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Growth of mixed $\text{K}_2\text{Ni}_x\text{Co}_{(1-x)}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystals for large supercooling without spontaneous crystallization in solution

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Abstract

A scheme for growing mixed $\text{K}_2\text{Ni}_x\text{Co}_{(1-x)}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (KCNSH) single crystals under conditions of supercooling at 5°C–10 °C without spontaneous crystallization in solution for more than a month has been proposed and implemented. The growth method is implemented according to the ‘rotor crystallizer’ scheme. The crystals grown were characterized by optical spectroscopy and x-ray topography. The crystals obtained demonstrated the optical properties necessary to create effective UV filters.

1. Introduction

Mixed $\text{K}_2\text{Ni}_x\text{Co}_{(1-x)}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (KCNSH) crystals are promising materials for UV–optical filters of the solar-blind spectral range 220–280 nm [1–4]. They have an increased radiation filtering efficiency in the specified range due to the suppression of spurious bandwidths in the non-working (visible) spectral region due to the absorption with nickel and cobalt hexahydrate complexes. Compared with crystals of individual components, mixed crystals have a high thermal stability [5].

It is known that mixed crystals grown from solutions are characterized by increased defect formation [6, 7]. Moreover, most of the defects that exist in crystals grown from low-temperature solutions are formed during their growth [8]. One of the most important factors affecting the defect formation in a growing crystal is spontaneous crystallization in a supersaturated solution. By themselves, the nuclei of a solid phase in a solution can serve as sources of crystal defects in the case of their capture by the crystallization front, i.e. in fact, they are among the first indicators of defective crystal growth. To reduce the effect of spontaneous crystallization on the defectiveness of a growing crystal, various filtration schemes for solutions were tested, including complex continuous filtration systems for the solution throughout the entire crystal growth process of the KDP family [9]. Reducing spontaneous crystallization in solutions is especially relevant for growing technically important crystals that require long growth cycles.

One of the types of compositional heterogeneity inherent in exclusively mixed crystals is mosaic microinhomogeneity, first discovered in K (Cl, Br) and K$_2$ (Cr, S) O$_4$ crystals [10] and confirmed on KCNSH crystals [11]. When mixed crystals are grown, fluctuations in the composition of the solution (for example, due to unsteady convection) can lead to local manifestations of the isomorphic substitution reaction—complex multidirectional processes of simultaneous dissolution of the crystal and the growth of the crystalline phase of a different composition [6, 7, 12]. This leads to the transformation of the crystal surface into a mosaic of randomly scattered zones of various compositions. It is assumed that the isomorphic substitution reaction can be suppressed by creating increased supercooling in the system [13]. In publications devoted to the growth of crystals from low-temperature solutions, low supercoolings (~0.5 °C) are used because of the high probability of the formation of spontaneous crystallization in solution.

The aim of this work was to develop a method for growing KCNSH crystals under conditions of large supercoolings without spontaneous crystallization in solution for a long period of time. This article describes the scheme for growing mixed $\text{K}_2\text{Ni}_x\text{Co}_{(1-x)}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (KCNSH) single crystals under supercooling conditions.
of 5°C–10°C without spontaneous crystallization in solution for more than a month. The growth method is implemented in the ‘rotary crystallizer’ scheme. The crystals obtained demonstrated the optical properties required to create effective UV filters.

2. Experimental part: crystal growing scheme and its implementation

In real growth systems, solution stability with respect to spontaneous nucleation depends on many factors, such as the purity of the initial components, temperature stability and the presence of temperature gradients in the growth zone, mechanical effects on the solution, pretreatment of the solution, hydrodynamic conditions, crystallizer device, etc. Growth conditions analysis in our previous works [4, 14–16] and some literature data [8, 9] showed that temperature and mechanical perturbations have a significant effect on the stability of a solution with respect to spontaneous nucleation. To reduce the influence of these disturbances, we have implemented a growing scheme in which the crystallizer with pretreated solution was installed in a thermostat with a temperature difference across the internal volume of no more than 1°C without forcing the solution to be mixed. The method of growing is implemented in the ‘rotary crystallizer’ scheme. A crystallizer with a seed mounted on a hermetically sealed lid is placed in a growth furnace, which has the possibility of rotation around a horizontal axis, which makes it easier to introduce seeds into the solution and prevent any evaporation of the solution from its surface, which is a critical parameter for the generation of spontaneous crystals [9]. In addition, before introducing the seed into the solution, the entire surface above the solution comes into thermodynamic equilibrium with the vapor phase, including all surfaces of the crystallizer with a cover, the shaper, and the seed. All these surfaces are covered with a film of condensate depleted in dissolved components, which prevents the generation of spontaneous crystals on these surfaces after they are introduced into the solution by upheaval of the crystallizer. The introduction of the seed crystal into the solution together with the fastening elements from the medium, which is not in thermodynamic equilibrium with the solution, will significantly increase the probability of spontaneous nucleation, which will lead to an increase in the defectiveness of the growing crystal and a decrease in the yield of the product. The nuclei of a solid phase in a solution can serve as sources of crystal defects in the case of their capture by the crystallization front. Separately growing spontaneous crystals are competitors for the seed crystal, reducing its growth rate by several times, which practically lead to a halt in the growth of the main seed crystal. By reducing the temperature and mechanical disturbances in the solution, we prevent the formation of spontaneous crystals, and by increasing supercooling, we suppress the isomorphic substitution reaction [13].

The ‘rotary crystallizer’ installation diagram (figure 1) includes a crystallizer in the form of a glass vessel with a sealed lid placed in a thermostat with a temperature difference in the internal volume of not more than 1°C.

![Figure 1](image_url)

Figure 1. The equipment scheme ‘rotary crystallizer’: 1—heat insulator, 2—cap, 3—crystallizer, 4—solution, 5—film heater, 6—thermocouple, 7—thermoregulator, 8—seed.
and the possibility of a 180° rotation around the horizontal axis during growth. The seed crystal is fixed in the shaper on the crystallizer lid. The shaper is a divided cylindrical container made of Teflon with a diameter of 20 mm and a height of 30 mm. The container has a seat for the seed, preventing it from falling in the upper position. The shaper with a seed is mounted on the lid with a mechanical holder. Monitoring and control of temperature conditions are carried out using a programmable controller of the Eurotherm type with an accuracy of ±0.05 °C.

The method of growing is as follows: a crystallizer with a solution overheated by 7 °C–10 °C relative to the liquidus temperature and a seed crystal on the lid is placed in a thermostat with the same temperature. Then the temperature of the thermostat drops to 2 °C–3 °C above the liquidus temperature and is kept for several hours. Then the crystallizer is turned upside down (together with the thermostat) and the temperature is lowered by 2 °C–3 °C below the liquidus temperature of the solution. In this state, crystal growth is carried out for a month or more with a gradual decrease in temperature by 1 °C–7 °C over the entire growth period.

At the end of the growth cycle, the crystallizer turns upside down and cools in a thermostat to room temperature. It should be noted that the selected temperature regimes exclude the appearance of spontaneous crystals, but naturally need to be corrected to optimize the growth rate.

The compositions of the crystals grown were analyzed by the atomic emission method in order to determine the nickel-to-cobalt ratio, and the structure of the crystals grown was investigated using x-ray diffraction analysis. Diffraction patterns of powder samples were recorded with a Siemens D-500 diffractometer in CuKα1 radiation.
radiation at the range of 2\(^\theta\) angles from 10 to 95\(^\circ\). The lattice parameters were calculated using the PowderCell software.

The transmission spectra of the crystals were measured immediately after the experiment without end surface treatment. The transmission spectra in the 190–1100 nm-wavelength range were recorded using a 'Perkin Elmer Lambda 45' automatic two-beam scanning spectrophotometer. The probing beam size was 2 \(\times\) 5 mm\(^2\). To evaluate crystal optical homogeneity, the measurements were made in the center and the periphery in 5 points.

3. Results and discussion

Within the framework of the growth conditions formulated in the previous section, the main driving force of crystallization is concentration convection due to the upward flow of the lightened solution after the deposition of the feeding component on the surface of the seed and countercurrents of supersaturated solution. Thermal convection under almost gradientless conditions, according to our estimates, is significantly inferior in mass transfer efficiency to concentration convection, as is molecular diffusion in a solution. The efficiency of mass transfer also depends on the design features of the crystallizer and the size of the seed crystal. The hydrodynamics...
of mixing the solution in this technology has a large inertia. Due to this, external perturbations (including temperatures) do not lead to significant changes in the growth rate. The latter affect the microhomogeneity of the growing crystal in composition.

Figure 2(a) shows an x-ray diffraction pattern of powder sample made from a KCNSH single crystal (figure 3(a)) of the composition K$_2$Co$_{0.115}$Ni$_{0.885}$(SO$_4$)$_2$·6H$_2$O. The atomic lattice belongs to the monoclinic space group P2$_1$/a. Unit-cell parameters of the KCNSH crystal were calculated from this x-ray diffraction pattern and amounted to $a = 8.998$ Å, $b = 12.177$ Å, $c = 6.129$ Å, $\beta = 105.07$ (degrees). Figure 2 also shows a touch-diagram of the K$_2$Ni(H$_2$O)$_6$ (SO$_4$)$_2$ phase (00-070-1826), which confirms the identity of the phases. Microscopic photographs (figures 2(b), (c)) show the morphology of the crystal cross sections at the seed-crystal interface and in volume after etching. The dislocation density revealed by etching pits is of the order of 10$^5$ cm$^{-2}$.

Figure 3 shows a mixed KCNSH crystal (170718) grown from a solution with a ratio of components of Ni / Co salts $= 2/1$ (mass of solution 2 kg, solution liquidus temperature 40 °C). A single crystal K$_2$Ni(SO$_4$)$_2$·6H$_2$O with a diameter of 20 mm and a height of 3 mm with a growth surface close to (110) served as the seed. The seed was introduced into the solution at a temperature of 42 °C and cooled with a thermostat at a rate of 0.5 °C h$^{-1}$ to a temperature of 37 °C. After that, slow cooling to a temperature of 32 °C at a rate of 0.17 °C day$^{-1}$ (30 days) followed and ageing at this temperature for 10 days. After that, the crystal was separated from the solution and cooled with the thermostat to room temperature. The thickness of the newly-grown layer was 20 mm. The average growth rate was 0.5 mm day$^{-1}$. Considering the growth rate at the exposure site at a temperature of 32 °C (10 days) 0.3 mm/day (the estimation from previous test measurement), we estimate the crystal growth rate at the section of slow cooling (30 days) as 0.57 mm/day. This value of the growth rate corresponds to the measured velocities in [16].

The transmission spectrum of the obtained crystal is shown in figure 3(b). The transmission in the UV region (75%) of a crystal with a thickness of 23 mm in terms of a thickness of 1 cm corresponds to the theoretical value for these crystals (~90%). In the visible region of the spectrum, transmission is absent (~0.01%), in the IR region of the spectrum, the peaks do not exceed 0.6%. This indicates the absence of scattering centers in them, and therefore their high structural perfection.

The x-ray topogram of a KCNSH crystal (170718) (figure 3(c)) and a photograph of a sample cut from this crystal parallel to the growth direction (figure 3(d)) show the absence of noticeable solution inclusions at the seed—crystal interface. For this reason, the number of dislocations has also decreased, according to data on the topogram ~10$^3$–10$^4$ cm$^{-2}$, whereas usually—by 1–2 orders of magnitude more. However, because of this, the level of residual stresses in the crystal is high, as evidenced by a powerful black band along the crystal-seed border (this is a kinematic contrast, indicating the presence of non-uniform elastic deformation), as well as cracks, which this time even formed inside the seed. As for the cracks in the crystal, they, apparently, are not directly linked to the seed, but are caused by a change in the crystal composition in the initial transition region (2–3 mm from the seed), although, probably, the stresses from the interface also contributed to it. We assume that this contribution is not very large, since cracks in the seed had to relieve the main stress. After the crack, the main part of the crystal looks structurally and optically homogeneous, which confirms the absence of scattering centers and the high structural quality revealed by the transmission of the crystal in the UV region, which corresponds to

![Figure 4. Transmission spectrum of a KCNSH crystal grown at an average rate of 0.83 mm day$^{-1}$.](image-url)
the theoretical value for these crystals (~90%). It is this main part of the crystal that is used to make UV filters. Residual stresses at the crystal-seed interface can be reduced by using a seed of the same composition as the growing crystal.

Another KCNSH crystal (181017) was grown in this crystallizer by analogy with the previous crystal using two growth areas (cooling and aging) and with the same composition of the solution. The average growth rate for 12 days was 0.83 mm day$^{-1}$. The thickness of the newly-grown layer on the seed was 10 mm. The calculated crystal growth rate at the temperature reduction site at a rate of 0.72 °C day$^{-1}$ was 1.1 mm day$^{-1}$. The transmission spectrum of this crystal is shown in figure 4. The transmission in the UV region (75%) coincides with that of the previous crystal; however, the thickness of this crystal is two times less (13 mm). In the visible region of the spectrum, the transmittance (~0.1%) is an order of magnitude larger than that of the previous crystal; in the IR region of the spectrum, the peak reaches 1.0%. We can state a certain decrease in the structural quality of this crystal, caused by its higher growth rate.

4. Conclusion

A scheme for growing mixed $K_2Ni_3Co_{1-x}\cdot f(SO_4)_{2}\cdot 6H_2O$ (KCNSH) single crystals under supercooling conditions of 5 °C–10 °C without spontaneous crystallization in solution for a month or more has been proposed and implemented. The method of growing is implemented in the ‘rotary crystallizer’ scheme. A crystallizer with a solution and a seed attached to the lid is placed in a growth furnace, which can be rotated around a horizontal axis, which makes it easy to introduce seeds into the solution and prevent any evaporation of the solution from its surface, which is a critical parameter for the generation of spontaneous crystals [8]. It was shown that the $K_2Co_{0.115}Ni_{0.885}SO_4\cdot 6H_2O$ crystal grown at an average rate of 0.5 mm day$^{-1}$ demonstrates a high level of transmission in the UV spectral range close to the theoretical value for these crystals (~90%). The x-ray topogram of the KCNSH crystal confirms the absence of noticeable solution inclusions at the seed-crystal interface and a decrease in the dislocation density by 1–2 orders of magnitude. Residual stresses at the crystal-seed interface can be reduced by using a seed of the same composition as the growing crystal. The method proposed in the article is a new approach for growing multicomponent systems. It is the first step in a new technology that opens up the possibility of creating a relatively simple and cheap method of producing crystals for UV filters.

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