Preparation and some properties of crystal Rb$_2$NiCl$_4$·2H$_2$O

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Abstract. The paper presents the results of studies on the growth of Rb$_2$NiCl$_4$·2H$_2$O crystals and the study of their properties. The conditions for the reproducible production of Rb$_2$NiCl$_4$·2H$_2$O single crystals by the method of controlled decrease of solubility are determined. The optical and thermal properties of crystals obtained in this way were studied.

1. Introduction
Optical filters with a passband in the UV range are used in devices of the "sun-blind technology" (SBT) [1]. Well-studied crystals for this application are sulfates of transition elements. These optical behavior is due to the presence of an octahedral nickel complex in their structure. Replacement of the structural components surrounding the transition metal atom can affect the optical characteristics of the complex. As the object of study, the compound was chosen Rb$_2$NiCl$_4$·2H$_2$O, since the octahedral environment of the transition metal is different from the well-studied binary cobalt and nickel sulfates [2, 3].

This paper describes the method of obtaining the crystal Rb$_2$NiCl$_4$·2H$_2$O, also presents the results of studies of optical and thermal properties.

2. Experimental Techniques

2.1. Synthesis
For the synthesis of Rb$_2$NiCl$_4$·2H$_2$O salt NiCl$_2$·6H$_2$O (pure grade), RbCl (extra-pure grade), distilled water were used.

Samples of RbCl and NiCl$_2$·6H$_2$O were mixed in an equimolar ratio and dissolved until the precipitate completely disappeared at elevated temperature, followed by filtration. Then, the solution was slowly cooled to room temperature to form a coarse-grained precipitate, followed by decontamination [4]. The obtained crystalline samples were dried at room temperature, followed by verification of the phase composition. For further syntheses of saturated solutions, this salt was used.

To study the temperature dependence of equilibrium concentrations in solution, the weight method was used. Saturated at the temperature of determination, the solution was taken in a weighing bottle, brought to constant weight. Then, water was evaporated dry from a liquid aliquot at room temperature. The mass difference of the weighing bottle before and after drying an aliquot was determined by the mass of the dissolved substance. According to the difference in masses of the dissolved substance and the liquid aliquot, the dependence on temperature in mass percent was built. (Table 1.)
Table 1. The temperature dependence of equilibrium concentrations in solution.

| T, °C | \(\omega (\text{Rb}_2\text{NiCl}_4 \cdot 2\text{H}_2\text{O})\), %mass |
|-------|----------------------------------|
| 25    | 49.7                             |
| 30    | 50.1                             |
| 35    | 50.5                             |
| 40    | 51.1                             |

Stock solutions for directional crystallization were prepared as follows. Saturated aqueous solution was filtered at elevated temperature. Then, the resulting solution was cooled to saturation temperature and poured onto an artificially faceted seed crystal obtained by spontaneous crystallization. Using a programmable PID controller, the temperature of the saturated solution with the seed crystal was cooled to the required values. The volume of the crystal thus obtained was sufficient for further investigation.

2.2. Techniques

X-ray phase analysis (XPA) of the powdered material samples was carried out at room temperature on a Rigaku Miniflex 600 desktop X-ray diffractometer (Japan) (X-ray tube with a copper anode, continuous shooting mode—2 grad/min, step width 0.02° in the angle range 20 5–75°, without sample rotation) in an ordinary atmosphere.

The optical properties were studied using a Cary 300 UV-Vis automatic double-beam spectrophotometer in the wavelength range of 200-800 nm at a speed of 300 nm/min. When measuring saturated aqueous solutions, standard quartz cuvettes with an internal width of 10 mm along the path of the spectrophotometer beam were used.

The behavior of the grown single crystals upon heating and cooling was studied by polarization microscopy and synchronous thermal analysis: differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. The thermal properties of the crystals were investigated in a dry nitrogen flow on an STA 449 F1 Jupiter (NETZSCH, Germany) combined TG–DSC analyzer in the temperature range of 298–473 K at the temperature-change rate of 2 K/min in Pt/Rh crucible.

3. Results and Discussion

The single crystal growth was carried out by the method of controlled temperature decrease from 35 to 30°C from a saturated aqueous solution with a seed crystal. After 48 hours of growth, the size of the seed crystal increased to 2*3*2 mm (Fig. 1a).

The results of studying optical transmission spectra demonstrate the presence of two bands with intensity maxima at wavelengths of 350 and 650 nm (Fig. 1a). Low intensity is associated with the presence of macrodefects in the volume of the crystal.

The thermal stability data, using the DSC/TGA method, indicate that the sample begins to lose mass at a temperature of ~ 50°C (Fig. 1c). A rather low temperature of the onset of mass loss may be due to the presence of water molecules in the crystal structure that are not related to the octahedral environment of nickel [2].

It should be noted that the indication of the obtained X-ray profile of the samples is impractical due to the low symmetry of the crystal (triclinic) [2]. The literature mentions the results of studies of the structure of \(\text{Rb}_2\text{NiCl}_4 \cdot 2\text{H}_2\text{O}\), while in the ICSD (single crystal) and PDF (powder) databases are not found.

The low temperature of the onset of mass loss of the crystal is not a fundamental limitation for its practical application in the framework of the SBT, since there are methods of protecting the surface of optical filters that significantly extend the temperature range of use [1].
Figure 1. a) Optical transmission spectrum of an $\text{Rb}_2\text{NiCl}_4\cdot2\text{H}_2\text{O}$ crystal.
b) X-ray profile of an $\text{Rb}_2\text{NiCl}_4\cdot2\text{H}_2\text{O}$ crystal.
c) DSC/TGA data $\text{Rb}_2\text{NiCl}_4\cdot2\text{H}_2\text{O}$ crystal
4. Conclusions
The temperature dependence of the solubility of the Rb$_2$NiCl$_4$·2H$_2$O compound was studied, which made it possible to obtain a single crystal with dimensions sufficient for a comprehensive study of its optical and thermal properties.

It was found that the optical transmission spectra of the crystal under study make it possible to use it in SBT devices.

The developed technique for obtaining crystals in the future will allow for structural studies with their subsequent deposition in the ICSD database.

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