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Physico-chemical investigation of systems
 $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O} - \text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{KNd}(\text{SO}_4)_2 - \text{SrSO}_4$

Relevance of the research

Rare earth elements and compounds based on them are used in many industries: the manufacture of superconductors, permanent magnets, ceramics and heat-resistant alloys. Rare earth elements: La, Ce, Pr, Nd, Sm, Eu are used as alloying components for steel and various alloys, as part of gas analyzers, in the manufacture of improved and upgraded ceramics, superconductors, supermagnetic, thermostatic, fluorescent and optical materials. Compounds of heavy rare earth elements have found application in medicine and in use as inorganic scintillators for radiation detection. The high demand and increased interest in the use and application of rare earth compounds makes it urgent to search for new directions in the chemistry of lanthanides and methods for obtaining their solid solutions.

It is known that $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{NaLn}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ are isostructural and form solid solutions upon co-crystallization at a temperature of 100-120°C. Whereas $\text{CaCO}_3 \cdot 2\text{H}_2\text{O}$ does not form solid solutions with $\text{NaLn}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ due to significant structural differences. In 1993, Japanese researchers synthesized for the first time a trigonal modification of $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$, which is very unstable and exists for 120 minutes, but it is capable of forming solid solutions with $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ due to their structural proximity. In 2022, the $\text{KLa}(\text{SO}_4)_2 \cdot \text{H}_2\text{O} - \text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ system was studied, in which the existence of a wide range of stable solid solutions at room temperature was established due to the structural proximity of these trigonal modifications $\text{KLa}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$. The search for the existence of solid solutions of other REE compounds at room temperature during co-crystallization with the trigonal modification of $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ is an urgent task that can simplify the process of obtaining materials with a high REE content.

The degree of development of the topic. Rare earth elements (1-2 wt. %) and strontium (1-2 wt. %) are contained in industrial waste of a technogenic nature,

for example, they are contained in phosphogypsum waste from the production of extraction phosphoric acid as a result of sulfuric acid decomposition of Khibiny apatites. In the works of N.N. Bushuev studied the interaction of various modifications of calcium sulfate with double sulfates of REE and sodium, in which the mechanism of heterovalent substitution of cations is considered, where the alkali metal ion Na^+ and the trivalent metal ion REE^{3+} are replaced by two atoms of the alkaline earth metal Ca according to the scheme: $\text{Ln}^{3+} + \text{Na}^+ \leftrightarrow 2\text{Ca}^{2+}$, where, $\text{Ln}^{3+} = \text{La, Ce, Nd}$ with the formation of wide areas of solid solutions based on trigonal modifications of $\text{NaLa}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. In recently published works, the $\text{KLa}(\text{SO}_4)_2 \cdot \text{H}_2\text{O} - \text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ system has been studied, and the formation of a wide range of solid solutions based on isostructural compounds $\text{KLa}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$, having a trigonal unit cell, has been established. gr. P3₁21. It should be noted that lanthanum La belongs to the d-element, which lacks f-electrons, unlike other lanthanides Ce, Pr, Nd, in which f-electrons are actively involved in the formation of a chemical bond. Perhaps for this reason, there is practically no information in the literature about the existence of trigonal modifications at room temperature, $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ in particular, and the crystallization of crystalline hydrate modifications $\text{KCe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{KPr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ in various other types has been noted. monoclinic modifications. Therefore, the search for conditions for the formation and existence of a trigonal modification of $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ is an urgent task that would enhance the reactivity of reagents in the formation of solid solutions with a trigonal modification of $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ due to their structural proximity.

Due to the isostructural structure of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ compounds, it can be assumed that using $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ as a crystal matrix for crystallization and co-precipitation of REE compounds is more appropriate, since the solubility of $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ is almost 80 times lower than $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$.

The aim of this work is to establish the features of phase formation and the existence of solid solution regions in the systems $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O} - \text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{KNd}(\text{SO}_4)_2 - \text{SrSO}_4$ in a wide temperature and concentration intervals. To establish the relationship between the reactivity of the reactants and their structure and the conditions of the chemical reaction during the formation of solid solutions.

The research tasks:

1. To establish the mechanism of the chemical process of crystallization and formation of solid solutions in the $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O} - \text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ system in aqueous solutions at a temperature of 25°C .
2. Determination of phase formation in the $\text{KNd}(\text{SO}_4)_2 - \text{SrSO}_4$ system in the temperature range up to 1000°C .
3. To establish the mechanism of formation and crystallization of solid solutions without the participation of K^+ ions during the joint crystallization of $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ with neodymium sulfate $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$.

Scientific novelty of the work

1. It is shown that as a result of the joint crystallization of $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$, a wide solid solution region is formed based on the trigonal modification of $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ in the concentration interval of 100–20 mol.% of the $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O} - \text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ system. The parameters of the unit cells of the solid solution samples have been determined. Heterovalent substitution of ions according to the scheme $2\text{Sr}^{2+} \leftrightarrow \text{K}^+ + \text{Nd}^{3+}$ stabilizes the structure of semi-hydrate solid solutions based on the initial isostructural trigonal modifications of $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$.
2. The conditions for the synthesis and preparation of two monoclinic polymorphic modifications $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (pr. gr. $\text{P2}_1/\text{c}$) and trigonal modification $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (pr. gr. P3_121) are established.
3. It is established that during heat treatment of samples of solid solutions of the system $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O} - \text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ partial dehydration of the samples occurs, and at temperatures above 400°C , complete dehydration and decomposition

of solid solutions are observed with the formation of individual $\text{KNd}(\text{SO}_4)_2$ phases and SrSO_4 .

4. For the first time, the high reactivity of the crystalline matrices of the trigonal modification of $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ and its dehydrated monoclinic modification, $\text{SrSO}_4 \cdot 0.1\text{H}_2\text{O}$, towards the isomorphic heterovalent inclusion of Nd^{3+} ions during cocrystallization with neodymium sulfate and the formation of unstable solid solutions without the involvement of potassium ions has been established.

5. The existence of a partially dehydrated modification of the composition of $\text{KNd}(\text{SO}_4)_2 \cdot 0.2\text{H}_2\text{O}$, which forms solid solutions with a crystalline matrix $\text{SrSO}_4 \cdot x\text{H}_2\text{O}$ ($0 \leq x \leq 0.1$), has been established.

6. In the temperature range of 25-900°C, a phase transformation diagram was established during the heating of $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$.

Theoretical and practical significance of the work:

1. The wide solid solution formation area based on the trigonal modification of $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ according to the scheme of heterovalent substitution of strontium ions for potassium and neodymium ions can be used for the separation of Nd concentrates.

2. The structural proximity of the compounds $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ contributes to the formation of a wide solid solution area based on $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$, which can be used in the development of processes for obtaining rare-earth elements concentrates.

3. Decomposition of samples during heating of the binary system $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O} - \text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ at temperatures above 400°C into anhydrous components $\text{KNd}(\text{SO}_4)_2$ and SrSO_4 can be used in the development of technology for extracting lanthanides

4. The formation of a wide solid solution region in the $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O} - \text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ system, in the absence of K^+ ions, is accompanied by the formation of a large number of vacancies in the cation sublattice, which leads to the thermodynamic instability of the solid solutions and their subsequent decomposition into the original components. This allows

Methodology and research methods

Modern physico-chemical research methods were used in the dissertation work: X-ray phase analysis (diffractometer - ARL EQUINOX 100, X-ray analysis (focusing camera-high resolution monochromator Guinier Camera G670, CuK α 1 radiation.), X-ray fluorescence analysis (energy dispersive X-ray fluorescence spectrometer - Shimadzu EDX-7000), differential thermal analysis and thermogravimetric analysis (synchronous thermal analyzer STD 409 PC), microscopic examination (scanning electron microscope JEOL JSM-6510LV).

Provisions to be defended

1. The results of the joint crystallization of $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$, where $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ is considered as a crystalline matrix for the extraction of Nd^{3+} ions due to the structural proximity of the initial reagents.
2. The results of the phase analysis study of the products of the thermal treatment of the solid solution samples of the $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ – $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ system and the anhydrous phases of $\text{KNd}(\text{SO}_4)_2$ and SrSO_4 .
3. The results of the study of the joint crystallization of $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ without the participation of potassium ions.
4. The scheme of phase transformations of $\text{KNd}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{KNd}(\text{SO}_4)_2$ in the temperature range of 25-900°C.