this work is to study phase transformations during heat treatment of solid solutions $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$ up to a temperature of 1000°C.

EXPERIMENTAL PART

As starting reagents, 2 M solutions of KCl, $NdCl_3$ and $SrCl_2$ were used, prepared from reagents $NdCl_3 \cdot 6H_2O$, KCl and $SrCl_2 \cdot 2H_2O$ of "chemically pure" grade. The prepared solutions of KCl, $NdCl_3$ and $SrCl_2$ were mixed, modeling the system [KCl + $NdCl_3$]-$SrCl_2$ with a step of 5 mol. % followed by the addition of a calculated amount of 2 M sulfuric acid. The resulting precipitates were subjected to X-ray phase and X-ray spectral analysis.

The elemental composition was determined by X-ray fluorescence analysis using an EDX-7000 X-ray spectrometer. The exact chemical composition of the formed precipitates of solid solutions of the $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$ system is specified in [13], which provides the corresponding volumes of the mixed 2 M solutions of KCl, $NdCl_3$, $SrCl_2$ and H_2SO_4 and the methodology for X-ray fluorescence determination of the elemental content of potassium, neodymium, and strontium. Table 1 presents the chemical composition of the initial theoretical and actually formed precipitates of solid solutions in terms of the molar content of $KNd(SO_4)_2 \cdot H_2O$ and $SrSO_4 \cdot 0.5H_2O$.

As can be seen from Table 1, the composition of the real precipitates differs from the theoretical composition by a higher content of $SrSO_4 \cdot 0.5H_2O$ and, accordingly, a decrease in the content of $KNd(SO_4)_2 \cdot H_2O$ due to its higher solubility in aqueous solutions with the participation of forming HCl solutions. The chemical composition of the solid solution samples of the $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$ system corresponds to the formula $K_xSr_{2\text{-}2x}Nd_x(SO_4)_2 \cdot H_2O$. In the concentration region with high content (20–100 mol. %) of $KNd(SO_4)_2 \cdot H_2O$, the solid solution samples crystallize in the structural type of the trigonal modification of $SrSO_4 \cdot 0.5H_2O$. In the concentration region with low and insufficient content (0–10 mol. %) of $KNd(SO_4)_2 \cdot H_2O$, the solid solution crystallizes in the structural type of the orthorhombic modification of $SrSO_4$. In the narrow concentration region of 10–20 mol. % $KNd(SO_4)_2 \cdot H_2O$, the solid solution crystallizes in the form of two phases: based on the trigonal modification of $SrSO_4 \cdot 0.5H_2O$ and the orthorhombic modification of $SrSO_4$.

The phase composition of the samples was studied using an ARL Equinox-100 diffractometer (Cu K_α-radiation). The single-phase nature of the solid solution samples was confirmed by indexing the corresponding X-ray diffraction patterns. X-ray analysis of the diffraction line profiles and refinement of the unit cell parameters of the crystalline samples were carried out using a G-670 HUBER camera-monochromator (Cu K_α-radiation, measurement step 0.005°) and the WinX-POW software package (version 2.20.2006) from STOE. The accuracy of determining the unit cell parameters did not exceed 0.002 Å.

Then the samples were subjected to thermogravimetric and X-ray phase analysis after appropriate exposure of the samples at various temperatures in the range of 20–1000°C. Thermogravimetric analysis (DTA-DTG) and differential scanning calorimetry were performed on a Netzch STA 409PC synchronous thermal analyzer in dynamic mode in an air flow (30 ml/min) when heated to 1000°C at a rate of 1–5 degrees/min.

RESULTS AND DISCUSSION

The literature contains information about the existence of different crystalline hydrate modifications of $KNd(SO_4)_2 \cdot H_2O$. In [6], information is provided about the existence of a monoclinic crystalline hydrate modification of $KNd(SO_4)_2 \cdot H_2O$, and in [9], we synthesized a trigonal (pseudohexagonal) crystalline hydrate modification of $KNd(SO_4)_2 \cdot H_2O$. In [8], an anhydrous monoclinic modification of $KNd(SO_4)_2$ was obtained by hydrothermal synthesis, and in [14], another anhydrous modification – triclinic – was obtained as a result of solid-phase synthesis at high temperatures. In this work, we have for the first time synthesized a second type of monoclinic crystalline hydrate modification of $KNd(SO_4)_2 \cdot H_2O$ with parameters close to the parameters of the monoclinic cell of $KPr(SO_4)_2 \cdot H_2O$ [15].

The available information needs to be systematized and the phase transformations during thermal treatment of crystalline hydrate modifications of $KNd(SO_4)_2 \cdot H_2O$ and anhydrous modifications of $KNd(SO_4)_2$ need to be studied. As a result of the conducted research, we have established the existence of six types of crystal structures of crystalline hydrate and anhydrous modifications of double sulfate of potassium and neodymium with a 1:1 composition. The parameters of the elementary cells of these compounds are presented in Table 2 (the structural characteristics confirmed in this work and earlier are marked with an asterisk).

Phase transformations during heating proceed according to the following scheme: $KNd(SO_4)_2 \cdot H_2O$ (monoclinic) $\xrightarrow{70\text{–}80\,^{\circ}\mathrm{C}}$ $KNd(SO_4)_2 \cdot H_2O$ (trigonal) $\xrightarrow{220^{\circ}\mathrm{C}}$ $KNd(SO_4)_2 \cdot 0.2H_2O$ (monoclinic) $\xrightarrow{380\text{–}400\,^{\circ}\mathrm{C}}$ $KNd(SO_4)_2$ (monoclinic) $\xrightarrow{675\,^{\circ}\mathrm{C}}$ $KNd(SO_4)_2$ (triclinic) $\xrightarrow{900\,^{\circ}\mathrm{C}}$ (melting with decomposition).

At room temperature, there are two types of monoclinic modifications of potassium neodymium double sulfate monohydrate $KNd(SO_4)_2 \cdot H_2O$. Both modifications have almost identical X-ray patterns and differ in minor changes in intensity and angles of diffraction line profiles. The authors of [6] obtained a monoclinic modification at room temperature by exchange reaction of solutions of neodymium sulfate $Nd_2(SO_4)_3$ and KCNS with unit cell parameters: $a = 10.0500(5)$, $b = 8.5250(4)$, $c = 10.3597(5)$ Å, $\beta = 118.486(2)^{\circ}$ and determined its crystal structure by studying a single crystal. Most often, mechanical mixtures of two monoclinic modifications of $KNd(SO_4)_2 \cdot H_2O$ crystallize simultaneously. During the prolonged evaporation of dilute solutions of $Nd_2(SO_4)_3$ and K_2SO_4, we synthesized for the first time a modification of $KNd(SO_4)_2 \cdot H_2O$ and determined its unit cell parameters: $a = 10.8453(18)$, $b = 15.395(3)$, $c = 10.0310(16)$ Å, $\beta = 112.356(9)^{\circ}$ (Table 1). The obtained parameters of the monoclinic modification of $KNd(SO_4)_2{\cdot}H_2O$ agree well with the unit cell parameters of the isostructural monoclinic modification of $KPr(SO_4)_2{\cdot}H_2O$ reported in [15]: $a = 10.866$, $b = 15.361$, $c = 10.031$ Å, $\beta = 112.360^\circ$.

Table 3 presents the results of the X-ray pattern indexing of the second monoclinic modification of $KNd(SO_4)_2{\cdot}H_2O$ with *hkl* indices, similar to those for the monoclinic modification of $KPr(SO_4)_2{\cdot}H_2O$. The Smith-Snyder criterion ($F_{30}>15$, indexing correctness factor) was 17.9, which indicates the correctness of the indexing.

When heated to 70–90°C, the monoclinic modifications transform into a trigonal pseudohexagonal modification $KNd(SO_4)_2{\cdot}H_2O$ (sp. gr. $P3_121$) (Table 2) without visible thermal effects on the thermograms. The parameters of the elementary trigonal cell of $KNd(SO_4)_2{\cdot}H_2O$ ($a = 7.139(2)$, $c = 6.638(2)$ Å) were determined by us in work [9], which showed the isostructurality of the trigonal modification of $KNd(SO_4)_2{\cdot}H_2O$ with the trigonal modification of $SrSO_4{\cdot}0.5H_2O$ (Table 2), having elementary cell parameters $a = 7.1805(11)$, $c = 6.5936(8)$ Å [10]. The content of crystalline hydrate water in all three modifications of $KNd(SO_4)_2{\cdot}H_2O$ remains constant. The structure of $KNd(SO_4)_2{\cdot}H_2O$ consists of NdO_9 polyhedra, KO_8 and SO_4 tetrahedra. One oxygen atom of the water molecule enters the coordination sphere of NdO_9, the remaining eight oxygen atoms in the coordination sphere of NdO_9 simultaneously belong to the SO_4 tetrahedra.

The study of structural differences between trigonal and two monoclinic modifications of $KNd(SO_4)_2{\cdot}H_2O$ requires separate fundamental studies of single crystal structures, which are beyond the scope of this work. However, the results of this work, our work [9], and work [6] allow us to draw some preliminary conclusions. The strict alternation of NdO_9 and KO_8 polyhedra in the structure of the trigonal modification of $KNd(SO_4)_2{\cdot}H_2O$ is absent and is purely statistical in nature. Strict alternation of NdO_9 and KO_8 polyhedra would lead to a doubling of the parameter *c* of the trigonal (pseudohexagonal) unit cell compared to the similar parameter of the trigonal (pseudohexagonal) unit cell of $CaSO_4 \cdot 0.5H_2O$. Strict alternation of LaO_9 and KO_8 polyhedra has been established only for the structure of the trigonal cell of $KLa(SO_4)_2 \cdot H_2O$, where La is a *d* -element. It is known that Nd belongs to *f* -elements. The absence of strict alternation of LnO_9 and KO_8 polyhedra or the tendency toward partial ordering leads to distortion of the trigonal pseudohexagonal cell and lowering of symmetry to monoclinic. In this case, the 120 ° angle of the trigonal cell decreases to 118°–119° in the monoclinic cell for a number of $KLn(SO_4)_2 \cdot H_2O$ compounds (Ln = Nd, Sm, Eu, Gd, Dy), for which KSCN solution was used as the starting solution. In this work, a monoclinic modification of $KNd(SO_4)_2 \cdot H_2O$ with a monoclinic angle $\beta = 112.356°$ was synthesized, using KCl solution as the starting material.

It has been established that during the formation of solid solutions in the system $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$, joint crystallization and interaction occur only between the trigonal modifications of $KNd(SO_4)_2 \cdot H_2O$ and $SrSO_4 \cdot 0.5H_2O$. The monoclinic modifications of $KNd(SO_4)_2 \cdot H_2O$ do not participate in the formation of solid solutions with $SrSO_4 \cdot 0.5H_2O$ and transform into the trigonal modification of $KNd(SO_4)_2 \cdot H_2O$, forming a wide homogeneity region of solid solutions at room temperature in the system $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$. It has been found that even a small amount (0.5 mol. %) of $SrSO_4 \cdot 0.5H_2O$ stabilizes the trigonal modification of $KNd(SO_4)_2 \cdot 0.5H_2O$. The mutual stabilization of the trigonal modifications of $KNd(SO_4)_2 \cdot H_2O$ and $SrSO_4 \cdot 0.5H_2O$ is provided by heterovalent substitution of K^+ (1.39 Å) and Nd^{3+} (1.01 Å) ions with two Sr^{2+} (1.20 Å) ions [16] due to the structural similarity of $KNd(SO_4)_2 \cdot H_2O$ and $SrSO_4 \cdot 0.5H_2O$. This feature explains the high absorption capacity of the $SrSO_4 \cdot 0.5H_2O$ modification for isomorphic capture of Nd^{3+} ions in the presence of K^+ ions.

The dehydration process of the trigonal modification of $KNd(SO_4)_2 \cdot H_2O$ occurs in the temperature range of 180–400°C in two stages. Figure 1 shows the thermogram of a pure sample of $KNd(SO_4)_2 \cdot H_2O$. According to calculations, at the first stage at a temperature of 240–250°C, 0.8 mol. % H_2O is removed with the formation of a compound of approximate composition $KNd(SO_4)_2 \cdot 0.2H_2O$, whose X-ray diffraction pattern is very similar to that of the dehydrated monoclinic modification of $SrSO_4 \cdot x H_2O$ ($0 <\leq 0.1$) with unit cell parameters presented in Table 2.

Determination of the exact content of crystal hydrate water in the structural type $KNd(SO_4)_2 \cdot 0.2H_2O$ requires more detailed analysis using thermogravimetry. The unit cell parameters of $KNd(SO_4)_2 \cdot 0.2H_2O$ could not be determined due to the strong blurring of the diffraction line profiles in the X-ray pattern. Complete dehydration of $KNd(SO_4)_2 \cdot H_2O$ is completed at a temperature of 400°C with the formation of an anhydrous monoclinic modification of $KNd(SO_4)_2$ with unit cell parameters presented in Table 2.

Figure 2 shows the thermogram of a solid solution sample with theoretical composition of 30 mol. % $KNd(SO_4)_2 \cdot H_2O$ + 70 mol. % $SrSO_4 \cdot 0.5H_2O$ (the actual composition corresponds to 21.8 mol. % $KNd(SO_4)_2 \cdot H_2O$ + 79.2 mol. % $SrSO_4 \cdot 0.5H_2O$). The single-phase nature of the sample was confirmed by indexing the X-ray diffraction lines (Table 4). Unit cell parameters: $a = 7.175(1)$, $c = 6.599$ Å, $V = 294.2(1)$ Å^3.

Figure 3 shows the thermogram of a solid solution sample with theoretical composition of 70 mol. % $KNd(SO_4)_2 \cdot H_2O$ + 30 mol. % $SrSO_4 \cdot 0.5H_2O$ (the actual composition corresponds to 48.2 mol. % $KNd(SO_4)_2 \cdot H_2O$ + 51.8 mol. % $SrSO_4 \cdot 0.5H_2O$). The single-phase nature of this sample was confirmed by indexing the lines of its X-ray diffraction pattern (Table 5). The unit cell parameters: $a = 7.161(2)$, $c = 6.622(1)$ Å, $V = 294.2(1)$ Å^3. The unit cell parameters of all compositions of solid solutions in the $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$ system were previously reported by us in [9]. The theoretical and precise actual compositions of the solid solution samples in the $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$ system are presented in Table 1.

Thermograms of the existing solid solution samples in the $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$ system across the entire concentration range have similar patterns. Unlike the pure $KNd(SO_4)_2 \cdot H_2O$ sample, the dehydration of solid solution samples occurs in a single stage and is completed at a temperature of 300–350°C (Figures 2, 3). The amount of water removed during heating completely matches the theoretical calculations. Complete removal of crystalline hydrate water from the solid solution samples is completed at 400°C, resulting in the formation of two individual phases: the monoclinic anhydrous modification of $KNd(SO_4)_2$ with unit cell parameters shown in Table 2, and the well-known orthorhombic anhydrous modification of $SrSO_4$ with parameters $a = 8.377$, $b = 5.350$, $c = 6.873$ Å, as determined in [17].

In the temperature range of 200-250°C, there is a fairly strong dehydration of solid solution samples, during which the structure based on the trigonal modification of $SrSO_4 \cdot 0.5H_2O$ transforms into the structural type of monoclinic dehydrated modification of $SrSO_4 \cdot 0.1H_2O$. The phase transition of the monoclinic anhydrous modification of $KNd(SO_4)_2$ into the triclinic anhydrous modification of $KNd(SO_4)_2$ proceeds without mass loss, is not accompanied by a noticeable thermal effect, and remains practically undetectable on the thermogram (Fig. 1). To determine the temperature of the phase transition from the monoclinic anhydrous modification of $KNd(SO_4)_2$ to the triclinic anhydrous modification of $KNd(SO_4)_2$, we synthesized the monoclinic modification by long-term annealing (100 h) of a $KNd(SO_4)_2 \cdot H_2O$ sample at a temperature of 400°C.

The thermogram of the obtained monoclinic modification sample of $KNd(SO_4)_2$ is presented in Fig. 4. The phase endothermic effect of the transition from monoclinic anhydrous to triclinic anhydrous modification is accompanied by a small thermal effect at a temperature of 638°C with preservation of the total mass of the sample.

The monoclinic anhydrous modification of $KNd(SO_4)_2$ exists in the temperature range of 400-635°C. The triclinic anhydrous modification of $KNd(SO_4)_2$ forms at 635°C and decomposes with the release of gaseous products at temperatures above 900°C. During this process, the formation of an intermediate compound $K_5Nd(SO_4)_4$ [14] is observed, followed by its decomposition to potassium and neodymium oxides above 1000 °C. These phase transformations can be represented by the following scheme:

$$5KNd(SO_4)_2 \rightarrow K_5Nd(SO_4)_4 + 2Nd_2O_3 + 6SO_2 + 3O_2,$$

$$2K_5Nd(SO_4)_4 \rightarrow 5K_2O + Nd_2O_3 + 8SO_2 + 4O_2.$$

X-ray phase analysis of annealed initial samples of the $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$ system and mechanical mixtures of anhydrous monoclinic or triclinic modifications of $KNd(SO_4)_2$ with the orthorhombic modification of strontium sulfate did not reveal any significant interaction in the temperature range from 400 to 900°C. As a result of the conducted studies, it was established that the monoclinic and triclinic modifications of $KNd(SO_4)_2$ do not interact with the orthorhombic modification of $SrSO_4$. Consequently, during the thermal treatment of samples of the $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$ system above 400-500°C, complete decomposition of solid solutions occurs with separation into anhydrous modifications of $KNd(SO_4)_2$ and $SrSO_4$, whose solubility in aqueous solutions differs significantly.

In works [18, 19] dedicated to the study of the anhydrous system $KLa(SO_4)_2$–$SrSO_4$, the existence of solid solutions based on the orthorhombic modification of $SrSO_4$ was established. These anhydrous solid solutions exist up to the decomposition temperature of $KLa(SO_4)_2$ (970°C). Unlike similar systems with lanthanum, in the studied system with neodymium, the absorption of neodymium and potassium ions is possible only in the crystalline hydrate system $KNd(SO_4)_2\cdot H_2O$–$SrSO_4\cdot 0.5H_2O$ due to the high absorption activity of $SrSO_4\cdot 0.5H_2O$.

In works [20–22], the processes of co-crystallization of cerium(III) sulfate and strontium sulfate in the presence of K^+ ions were studied. The authors of these works did not associate the obtained precipitates of triple sulfates of cerium, strontium, and potassium with the absorption activity of strontium sulfate due to the thermodynamic instability of $SrSO_4\cdot 0.5H_2O$. Unlike the authors of [20–22], we concluded that $SrSO_4\cdot 0.5H_2O$ has high absorption activity due to its stabilization through heterovalent substitution of two strontium ions with Nd^{3+} and K^+ ions, forming stable solid solutions. In the anhydrous binary system $KNd(SO_4)_2$–$SrSO_4$, during thermal treatment, the solid solutions decompose as a result of complete dehydration above 400–500°C.

CONCLUSION

The following scheme of phase transformations during heating of $KNd(SO)_2\cdot H_2O$ to 1000°C is proposed:

$KNd(SO_4)_2\cdot H_2O$ (monoclinic) $\xrightarrow{70\text{-}80^\circ C}$ $KNd(SO_4)_2\cdot H_2O$ (trigonal) $\xrightarrow{220^\circ C}$ $KNd(SO_4)_2\cdot 0.2H_2O$ (monoclinic) $\xrightarrow{380\text{-}400^\circ C}$ $KNd(SO_4)_2$ (monoclinic) $\xrightarrow{675^\circ C}$ $KNd(SO_4)_2$ (triclinic) $\xrightarrow{900^\circ C}$ (melting with decomposition).

The existence of two monoclinic modifications of $KNd(SO)_2\cdot H_2O$ at room temperature has been established. Upon slight heating above 70-80°C, the monoclinic modifications of $KNd(SO)_2\cdot H_2O$ transform into the trigonal modification. When any modifications of $KNd(SO)_2\cdot H_2O$ interact with the trigonal modification of $SrSO_4\cdot 0.5H_2O$, only the trigonal modification of $KNd(SO)_2\cdot H_2O$ is stabilized, forming a wide homogeneity range of solid solution in the $KNd(SO_4)_2\cdot H_2O$-$SrSO_4\cdot 0.5H_2O$ system.

Dehydration during heating of $KNd(SO_4)_2 \cdot H_2O$ at 250°C leads to the formation of a partially dehydrated modification with approximate composition $KNd(SO_4)_2 \cdot 0.2H_2O$, which forms a wide range of solid solutions in the $KNd(SO_4)_2 \cdot 0.2H_2O$-$SrSO_4 \cdot 0.1H_2O$ system in the temperature range of 250-380°C. The completely dehydrated monoclinic modification of $KNd(SO_4)_2$ is formed during heating of the trigonal modification $KNd(SO_4)_2 \cdot H_2O$ to 400°C and with further heating to 635°C transforms into triclinic modification $KNd(SO_4)_2$. It has been established that monoclinic and triclinic anhydrous modifications of $KNd(SO_4)_2$ do not form solid solutions with orthorhombic modification of $SrSO_4$. The obtained results may be useful in developing processes of absorption and desorption of Nd^{3+} ions by crystalline matrices $SrSO_4 \cdot 0.5H_2O$ and $SrSO_4$.

ACKNOWLEDGMENT

The authors express their gratitude to Ph.D. D.S. Zinin for assistance in conducting X-ray fluorescence analysis of solid solution samples.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest

REFERENCES

1. *Jiustel T., Nikol Y., Ronda C.* // Angew. Chem. Int. Ed. 1998. V. 37. P. 3084.

2. *Kuzmina N.P., Eliseeva S.V.* // Russ. J. Inorg. Chem. 2006. V. 51. P. 73. https://doi.org./10.11.34/S0036023606010141

3. *Novikova G.Ya ., Morgalyuk V.P., Yanovich E.A* . // Russ. J. Inorg. Chem. 2021. V. 66. No. 8. P. 1054 . https://doi.org/1031857/S0044457X21080183

4. *Buyer C., Enseling D., Shlind J.* // Crystals. 2021. V. 11. № 6. P. 513. https://doi.org./10.3390/cryst 11060575

5. *Feldmann C., Justel T., Ronda C.* // Adv. Funct. Matter. 2003. V. 13. P. 511.

6. *Kazmierczak C., Hening A.* // J. Solid State Chem. 2010. V. 183. № 9. P. 2087. https://doi.org/10.1016/j.jssc 2010.07.024

7. *Iskhakova L.D., Plyushchev V.E.* // Russ. J. Inorg. Chem. 1970. V. 15. No. 9. P. 2526.

8. *Ishakova L.D., Gasanov Y.M., Trunov V.R.* // J. Struct. Chem. 1988. V. 29. P. 242. https://doi org/1007/BF00747987

9. *Bushuev N.N., Tatosyan G.K.* // Russ. J. of Inorg. Chem. 2023. V. 68. № 10. P. 1475. https://doi.org/10.1134/S0036023623601824

10. *Takahashi Satoshi, Seki Masanobu, Setoyama Katsumi* // Bull. Chem. Soc. Jpn. 1993. V. 66. P. 2219. https://doi.org/10/1246/bcsj.66.2219

11. *Takahashi S.* Kougakin Universit. Japan. Private communication 1993 (ICDD 44-0375).

12. *Bushuev N.N., Sysoev A.A. Velikodny Yu.A .* // Russ. J. Inorg. Chem. 2023. V. 68. № 4. P. 396. https://doi.org/10.1134/S0036023622602628

[

13. *Bushuev N.N., Zinin D.S., Tatosyan G.K., Sviridenkova N.V.* // J. Anal. Chem. 2024. V. 79. № 11. P. 1561. https:// doi org / 10.1134/S1061934824700977

14. *Degtiarev P.A., Pokrovskii A.N., Kovba L.M., Kortnaia F.M.* // J. Solid State Chem. 1977. V. 22. № 4. P. 419. https://doi.org/ 10.1016/0022-4596(77)90019-6

15. *Iskhakova L.D., Sarukhanyan N.L., Shchegoleva T.M. et al.* // Kristallografiya. 1985. V. 30. P. 474.

16. *Shannon R.D., Prewitt C.T.* // Acta Crystallogr., Sect. B. 1969. V. 25. P. 925. https://doi.org/ 10.1107/S0567740869003220

17. *Garske D., Peacor D.* // Z. Kristallchem. 1965. V. 121. P. 204.

18. *Bushuev N. N., Tyu · lbendzhyan G. S., Egorova A. N. et al.* // Russ. J. Inorg. Chem. 2021. V. 66. № 3. P. 405. https://doi.org/10.1134/S0036023621030049

19. *Bushuev N.N., Egorova A.N., Plotko I.I.* // Inorg. Materials. 2022. V. 58. № 11. P. 1202. https://doi/10.31857/S0002337X22100050

Bushuev N.N., Egorova A.N., Plotko I.I. // Inorg. Mat. 2022. V. 58. № 11. P. 1162. https://doi/10.1134/S0020168522100053

20. *Tsizin G.I., Malofeeva G.I., Tobelko K.I. et al.* // J. Anal. Chem. 1983. V. 38. № 6. P. 1027.

21. *Tobelko K.I., Tsizin G.I., Malofeeva G.I. et al.* // Russ. J. Inorg. Chem. 1983. V. 28. № 4. P. 889.

22. *Tsizin G.I., Tobelko K.I., Malofeeva G.I. et al.* // Russ. J. Inorg. Chem. 1983. V. 28. № 9. P. 2256.

Table 1. Chemical composition of precipitate samples of solid solutions in the $KNd(SO_4)_2 \cdot H_2O$–$SrSO_4 \cdot 0.5H_2O$ system, mol. %

Theoretical composition		Actual composition	
$SrSO_4 \cdot 0.5H_2O$	$KNd(SO_4)_2 \cdot H_2O$	$SrSO_4 \cdot 0.5H_2O$	$KNd(SO_4)_2 \cdot H_2O$
90	10	90.5	9.5
80	20	85.1	14.9
70	30	79.2	21.8
60	40	72.5	27.5
50	50	66.4	33.6
40	60	58.1	41.9
30	70	51.8	48.2
20	80	43.9	56.1
10	90	31.7	68.3

Table 2. Unit cell parameters of some compounds

No.	Compound	*a* , Å	*b* , Å	*c* , Å	β, deg	Space gr.	Reference
1	$KNd(SO_4)_2 \cdot H_2O$	10.0500(5)	8.5250(4)	10.3597(5)	118.486(2)	$P2_1/c$ monocl.	[6]
2	$KNd(SO_4)_2 \cdot H_2O$	10.8453(18)	15.395(3)	10.0310(16)	112.356(9)	$P2_1/c$ monocl.	*
3	$KNd(SO_4)_2 \cdot H_2O$, $SrSO_4 \cdot 0.5H_2O$	7.139(2), 7.1805(11)		6.638(2), 6.5936(8)		$P3_121$ trigon., $P3_121$ trigon.	* [9*] [10], [12*]
4	$KNd(SO_4)_2 \cdot 0.2H_2O$ $SrSO_4 \cdot xH_2O$ anhydr.	6.9023(16)	7.154(2)	6.5936(8)	102.68(1)	$P2_1/c$ monocl.	* [11]
5	$KNd(SO_4)_2$ monoclinic	8.551(1)	7.159(1)	10.721(1)	92.42(1)	$P2_1/c$ monocl.	*[8]
6	$KNd(SO_4)_2$ triclinic	6.9190(20)	5.307(1)	9.0530(20)	α = 92.029 β = 96.870 γ = 90.800	*P* 1 tricl.	* [14]

*Structural characteristics of these compounds are confirmed in this work and in works previously published by the authors.

Table 3. Indexing of X-ray diffraction lines of the second monoclinic modification $KNd(SO_4)_2 \cdot H_2O$

2θ , deg	*h k l*	2θ , deg	Exp. –calc.	*I/I* , %	d_{exp}, Å	d_{calc}, Å
11.487	0 2 0	11.516	–0.0297	5.7	7.6975	7.6777
14.501	1 2 0	14.514	–0.0169	61.7	6.1036	6.0966
14.958	0 2 1	14.966	–0.0087	88.1	5.9182	5.9148
17.678	2 0 0	17.671	0.0067	21.8	5.0131	5.0150
18.614	2 1 0	18.598	0.0166	3.5	4.7630	4.7672
19.158	0 0 2	19.119	0.0391	11.3	4.6290	4.6384
19.465	1 3 0	19.454	0.0105	14.7	4.5567	4.5591
20.223	–2 2 1	20.232	–0.0092	16.0	4.3876	4.3856
20.532	–2 0 2	20.533	–0.0009	20.0	4.3222	4.3220
23.148	0 4 0	23.151	–0.0030	15.5	3.8393	3.8388
23.891	2 1 1	23.583	0.0378	5.7	3.7216	3.7274
24.812	1 4 0	24.814	–0.0022	43.4	3.5855	3.5852
25.354	–1 4 1	25.366	–0.0117	3.4	3.5100	3.5084
25.865	0 3 2	25.902	–0.0372	22.3	3.4419	3.4371
26.963	–2 3 2	26.979	–1.0160	46.0	3.3042	3.3022
27.861	1 4 1	27.849	0.0121	100.0	3.1997	3.2010
28.739	–3 2 2	28.746	–0.0067	84.0	3.1039	3.1032
29.041	2 3 1	29.035	0.0055	80.6	3.0723	3.0729
29.913	–2 2 3	29.911	0.0021	66.2	2.9846	2.9848
30.230	0 4 2	30.196	0.0349	9.1	2.9540	2.9574
30.446	1 5 0	30.415	0.0310	34.3	2.9336	2.9365
30.885	–1 5 1	30.875	0.0107	32.2	2.8929	2.8939
32.043	–1 3 3	32.015	0.0280	2.5	2.7910	2.7934
32.975	2 4 1	32.956	0.0192	12.5	2.7142	2.7157
33.525	–4 0 2	33.516	0.0090	21.8	2.6709	2.6716
33.996	–4 1 2	34.035	–0.0393	4.3	2.6350	2.6320
35.319	–3 4 2	35.277	0.0415	12.4	2.5393	2.5421
35.649	–1 4 3	35.641	0.0079	22.1	2.5165	2.5170
35.935	–2 0 4	35.922	0.0129	11.8	2.4971	2.4979
36.188	1 6 0	36.195	–0.0065	24.5	2.4802	4.4798
36.762	–1 1 4	36.740	0.0217	5.6	2.4428	2.4442
37.040	–4 1 3	37.007	0.0330	3.8	2.4251	2.4272
38.165	–1 2 4	38.163	0.0020	3.2	2.3562	2.3563
38.359	–3 1 4	38.315	0.0441	10.6	2.3447	2.3473
38.666	3 0 2	38.368	–0.0326	2.1	2.3268	2.3249
39.005	–2 6 1	38.991	0.0135	10.6	2.3074	2.3081
39.522	2 6 0	39.500	0.0226	20.6	2.2783	2.2796
39.671	–3 2 4	39.690	–0.0191	11.8	2.2701	2.2691
39.898	–1 5 3	39.880	0.0177	2.3	2.2577	2.2587
40.562	0 2 4	40.603	–0.0409	19.4	2.2223	2.2201
40.941	–4 4 1	40.909	0.0323	14.4	2.2026	2.2042
41.089	4 1 1	41.095	–0.0063	22.9	2.1950	2.1947
41.776	–4 0 4	41.765	0.0112	12.6	2.1605	2.1610
42.166	1 7 0	42.133	0.0326	12.5	2.1414	2.1430
42.479	–1 7 1	42.481	–0.0020	20.5	2.1263	2.1262
42.929	1 6 2	42.908	0.0210	5.1	2.1051	2.1061
43.164	–2 4 4	43.174	–0.0094	4.4	2.0941	2.0937
43.678	1 4 4	43.637	0.0403	7.6	2.0707	2.0725
44.295	–3 6 2	44.299	–0.0036	34.1	2.0433	2.0431
44.565	3 6 0	44.550	0.0152	10.0	2.0315	2.0322
45.722	0 7 2	45.715	0.0069	6.5	1.9828	1.9830

45.963	0 6 3	45.996	–0.0330	9.0	1.9729	1.9716
46.591	–1 1 5	46.661	–0.0200	5.0	1.9478	1.9470
46.857	–2 5 4	46.844	0.0134	9.6	1.9373	1.7379

Table 4. X-ray characteristics of the sample 30% $KNd(SO_4)_2 \cdot H_2O$ + 70% $SrSO_4 \cdot 0.5H_2O$

d , Å	2θ, deg	*I/I* ,	*h*	*k*	*l*
6.2142	14.241	53.52	1	0	0
4.5233	19.609	16.04	1	0	1
3.5845	24.818	44.07	1	1	0
3.1077	28.701	71.66	2	0	0
2.9140	30.655	100.00	1	0	2
2.4302	36.958	14.66	1	1	2
2.3493	38.280	6.97	2	1	0
2.2616	39.825	4.77	2	0	2
2.2122	40.753	28.50	2	1	1
2.1994	41.001	11.99	0	0	3
2.0743	43.597	2.50	1	0	3
1.9755	45.898	9.91	3	0	1
1.9130	47.489	48.22	2	1	2
1.8751	48.509	3.62	1	1	3
1.7949	50.828	12.89	2	0	3
1.7543	52.090	18.68	3	0	2
1.7237	53.087	14.24	3	1	0
1.6681	55.004	2.03	3	1	1
1.5954	57.737	6.78	1	0	4
1.5761	58.513	3.36	2	2	2
1.5535	59.450	0.95	4	0	0
1.5279	60.548	4.42	3	1	2
1.5106	61.316	1.35	4	0	1
1.5106	61.316	1.35	3	0	3
1.4991	61.836	5.16	1	1	4
1.4569	63.837	1.84	2	0	4
1.4051	66.489	2.99	4	0	2
1.3922	67.182	1.98	2	3	1
1.3522	67.182	1.98	2	2	3
1.3566	69.195	2.81	3	3	3
1.3502	69.570	7.85	2	2	4
1.3084	72.130	4.99	3	3	2
1.2907	73.279	4.79	3	3	4
1.2541	75.786	2.20	4	4	2
1.2146	78.714	1.33	2	2	5
1.1952	80.249	2.07	3	3	0
1.1916	80.543	0.75	3	3	4
1.1629	82.963	1.05	5	5	2
1.1544	83.707	0.84	4	4	3
1.1310	85.855	1.10	4	4	4
1.1153	87.358	1.87	5	1	0

1.1062	88.266	2.19	4	2	2
1.1005	88.845	0.85	5	1	1
1.0791	91.093	1.76	3	2	4

Table 5. X-ray characteristics of the sample 70% $KNd(SO_4)_2 \cdot H_2O$ + 30% $SrSO_4 \cdot 0.5H_2O$

d , Å	2θ, deg	*I/I* , %	*h*	*k*	*l*
6.1996	14.274	35.67	1	0	0
4.5214	19.618	13.24	1	0	1
3.5759	24.879	40.16	1	1	0
3.1012	28.763	65.10	2	0	0
2.9173	30.620	100.00	1	0	2
2.4310	36.946	12.15	1	1	2
2.3444	38.362	4.93	2	1	0
2.2602	39.851	3.67	2	0	2
2.2073	40.847	31.02	2	1	1
2.0778	43.519	1.85	1	0	3
1.9719	45.986	6.62	3	0	1
1.9117	47.522	34.30	2	1	2
1.8774	48.445	2.97	1	1	3
1.7964	50.781	7.65	2	0	3
1.7529	52.135	12.57	3	0	2
1.7205	53.194	9.69	3	1	0
1.6650	55.115	1.27	3	1	1
1.5983	57.622	6.07	1	0	4
1.5746	58.572	2.58	2	2	2
1.5259	60.636	3.50	3	1	2
1.5021	61.702	4.42	1	1	4
1.4584	63.763	1.54	2	0	4
1.4032	66.588	3.88	4	0	2
1.3900	67.302	2.51	2	2	3
1.3518	69.477	11.28	2	1	4
1.3069	72.230	5.56	3	2	2
1.2918	73.204	6.17	3	0	4
1.2525	75.898	2.66	4	1	2
1.2394	76.847	0.44	5	0	0
1.2154	78.659	1.97	2	2	4
1.1930	80.429	3.93	3	3	0
1.1605	83.167	1.60	5	0	2
1.1527	83.858	1.85	2	1	5
1.1313	85.826	1.47	4	0	4
1.1139	87.499	3.32	5	1	0
1.1036	88.528	4.03	0	0	6
1.0790	91.102	2.10	3	2	4

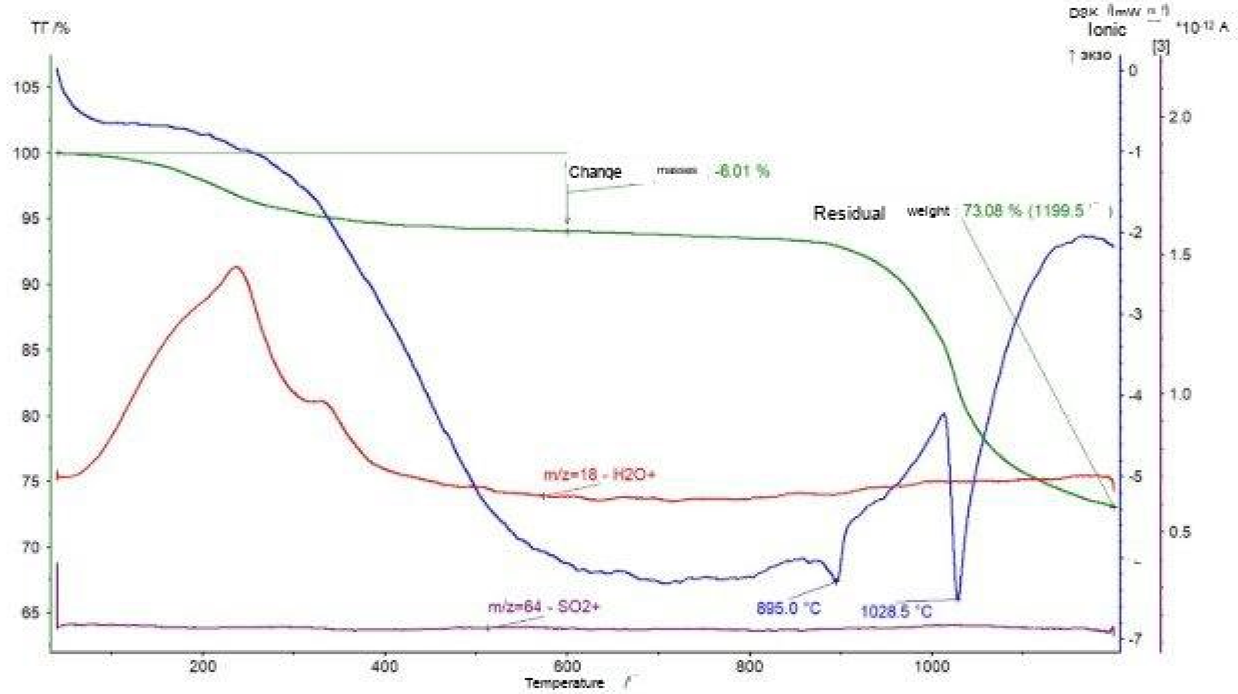

Fig. 1. Thermogram of pure (100%) $KNd(SO_4)_2 \cdot H_2O$.

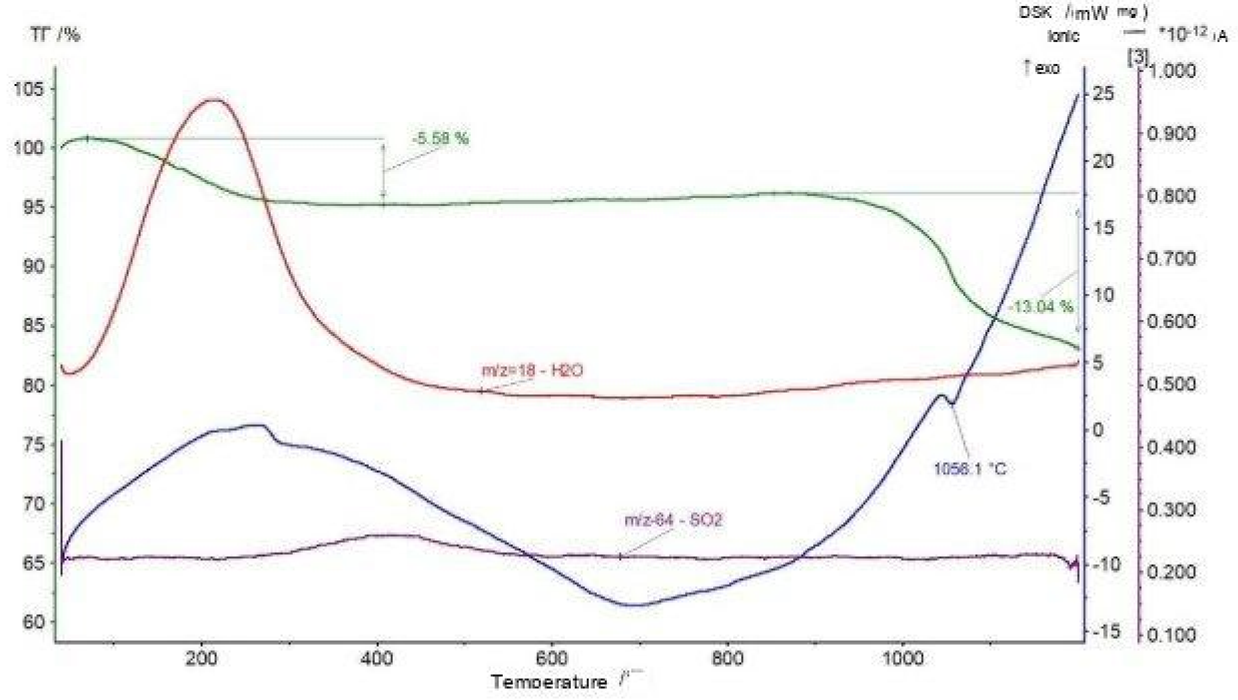

Fig. 2. Thermogram of 30% $KNd(SO_4)_2 \cdot H_2O$ + 70% $SrSO_4 \cdot 0.5H_2O$.

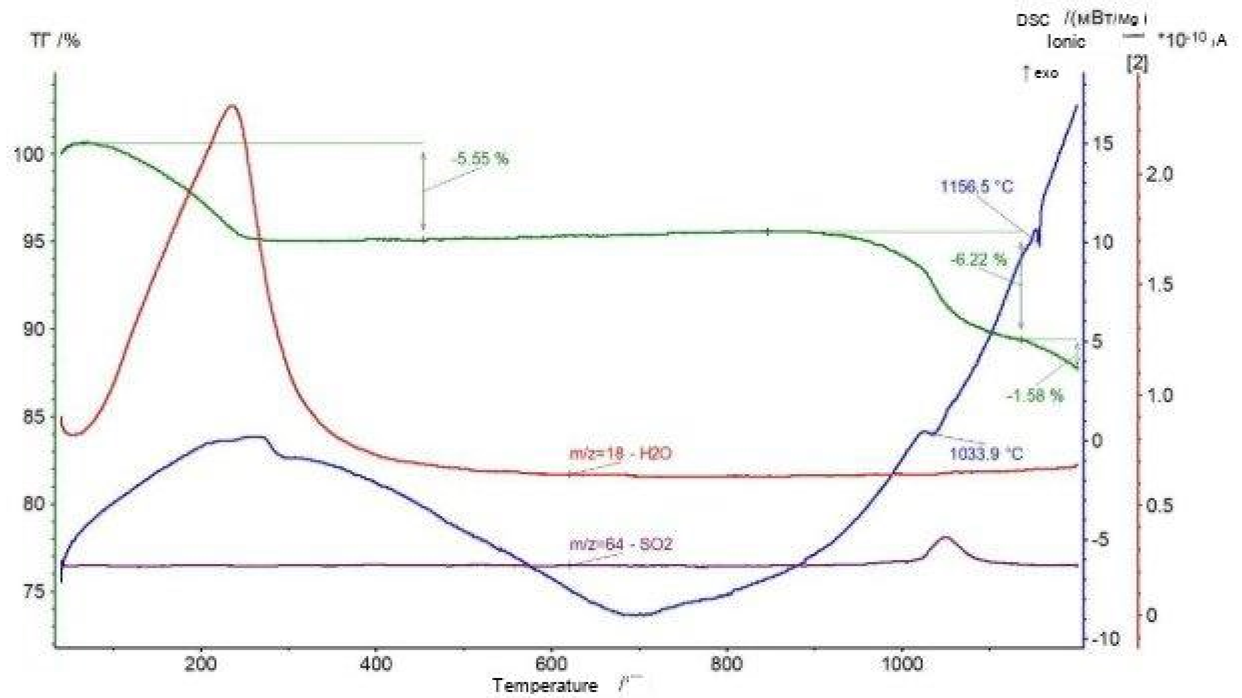

Fig. 3. Thermogram of 70% $KNd(SO_4)_2 \cdot H_2O$ + 30% $SrSO_4 \cdot 0.5H_2O$.

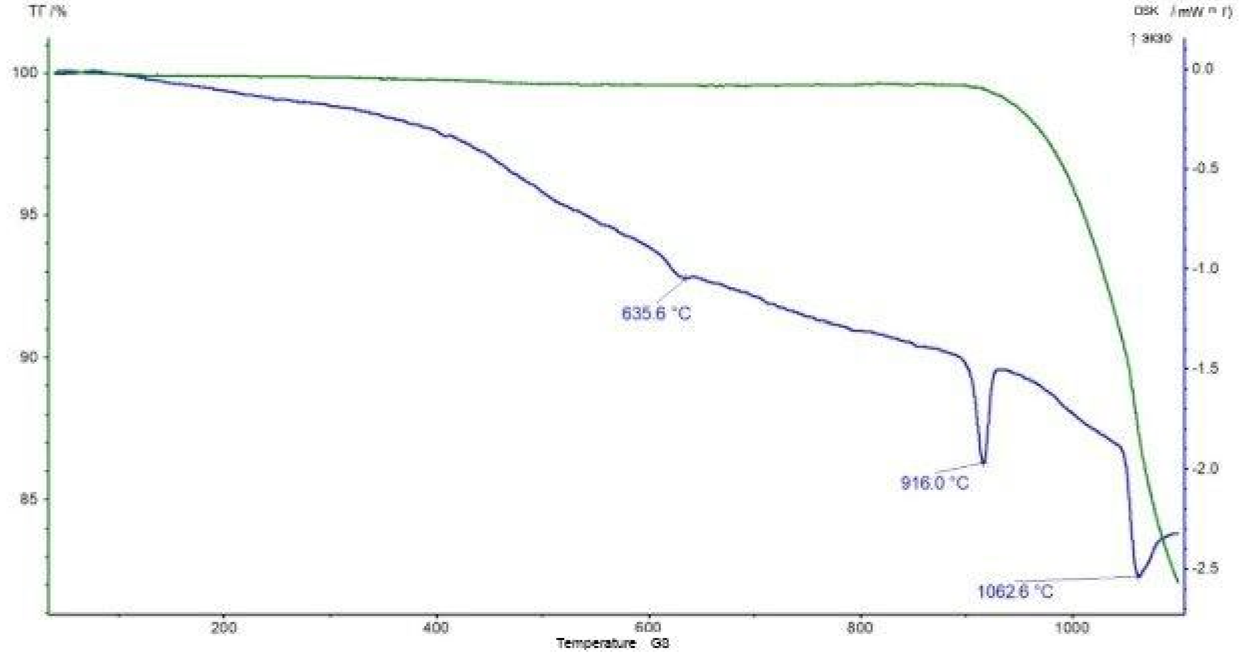

Fig. 4. Thermogram of anhydrous monoclinic modification of $KNd(SO_4)_2$.