

Review

# The Problem of Formation of Mixed Crystals and High-Efficiency K<sub>2</sub>(Co, Ni)(SO<sub>4</sub>)<sub>2</sub> • 6H<sub>2</sub>O Optical Filters

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**Abstract:** This review, for the first time, summarizes the results of studies of the defect formation mechanisms in mixed crystals grown from aqueous solutions. The general mechanism of interaction of a crystal with a foreign solution is described (reaction of isomorphous replacement). As a result of this reaction, the crystal surface turns into a mosaic of local areas where multidirectional processes (dissolution and growth) occur simultaneously. Data on mosaic microinhomogeneity, which is a new type of composition inhomogeneity inherent solely to multicomponent crystals, is presented. A new mechanism for the mismatch stress relaxation in heterocompositions of brittle crystals grown from low-temperature solutions is described; in this case, the formation of misfit dislocations is impossible and stress relaxation occurs due to the formation of numerous inclusions at the interface. The general concept of growing high-quality mixed crystals from solutions is described, using the example of  $K_2(Co, Ni)(SO)_2 \cdot 6H_2O$  (KCNSH) mixed crystals.

**Keywords:** solution crystal growth; mixed crystals; isomorphous replacement; mechanism of stress relaxation; optical filters; solar-blind technology

## 1. Introduction

The phrase mixed crystals here describes substitutional solid solutions of isomorphous components. The possibility of growing crystals of solid solutions is of prime importance for creating materials with specific properties. However, until now, growing such crystals from aqueous solutions has encountered insurmountable difficulties due to their extremely poor quality.

The most obvious problems of growing mixed crystals are associated with their strong zonal and sectorial inhomogeneity and, as a consequence, high internal stresses, cracks, and a large number of inclusions. Due to the huge number of defects in mixed crystals, there have not yet been any examples of their practical use.

The main problem of crystallization in multicomponent systems is due to the presence of additional degrees of freedom. Thus, according to the Gibbs phase rule, a three-component system consisting of a solvent (water) and two salts has two degrees of freedom (temperature and composition) at constant pressure. This means that, at a given temperature, there is a continuous series of saturated solutions and the same number of crystals, the compositions of which correspond to the equilibrium conditions with these solutions. If a crystal comes into contact with a foreign solution, complicated processes begin to occur on its surface, leading to the formation of defects.

The motivation for writing this article was the desire to summarize the results of studies of the processes which occur during the growth of mixed crystals from aqueous solutions, and to demonstrate their fundamental importance for solving practical problems. This paper is a brief overview of the results published prior to our studies, a summary of our most important published results, and also includes some new and previously unpublished experimental data. Such a summarized presentation is given for the first time and helps to draw a general pattern of the defect formation processes in mixed crystals. It was this integral vision of the problem that helped us to use the previously obtained fundamental results in solving the applied problem of developing optical filters based on mixed  $K_2(Co, Ni)(SO)_2.6H_2O$  (KCNSH) crystals, which are solid solutions of  $K_2Co(SO)_2.6H_2O$  (KCSH) and  $K_2Ni(SO)_2.6H_2O$  (KNSH). These crystals are considered as a promising material for solar-blind optical filters; therefore, the solution to the problem of their structural perfection is of great practical importance.

## 2. Morphological Effects in Liquid-Phase Epitaxy

For the first time, unusual phenomena (dissolution of the substrate, growth of the new phase with simultaneous dissolution of the substrate) during isothermal contact of mutual non-equilibrium (in composition) the multicomponent liquid phase and the crystal were observed during liquid-phase heteroepitaxy (LPE) of solid solutions of III–V compounds, and were explained in a series of works by Yu. Bolkhovityanov [1–3], based on his developed model of the formation of a stress diffusion layer (skin-layer) on the substrate surface.

Bolkhovityanov considered the thermodynamics of the phase interaction in a three-component system. In this model, it was assumed that the crystal contained two components, and the third one was either a solvent or a component associated with the first two by stoichiometric ratios. The difference in thermodynamic potentials of the two contacting phases of arbitrary compositions is given by

$$\Delta G(T_0, x_0, x) = xRT_0 \ln \frac{x}{x_0} + (1 - x)RT_0 \ln \frac{1 - x}{1 - x_0} - \beta (x - x_0)^2, \tag{1}$$

where  $x_0$  is the concentration of one of the components in the crystal that is in equilibrium with a given liquid phase, and x is its concentration in the crystal whose composition does not correspond to the equilibrium conditions. The dependences calculated by Equation (1) for the In-Ga-As-In<sub>x</sub>Ga<sub>1-x</sub>As system are shown in Figure 1. It can be seen that with any deviation of the crystal composition from the equilibrium value, the change of free energy becomes greater than zero, which will lead to crystal dissolution.



**Figure 1.** The change of free energy  $\Delta G_m$  calculated by Equation (1) when the composition of the solid phase x deviates from the equilibrium value  $x_0$  for  $In_xGa_{1-x}As$  solid solution ( $T_0 = 800 \ ^\circ C$ ,  $\beta = 3.45$  Kcal/mol [2]).

However, this important result was barely used by Bolkhovityanov. The main role in his model was assigned to the stressed skin-layer which very quickly forms at the interface as a result of solid-state

diffusion, and whose composition will be in equilibrium with the liquid phase. This skin-layer protects the substrate surface from the dissolution. According to his hypothesis, dissolution occurs in the breaks of the skin-layer if this skin layer is not continuous, due to the elastic stresses resulting from lattice mismatch between the skin layer and the substrate. He suggested that this would be the case when the skin-layer lattice parameters were smaller than those of the substrate. In this case, an island texture will be formed. Otherwise, the skin-layer will be continuous and will provide the growth of a continuous epitaxial layer.

Obviously, such reasoning is explained by the known fact that elastic stresses increase the crystal internal energy, and therefore, decrease the effective supersaturation in the crystal-solution system:

$$\mu_{\varepsilon kp} = \mu_{0cr} + U_{\varepsilon}, \ \Delta \mu_{\varepsilon} = \mu_{sol} - \mu_{\varepsilon cr} = \Delta \mu_0 - U_{\varepsilon}, \tag{2}$$

where  $U_{\varepsilon}$  is the specific deformation energy,  $\mu_{sol}$ ,  $\mu_{0cr}$ , and  $\mu_{\varepsilon cr}$  are the chemical potentials of the solution, unstressed, and stressed crystals, respectively. Thus, the elastic stresses in the crystal shift the process towards dissolution. In particular, it explains the effect of selective etching.

However, it should be noted that the skin-layer hypothesis has never been confirmed experimentally. Moreover, a number of objections can be put forward against this hypothesis. Let's assume that at the initial moment, the components are uniformly distributed over the crystal. Then, after the first elementary act (atomic jump between adjacent monolayers), the surface concentration of one component will increase, while the other will decrease. One elementary act will not be enough to establish equilibrium if the crystal composition significantly deviates from the equilibrium with the solution. So, all subsequent diffusion acts of each component will be directed to the area with its higher concentration (that is, in the direction of the concentration gradient of the component) that contradicts the first Fick's law.

At the same time, accounting the misfit stresses allows one to describe the observed metastable equilibrium of the supercooled melt with the substrate, which will be discussed below, in fairly good agreement with the experiment.

Almost simultaneously with Bolkhovityanov's studies, similar effects were observed by A. Glikin's group at St.-Petersburg University regarding the growth of mixed crystals from aqueous solutions [4–13]. Based on numerous observations of processes in aqueous systems with  $(Co,Ni)(NH_4)_2(SO_4)_2 \cdot 6H_2O$ ,  $(Cr,Al)K(SO_4)_2 \cdot 12H_2O$ ,  $(Mg,Ni)SO_4 \cdot 7H_2O$ ,  $(Fe,Ni)SO_4 \cdot 7H_2O$ ,  $K_2(SO_4,CrO_4)$  salts, the relationship between the surface morphology formation and the solubility ratio of the system components was demonstrated. The observed processes were interpreted as the replacement of a part of the crystal volume by a crystalline phase of different composition; accordingly, this process was called the reaction of isomorphous replacement.

Despite the difference between the growth processes, the morphology of the textures formed in the melt and in the solution was very similar: in some cases, it was possible to achieve the formation of a continuous epitaxial layer, while in others, a system of islands formed, which were often located in the center of etch pits.

However, a reasonable mechanism for such surface processes has not been proposed in any of the aforementioned works [1–13], so the criteria for the formation of one or another surface morphology were not clear either.

#### 2.1. In situ Atomic Force Microscopy [14]

In [14], in situ atomic-force microscopy (AFM) study of the interaction of a (010) rubidium acid phthalate (RbAP) crystal with a potassium acid phthalate (KAP) solution was performed. In the first stage (during the first 3–4 min), a rather intensive layer-by-layer dissolution of the sample with an approximately normal rate of about 5  $\mu$ m/min was observed. Approximately five minutes later, the rate decreased considerably and comprised R  $\approx$  0.5  $\mu$ m/min. So, within 10 min, the dissolution slowed approximately ten times. The primary dissolution of the substrate was replaced by the rapid nucleation and growth of islands. After about 1 min, the crystal surface acquired the appearance shown in Figure 2a. Further, this pattern changed very slowly, and the channels between the islands were not overgrown throughout the experiment (Figure 2b).



**Figure 2.** The (010) surface of the RbAP crystal after 12-min-long (**a**) [14] and 1.5-h-long (**b**) [15] interaction with the RbAP solution (optical microscope). Reprinted from J. of Crystal Growth, vol. 261, Voloshin, A.E., Kovalev, S.I., Rudneva, E.B., Glikin, A.E., Phenomena and mechanisms of mixed crystal formation in solutions II. Mechanism of interface processes, p. 105–117 © 2004 Elsevier B.V.

However, the dissolution continues between the islands forming the channels penetrating into the crystal volume. Figure 3 shows three-dimensional images of the surface inside the channels reconstructed from the AFM images. New islands can occur within the channels. The formation of the protrusion "1" and the pit "2" at the channel bottom can be seen in Figure 3a. This shows that inside the channels, the mechanisms of growth and dissolution also work simultaneously, as they do the surface. Further dissolution of the substrate between the islands leads to a gradual deepening and simultaneous narrowing of the channel due to new phase crystallization on its walls (Figure 3b,c).



**Figure 3.** Three-dimensional reconstruction of AFM images of the surface of the RbAP crystal interacting with the KAP solution: (a) 14 min, (b) 24 min, and (c) 28 min after the introduction of the solution [14]. Reprinted from J. of Crystal Growth, vol. 261, Voloshin, A.E., Kovalev, S.I., Rudneva, E.B., Glikin, A.E., Phenomena and mechanisms of mixed crystal formation in solutions II. Mechanism of interface processes, p. 105–117 © 2004 Elsevier B.V.

It also should be noted that the islands formed at the beginning of the experiment were also subjected to slow dissolution due to a change of the solution composition with time, leading to changes in their initial appearance (Figure 2b).

## 2.2. Morphological Effect of the Reaction of Isomorphous Replacement [14]

The AFM studies have shown that the substrate dissolution is the initial stage of the interaction of the crystal and the "foreign" solution. Obviously, it continues until supersaturation in the solution

subsurface layer becomes sufficient for the new phase crystallization. This dissolution is due to purely thermodynamic reasons that directly follow from the Equation (1). It reflects the fastest way of the system motion to the equilibrium state. No new crystal or layers are formed on the surface of the original crystal during this dissolution.

Since generally the ratio of isomorphic components in the crystal and in the solution is different, the composition of the solution in the subsurface layer changes during the crystal dissolution. Therefore, the composition of the islands of the new phase also differs from the composition of the original crystal. It is close to equilibrium with the solution in the subsurface layer, so the islands protect the crystal from further dissolution; however, dissolution continues between the islands.

The possibility of crystallization of the new phase and the mechanism of its growth are determined by the ratio of the rates of the diffusion in the solution, the dissolution of the initial crystal, and the growth of the new crystalline layer. If the diffusion rate is greater than the dissolution rate (for example, with intensive stirring), then the supersaturation necessary for crystallization will never be achieved, and the crystal will dissolve completely. Otherwise, the supersaturation in the solution subsurface layer will gradually increase until the crystallization of the new phase begins, and further, until the sum of the rates of its growth and the diffusion in the solution becomes equal to the substrate dissolution rate. If the dissolution is not very intense, such equalization of the rates may occur already at a sufficiently low supersaturation, and then the growth of the new layer will follow a spiral mechanism.

Such a process was observed in situ in the laser interferometer at the interaction of mixed KCNSH crystals with foreign mixed solutions  $K_2(Co, Ni)(SO_4)_2 \cdot 6H_2O$  [16]. In this case, the growth of the new layer began on the tops of active hillocks and spread to their feet.

If the supersaturation in the solution subsurface layer reaches a value sufficient for growth by the mechanism of two-dimensional nucleation, then intensive deposition of islands begins over the entire crystal surface. Since crystallization occurs very quickly in this case, it is most likely that supersaturation will drop sharply as a result. Also, it significantly reduces the crystal surface available for dissolution. For this reason, the influx of the substance into the solution will slow down greatly. In this case, further growth of islands will occur by the spiral mechanism and the formation of new islands will stop.

Thus, dissolution plays an active role in the transformation of the substrate surface at all stages of its interaction with a foreign solution.

Finally, one can divide the whole process into three stages (Figure 4): (a) the primary dissolution of the substrate and formation of supersaturated solution boundary layer, (b) precipitation and fast growth of islands, and (c) further slow growth of islands combined with substrate dissolution between them.



**Figure 4.** Stages of epitaxial structures formation: (**a**) initial dissolution of the substrate, (**b**) precipitation of islands, (**c**) further growth of islands during substrate dissolution [14]. <sup>3</sup> Reprinted from J. of Crystal Growth, vol. 261, Voloshin, A.E., Kovalev, S.I., Rudneva, E.B., Glikin, A.E., Phenomena and mechanisms of mixed crystal formation in solutions II. Mechanism of interface processes, p. 105–117 © 2004 Elsevier B.V.

Let's consider the model of the process in more detail. Here, it is assumed that the precipitation of new islands has already finished, and that the growth of already existing ones occurs only due to the substrate dissolution between them and the matter transfer to the side walls of the channels. In other words, material transport outside the channels and the normal growth of the islands are ignored. It is also assumed that the process runs at a constant temperature and that there is a continuous series of solid solutions. We denote the specific area of the surface free of islands at a certain point in time as S, and the average depth of the channels formed up to this moment as h (Figure 5).



**Figure 5.** Schematic illustrating the tangential growth of islands during dissolution of the substrate between the islands: (**a**) section (**b**) view from the top [14]. Reprinted from J. of Crystal Growth, vol. 261, Voloshin, A.E., Kovalev, S.I., Rudneva, E.B., Glikin, A.E., Phenomena and mechanisms of mixed crystal formation in solutions II. Mechanism of interface processes, p. 105–117 © 2004 Elsevier B.V.

Let's consider the material balance of the process. If the channel depth between the islands increases by *dh* as a result of dissolution, then the crystalline phase volume *Sdh* enters the solution that leads to an additional solution supersaturation. This results in the crystallization of the layer with a thickness of *dr* on the channel walls (Figure 5b), leading to a change in the free substrate surface area by -dS, while the volume of the crystallized phase is *hdS*. However, the compositions of the substrate and the crystallized layer are different; therefore, the coefficient  $\omega$  is entered into the material balance equation, which takes into account changes in the volume and the solubility of the crystalline phase, depending on its composition changes. Then, the equation of material balance takes the form

$$\begin{aligned} \omega Sdh &= -hdS\\ S &= S_0 \Big|_{h=h_0} \end{aligned} \tag{3}$$

where  $S_0$  and  $h_0$  are the initial free surface area and the initial average height of the islands, respectively. Solving the problem (3) under the assumption that  $\omega$  = const during the process gives

$$S = S_0 \left(\frac{h_0}{h}\right)^{\omega}.$$
(4)

If we consider the process for an infinite time, then in its course, the depth of the channels will change from  $h_0$  to  $\infty$ . Then, in order for the islands coalesce and form a continuous layer, it is necessary to dissolve the volume *V* of the substrate equal to

$$V = \int_{h_0}^{\infty} Sdh = S_0 h_0^{\omega} \int_{h_0}^{\infty} \frac{dh}{h^{\omega}} = \begin{cases} \frac{h_0 S_0}{\omega - 1} & \text{at } \omega > 1, \\ \infty & \text{at } \omega \le 1 \end{cases}.$$
(5)

This means that if  $\omega > 1$ , the epitaxial layer grows faster than the substrate is dissolving, and in this case, the formation of a continuous layer requires the dissolution of a certain finite volume of the substrate. If  $\omega \le 1$ , then an infinitely large volume of the substrate will be dissolved, meaning that it is impossible to form a continuous epitaxial layer. Thus, the parameter  $\omega$  can be regarded as a criterion for the type of morphological texture formed during the reaction of isomorphous replacement.

The approximate shape of the layer-substrate interface was derived from Equation (4) under the assumption that the islands have a cylindrical shape of radius *r*, and their number per surface unit is  $\rho$  [14]. Then  $S = 1 - \rho \pi r^2$ , and

$$h = h_0 \left(\frac{1 - \rho \pi r_0^2}{1 - \rho \pi r^2}\right)^{1/\omega}.$$
(6)

Figure 6a,b show the shape of the channels calculated for  $\omega = 1/2$  and  $\omega = 2$  and the layer-substrate interface for  $\omega = 4$  when p = 10000 mm<sup>-2</sup>,  $h_0 = 3 \mu m$  and  $r_0 = 5 \mu m$ . For comparison, Figure 6c shows a photograph of the cross section of the InAs/GaP epitaxial structure published in [1]. The similarity of the profiles in Figure 6b,c confirms the validity of the proposed mechanism.



**Figure 6.** Layer-substrate interface: (**a**) shape of the channels between the islands calculated at  $\omega$  = 2 and  $\omega$  = 1/2. (**b**) layer-substrate interface calculated at  $\omega$  = 4, (**c**) part of the cross section of the InAs/GaP (111)B structure formed during the contact of the saturated melt with the substrate (see Figure 7 in [1]) [14]. Reprinted from J. of Crystal Growth, vol. 261, Voloshin, A.E., Kovalev, S.I., Rudneva, E.B., Glikin, A.E., Phenomena and mechanisms of mixed crystal formation in solutions II. Mechanism of interface processes, p. 105–117 © 2004 Elsevier B.V.

#### 2.3. Volume Effect of the Reaction of Isomorphous Replacement

It follows from the Equation (3) that parameter  $\omega$  equals to the ratio of the volume of the grown epitaxial layer  $\Delta V_l$  to the dissolved substrate volume  $\Delta V_c$ , i.e., it describes the change in the volume of the crystalline phase over the course of isomorphous replacement:

$$\omega = \Delta V_l / \Delta V_c. \tag{7}$$

Thus, it characterizes the volume effect of the reaction. The detailed derivation of the expression for  $\omega$  is given in [14] by considering the processes of crystal dissolution and the growth of a new crystalline phase in a hypothetical binary system of isomorphic compounds *A* and *B* in the Schreinemakers diagram. Schreinemakers diagram is a plot of the dependence of the component A content ( $v_A$ ) on the component B content ( $v_B$ ) in saturated solutions, i.e. the mutual solubility of the solid components where the coordinate axes indicate the volumes of the crystalline phases dissolved in a fixed amount of the solvent (e.g., in 100 cm<sup>3</sup>). The expression was obtained

$$\omega = \frac{1 - c(dv_B/dv_A + 1)}{1 - l(dv_B/dv_A + 1)}.$$
(8)

Here, *c* and *l* are the volume fractions of component *A* in the initial crystal and in the crystalline phase equilibrium with the given solution, respectively, and  $v_A$  and  $v_B$  are the contents of A and B in the solution.

In the case of interaction of pure components of the system (c = 1, l = 0), Equation (8) is transformed into

$$\omega = -dv_B/dv_A.$$
(9)

Thus, the volume effect of the reaction of isomorphous replacement depends on the differences in the compositions of the crystalline phases and on the ratio of the solubility of the components at the figurative point of the solution in the phase diagram.

At the same time, we should indicate that criterion (8) is only approximate because it assumes that volume factor  $\omega$  remains constant over the course of the reaction. In fact, during the reaction, the composition of the solution changes due to the dissolution of the crystal and the crystallization of the new phase, and therefore, in accordance with Equation (8), *c* and *l* change. However, these changes can be neglected if the solution volume is much larger than the volume of the crystal.

## 2.4. Micromosaic Inhomogeneity of Mixed Crystals

Thus, the reaction of isomorphous replacement is a complex multidirectional process of simultaneous crystal dissolution and growth of another crystalline phase. This leads to the transformation of crystal surface into a mosaic of randomly scattered areas of various compositions. As a result, a mosaic microinhomogeneity is formed in the crystal bulk, a new type of inhomogeneity which occurs only in mixed crystals.

The first studies of mosaic microinhomogeneity in (Pb,Ba)(NO<sub>3</sub>)<sub>2</sub>, K(Br,Cl), and (K,Rb)HC<sub>8</sub>H<sub>4</sub>O<sub>4</sub> crystals by X-ray microtomography were described in [17–19]. However, this method is characterized by numerous artefacts. In addition, the size of the detected mosaic (~50–100  $\mu$ m) is close to the method resolution (~50  $\mu$ m). Later, in [20], another study of micromosaicity in the synthesized mixed (Co,Ni)K<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (KCNSH) crystals by the energy-dispersive method was performed.



**Figure 7.** Images of KCNSH crystal in characteristic (**a**) Co and (**b**) Ni X rays, and (**c**) the sum of images in panels (**a**,**b**) [20]. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature. Cryst. Rep., Mosaic microinhomogeneity in crystals of (Co,Ni)K2(SO4)2·6H2O solid solutions, Grigoryeva, M.S., Vasilyeva, N.A., Artemov, V.V., Voloshin, A.E. © Pleiades Publishing, Inc., 2014.

Figure 7a,b present Co and Ni distribution patterns. Figure 7c presents a summed image of Co and Ni distributions in the crystal obtained by superimposing the initial images (Figure 7a,b). The sum of the contents of the cobalt and nickel components in a solid solution should amount to 100% and, therefore, be constant. Figure 7 shows that the inhomogeneity of the summary image is much smaller than that of the initial ones, confirming the presence of mosaic microinhomogeneity of Co and Ni in the crystal. The characteristic size of the mosaic elements varies in the range of 70–200  $\mu$ m.

Our recent study [21] of KCNSH mixed crystals grown from solutions with a mass ratio of the isomorphic components KCSH:KNSH = 1:2 has shown a clear dependence of the value of micromosaic Ni inhomogeneity  $|\delta c_{\text{Ni}}|$  on the solution supercooling  $\Delta T$  (Figure 8). Linear extrapolation to the value  $|\delta c_{\text{Ni}}| = 0$  shows that a complete suppression of the mosaic inhomogeneity can be expected at  $\Delta T = 0.8$ –0.9 °C.



Figure 8. Dependence of the mosaic microinhomogeneity of the Ni content in KCNSH crystals on the solution supercooling [16].

#### 2.5. Study of Quasi-Equilibrium States

As it follows from Sections 2.1 and 2.2, the interaction of mutual nonequilibrium phases starts with the crystal dissolution, which is the cause of subsequent epitaxial processes. However, the excess thermodynamic potential (1) of such a system can be compensated for by solution supercooling. In this case, the system acquires a metastable equilibrium, which prevents both the dissolution of the crystals and the growth of the new phase. This state was predicted theoretically and then confirmed by indirect data on semiconductor systems [2,3]. Later, such states were observed in situ in water-salt systems  $K_2SO_4$ - $K_2CrO_4$  [9], Ni(NH<sub>4</sub>)(SO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O-Co(NH<sub>4</sub>)(SO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O [12], KAP-RbAP [14] and KDP-ADP [15]. For the last three systems, critical supercooling was measured in the whole composition range of the mixed solutions by the method described in [14]. The results are shown in Figure 9.



**Figure 9.** Quasi-equilibrium states in the supercooled mixed solutions: (a)  $Ni(NH_4)(SO_4)_2 \cdot 7H_2O$  and  $Co(NH_4)(SO_4)_2 \cdot 7H_2O$  crystals in the solutions saturated at 29 °C [12]; (b) KAP and RbAP crystals in the solutions saturated at 39 °C [14]; (c) KDP and ADP crystals in the solutions saturated at 35 °C [15]. Reprinted from J. of Crystal Growth, vol. 261, Voloshin, A.E., Kovalev, S.I., Rudneva, E.B., Glikin, A. E., Phenomena and mechanisms of mixed crystal formation in solutions II. Mechanism of interface processes, p. 105–117 © 2004 Elsevier B.V.

This quasi-equilibrium state is very unstable. Any small change in supercooling (by 0.1 °C) leads to disequilibrium. An increase of supercooling leads to a net growth of a new crystalline phase, while supercooling reduction resumes the reaction of isomorphous replacement under which the dissolution of crystal begins, and it is accompanied by the growth of islands. In this case, the lower the supercooling, the more intense the crystal dissolution and the growth of islands. This, in particular, explains the decrease of the mosaic microinhomogeneity with an increase of supercooling (Figure 8).

The dissolution role in the formation of a surface layer is also seen from the experiments on the interaction of the (100) surface of a KAP crystal with the RbAP solution (Figure 10) [14]. Crystals were placed into a saturated solution and supercooled by 3.5 °C. In both cases, the formation of a continuous layer was observed, but in the first case, it was formed from an island texture (Figure 10a), whereas in

the second, the smooth epitaxial layer was grown (Figure 10b). The wavy surface relief of both samples is caused by the sawing of the crystals perpendicular to the (010) cleavage planes.



**Figure 10.** (100) face of a KAP crystal after 3-h-long reaction with (**a**) saturated and (**b**) supercooled (by 3.5 °C) RbAP solution at room temperature [14]. Reprinted from J. of Crystal Growth, vol. 261, Voloshin, A.E., Kovalev. S.I., Rudneva, E.B., Glikin, A.E., Phenomena and mechanisms of mixed crystal formation in solutions II. Mechanism of interface processes, p. 105–117 © 2004 Elsevier B.V.

## 2.6. The Mechanism of Stress Relaxation at Crystal Growth from Low-temperature Solutions

The results of the experiments on epitaxial growth of RbAP layers onto a KAP substrate (Figure 10) raise the question: why don't these heterostructures crack? Indeed, as seen in the Table 1, the KAP/RbAP lattice mismatch changes from 1.7 to 4.3%. At these huge values, the misfit stresses could be relaxed only by generation of a misfit dislocation grid of very high density. However, dislocation generation and motion are strongly suppressed at low temperatures. For example, at room temperature in Ge, the critical stress of dislocation generation is an order of magnitude less, and the dislocation mobility is 6 orders of magnitude less than at the melting point [22]. Therefore, the question of the elastic stress relaxation mechanisms at low temperature crystal growth is not easy and requires special study.

Lattice Parameter	КАР	RbAP	Misfit, %
Space group	P2		
<i>a</i> , Å	6.47	6.58	1.7
<i>b,</i> Å	9.61	10.02	4.3
<i>c,</i> Å	13.26	12.99	-2.1

Table 1. Lattice parameters of KAP and RbAP crystals [23].

This problem was studied in [24] on the series of KCSH/KNSH bicrystals. The samples were grown by decreasing the solution temperature method in a standard 1.8 L crystallizer with initial solution supercooling to 4.5 °C. With the use of KNSH crystals of ~ $10 \times 10 \times 20$  mm as substrates, the sizes of the grown KCSH/KNSH bicrystals reached as much as  $55 \times 40 \times 45$  mm.

Two samples were cut from the grown bicrystal: sample I was cut parallel to the substrate surface, and sample II was cut perpendicular to the substrate surface (Figure 11a). On the X-ray topograph of sample I, there are no images of misfit dislocations at the interface in the sample plane (Figure 11b), while in both samples (Figure 11b,c), on the side interfaces 1, one can see the solution inclusions 2 and dislocation bundles 3, which make a small angle with a normal interface. The dislocation density in the bundles was estimated to be  $10^5-10^6$  cm<sup>-2</sup>. It should be noted that the dislocation density in KNSH and KCSH crystals is usually of the order of  $10^1-10^2$  cm<sup>-2</sup>.

KNSH

(c)



(d)

Figure 11. Schematic diagram of cutting the samples for X-ray topography (a), X-ray topographs of the sample I (b) and sample II (c) and photographs of the interface in the sample II (d). 1---interface, 2—solution inclusion, 3—dislocations [24]. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature. Cryst. Rep., A study of the mechanisms of defect formation in K2Ni(SO4)2.6H2O/K2Co(SO4)2.6H2O bicrystals grown from aqueous solutions, Grigor'eva,. M.S., Voloshin, A.E., Rudneva, E.B., Manomenova, V.L., Khakhanov, S.N., Shklover, V.Ya. © Pleiades Publishing, Inc., 2009.

Figure 11d shows the bubbles (solution inclusions) at the interface of the sample II. Their average diameter is 10  $\mu$ m and density is about 5  $\times$  10<sup>5</sup> cm<sup>-2</sup>. Many of these inclusions are sources of dislocations inclined to the interface (Figure 11b,c). This is, in particular, shown by similar density magnitudes for dislocations and inclusions.

It is known that inclusions can effectively relax elastic stresses. The theory of multidomain structures [25] predicts that inclusions of another phase whose elasticity modulus differs from that of the main matrix can effectively relax stresses even without dislocations. The mother liquor inclusions can be considered as phase inclusions with zero modulus of elasticity; therefore, they should decrease the mismatch stresses.

Thus, the formation of inclusions can be an alternative to dislocations for the elastic stress relaxation at low-temperature crystallization. However, to provide it, one should understand how exactly elastic stresses in a crystal affect the capturing of inclusions. For this purpose, in situ study of inclusion formation during epitaxial growth in the (NH<sub>4</sub>)<sub>2</sub>Co(SO)<sub>2</sub>·6H<sub>2</sub>O (ACSH) - (NH<sub>4</sub>)<sub>2</sub>Ni(SO)<sub>2</sub> · 6H<sub>2</sub>O (ANSH) and KCSH-KNSH systems was conducted [26].

A drop of the KCSH (ACSH) saturated solution was deposited onto a KNSH (ANSH) crystalline substrate surface so that the latter was completely immersed. The crystallization of the composition was observed using a LEXT OLS 3100 microscope in the optical and confocal modes. The series of photographs is presented in Figures 12 and 13.



**Figure 12.** Crystallization of ACSH layers on the ANSH (110) face: (a) 4, (b) 20, (c) 49 and (d) 319 s after coming into contact with the ACSH solution. *1*—is a macrostep [26]. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature. Crystallography Reports, Formation of Solution Inclusions in Bicrystals of Potassium–Cobalt/Potassium–Nickel and Ammonium–Cobalt/Ammonium–Nickel Sulfates, Grebenev, V.V., Grigor'eva, M.S., Voloshin, A.E. © Pleiades Publishing, Inc., 2010.



**Figure 13.** Crystallization of KCSH layers on the KNSH (001) face: (**a**) 4, (**b**) 52, (**c**) 128, and (**d**) 358 s after coming into contact with the KCSH solution. *1*—macrostep, 2—inclusions [26]. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature. Crystallography Reports, Growth and properties of mixed K2NixCo1–x(SO4)2·6H2O crystals, Vasilyeva, N.A., Grigoryeva, M.S., Grebenev, V.V., Voloshin, A.E. © Pleiades Publishing, Inc., 2013.

In both cases, the steps are born on the sample edges and form macrosteps of micron height. In the ACSH/ANSH system, the steps are fairly straight and close in the sample center without the formation of inclusions (Figure 12). In contrast, in the KCSH/KNSH system, the steps are strongly curved and close in the sample center forming the series of inclusions (Figure 13). It should be noted that the mismatch of the KCSH-KNSH lattices in (001) plane is several times larger than that in the ACSH-ANSH (Table 2).

Lattice	ACSH/ANSH			KCSH/KNSH		
Parameter	ACSH [27]	ANSH [28]	Misfit, %	KCSH [29]	KNSH [30]	Misfit, %
Space group	P2 <sub>1</sub> /c			P2 <sub>1</sub> /c		
<i>a</i> , Å	9.25	9.241	0.097	9.045	8.98	0.72
<i>b,</i> Å	12.52	12.544	-0.192	12.193	12.159	0.275
<i>c,</i> Å	6.24	6.243	-0.048	6.146	6.125	0.342
β, deg	107.1	106.97	0.121	104.31	105.6	-0.734

Table 2. Lattice parameters of ACSH, ANSH, KCSH and KNSH crystals.

The dependence of the step bending on the lattice mismatch becomes clear due to the X-ray topography of the KAP/RbAP composition (Figure 14a, [31]). It shows that a dark contrast is formed along the layer boundary (Figure 14b). This is so called diffraction kinematic contrast, arising in areas with non-uniform elastic deformation [32]. In our case, such an area arises in the substrate near the edge of the layer as a zone of the misfit elastic stress relaxation between the layer and the substrate. Obviously, the larger the lattice mismatch, the stronger the deformation near the edge of the layer. According to Equation (2), effective supersaturation is reduced in this area. However, a protrusion formed for any reason at the edge of the layer (of the macrostep) will fall in the less deformed area

with greater effective supersaturation and will start to grow more rapidly than the main macrostep. In this way, morphological instability is developed at a high level of the lattice mismatch between the layer and the substrate. This results in the capture of inclusions.



**Figure 14.** X-ray topograph of the sample after 48 h-long interaction of the RbAP crystal with the KAP solution (**a**) [31] and the enlarged area A (**b**) [15]. Reprinted from J. Cryst. Growth, vol. 255, Glikin, A.E., Kovalev, S.I., Rudneva, E.B., Kryuchkova, L.Yu., Voloshin, A.E. Phenomena and mechanisms of mixed crystal formation in solutions. I. General concept on the example of the system  $KHC_8H_4O_4$ -RbHC $_8H_4O_4$ -H<sub>2</sub>O, p. 150–162 © 2003 Elsevier B.V.

In other words, the capture of inclusions initiated by the elastic stresses emerging during crystal growth finally leads to stress relaxation due to these inclusions. This is illustrated by the experiment growing the RbAP crystal on the KAP crystal. The lattice mismatch in RbAP/KAP system is 20–40 times larger than in ACSH/ANSH one. Therefore, one layer of inclusions is not enough to eliminate stresses at the hetero-interface. As a result, a whole area of inclusions with a thickness of several millimeters is formed (Figure 15). After this, the RbAP crystal grew almost free from defects.



Figure 15. Photograph of the RbAP/KAP bicrystal [15].

In particular, this example shows that the formation of inclusions can occur not only at the hetero-interface, but can be caused by the presence of any internal stresses in the crystal which are greater than a certain critical value.

Thereafter, the conclusion about the formation of inclusions as a result of high misfit stresses has been repeatedly confirmed by our studies of the growth of mixed crystals on foreign substrates (some examples are shown in the Figure 16). As will be shown below, only the complete identity of the crystal and substrate compositions makes it possible to avoid the formation of inclusions.



Figure 16. X-ray topographs of the crystals grown on the KNSH substrates: (a) KCSH, (b)  $K_2Co_{0.28}Ni_{0.72}(SO_4)_2 \cdot 6H_2O$ , (c)  $K_2Co_{0.18}Ni_{0.82}(SO_4)_2 \cdot 6H_2O$  [16].

## 3. Growth of High-Perfect K<sub>2</sub>Ni<sub>x</sub>Co<sub>1-x</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O Mixed Crystals for UV Light Applications

#### 3.1. General Characteristic of the Defect Structure of KCNSH Mixed Crystals

In recent years, materials showing promise for use in the ultraviolet (UV) optical range have been intensively studied. Crystals for solar-blind technology represent a significant segment of materials for the UV range. It is known that the ozone layer of the Earth efficiently absorbs solar light in the wavelength range of 200–300 nm. UV radiation sources (such as electric discharges and flame) can be detected in this solar-blind spectral range because they have a significant emission components in the wavelength range of 250–280 nm. The effective band pass filter which is transparent in the 200–300 nm range and opaque in other ranges is an important element of devices for the registration of radiation in the solar-blind range. It makes it possible to use registration devices of UV radiation sources in sunlight. At present, the main materials for solar-blind filters are simple and complex nickel and cobalt sulfates [33].

Crystals of nickel sulfate and nickel Tutton's salts have similar spectra of optical transmissions. Unfortunatly, they have not only high transmittance in the UV range (at  $\lambda = 240-290$  nm), but also a transparency window in the visible light range (around  $\lambda = 500$  nm). This property is a disadvantage because such crystals do not effectively filter the radiation in the visible range. Tutton cobalt salts crystals, for example, potassium cobalt sulfate hexahydrate K<sub>2</sub>Co(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (KCSH), are also transparent in the range  $\lambda = 240-290$  nm. But the existence of an absorption band in the 350–750 nm range [33] makes it possible to fully or partially suppress a transmission peak at around 500 nm, which is characteristic of nickel salts.

Considering that cobalt sulfate and nickel sulfate crystals are isomorphic, obtaining mixed crystals of the solid solution  $K_2Co_xNi_{1-x}(SO_4)_2 \cdot 6H_2O$  (KCNSH) could be a way to effectively suppress radiation in the visible part of the spectrum. It was found that mixed KCNSH single crystals are transparent in the 240–290 nm range. They show high absorption efficiency in the visible range [34–36] due to the overlapping of the absorption bands of six-water complexes of nickel and cobalt ions that suppress transmission in the visible range. In addition, these crystals have higher thermal stability compared to crystals of individual components [37].

However, the mixed crystals grown from solutions are characterized by increased numbers of defects. At low supersaturation, the appearance of the reaction of isomorphous replacement is possible due to solution composition fluctuations and unstable hydrodynamics. This will lead to the formation of mosaic microinhomogeneity (Figures 7 and 8). It is possible to suppress these processes by creating a certain supercooling that prevents dissolution and provides crystal growth only as well as by maintaining a stable flow hydrodynamics [21].

Besides this, as a rule, isomorphic components enter into the mixed crystal lattice in a different way. This means they have different distribution coefficients depending on the crystal face atomic structure. Due to changes in the solution composition during crystal growth and different compositions of different growth sectors, the strong zonal and sectorial inhomogeneity are inherent to mixed crystals. As mixed crystals are characterized by a high level of internal stresses, they typically contain cracks and a large number of solution inclusions. It was shown by X-ray topography that the main source of elastic stresses in KCNSH crystals is a sectorial inhomogeneity [36] (Figure 17a). Figure 17b clearly shows that most cracks in this crystal are related to the sectorial boundaries [36]. A high level of stresses results in the formation of inclusions that decrease UV transmittance compared to KNSH crystal due to light scattering (Figure 17a). This problem can be effectively solved by growing crystals in shapers, where only one crystal face grows [38].



**Figure 17.** X-ray topograph [36] (**a**), photography [36] (**b**) and spectrum in comparison with KNSH crystal [16] (**c**) of KCNSH crystal grown on the open platform by temperature decreasing technique in static regime at component ratio KCSH:KNSH = 1:2 in the mother solution. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature. Crystallography Reports, Growth and properties of mixed K2NixCo1–x(SO4)2·6H2O crystals, Vasilyeva, N.A., Grigoryeva, M.S., Grebenev, V.V., Voloshin, A.E. © Pleiades Publishing, Inc., 2013.

However, another very strong source of stresses in mixed crystals is the nonstationarity of their composition, which arises in the initial transient regime, when a diffusion boundary layer is formed near the crystal-solution interface [39,40]. The zone of intensive composition variation in KCNSH crystals extends over a distance of 1 to 4 mm from the seed [38,41], depending on the crystal growth rate and the intensity of the solution stirring. The region of the initial transient is increased with decreasing the crystal growth rate and solution stirring intensity [40]. Figure 18 shows the experimental data [41] on the distribution of K<sub>2</sub>Co(SO<sub>4</sub>)·6H<sub>2</sub>O over the length of two crystals grown from solutions with component ratios of KCSH:KNSH = 1:2 and 1:1 on (110)-seeds at a rate of 0.8 mm/day. It is possible to compensate for the shift of the crystal composition in the initial transient by adjusting the solution composition.



**Figure 18.** The distribution of  $K_2Co(SO_4).6H_2O$  over the length of KCNSH crystals grown from solutions with the components ratios KCSH:KNSH = 1:2 and KCSH:KNSH = 1:1 without feeding: experiment and calculation by Equation (14) [41]. Reprinted from J. of Crystal Growth, vol. 500, Voloshin, A.E., Manomenova, V.L., Rudneva, E.B., Vasilyeva, N.A., Masalov, V.M., Zhokhov, A.A., Emelchenko, G.A. Growth of high-perfect mixed K2NixCo1-x(SO4)2.6H2O crystals for fabrication of high-efficiency UV optical filters, p. 98–103 © 2018 Elsevier B.V.

It is also necessary to consider that the composition of mixed crystals is sensitive to the growth conditions. For example, the contents of Ni and Co in KCNSH crystals depend on the growth temperature and supersaturation [42]. Therefore, the method of slow cooling cannot ensure the constancy of the chemical composition of the growing crystal.

All these problems were effectively solved in [41] by growing crystals in shapers by the temperature difference technique, continuously feeding the mother solution.

#### 3.2. Experimental Setup

The setup described in [41] was used for growing the KCNSH crystals (Figure 19). To control the solution's composition, the setup was equipped with syringe dispensers (13) and a special cover of the vessel that made it possible to extract the condensate. The crystal was mounted in the upper crystallizer part and the growth ran from top to bottom to avoid the formation of parasitic crystals on the shaper elements.



**Figure 19.** The scheme of the setup for the crystal growth at a controlled temperature difference with maintenance of the solution composition. 1—crystal; 2—crystallizer; 3—submersible centrifugal pump; 4—the vessel with growth solution; 5—thermostat; 6—heating element; 7—the temperature sensor; 8—the peristaltic pump for the condensate extraction; 9—the feeding of the KCSH and KNSH solutions; 10—intermediate cooler; 11—the cooler thermostat; 12—the motor of submersible centrifugal pump; 13—the syringe dispensers [41]. Reprinted from J. of Crystal Growth, vol. 500, Voloshin, A.E., Manomenova, V.L., Rudneva, E.B., Vasilyeva, N.A., Masalov, V.M., Zhokhov, A.A., Emelchenko, G.A. Growth of high-perfect mixed K2NixCo1-x(SO4)2·6H2O crystals for fabrication of high-efficiency UV optical filters, p. 98–103 © 2018 Elsevier B.V.

#### 3.3. Calculation of the Solution Feeding Modes [41]

## 3.3.1. Non-Stationary Feeding Mode

During the initial transient process (non-stationary mode of mass transfer), in the liquid phase near the interface, a boundary diffusion layer formed. In this process, the concentration of the components in the solution at the interface continuously changed; it increased if  $k_0 < 1$ , or decreased if  $k_0 > 1$  (see Table 3), and the crystal composition changed accordingly. At the same time, the composition of the solution far from the interface did not change. In order to ensure the constancy of the crystal composition, it was necessary to maintain a constant solution composition near the interface. This could be realized by adjusting the solution composition in the crystallizer bulk according to a special law. Such a calculation can be made if we know the law of change in the solution composition at the interface. This work was performed in [38].

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R	the normal crystal growth rate
x	the distance from the seed
$K_0$	the generalized equilibrium distribution coefficient of the components
$K^*$	the generalized equilibrium distribution coefficient of the components in a stationary mode
K(x)	effective generalized coefficient of distribution of the components in the initial transient at the crystal length x
$k_0$	the equilibrium distribution coefficient of KCSH
$k^*$	the effective distribution coefficient of KCSH in the stationary mode
k(x)	the effective distribution coefficient of KCSH in the initial transient at the crystal length x
$C_{\infty}$	the KCSH mole fraction in the salt mass in the bulk of the solution
$C_0$	the KCSH mole fraction in the salt mass in the solution at the interface
c(x)	the average mole fraction of KCSH in the crystal cross section with the coordinate x
$c_0$	the initial mole fraction of KCSH in the crystal
с*	the KCSH mole fraction in the crystal in the stationary mode
δ	the thickness of the solution diffusion boundary layer
D	the diffusion coefficient in the solution

**Table 3.** The designations used.

The analysis of the processes at this stage was carried out by the complete solution of the problem of convective diffusion in the Burton-Prim-Slichter model described by the formula [40]

$$k(x) = c(x) / C_{\infty} = k^* - (k^* - k_0)e^{-\alpha x}.$$
(10)

$$\alpha = \frac{R}{D} \frac{k_0}{k^*} \frac{1}{1 - (1 + \Delta)e^{-\Delta}}, k^* = \frac{c^*}{C_{\infty}} = \frac{k_0}{k_0 + (1 - k_0)e^{-\Delta}}, \Delta = \frac{R\delta}{D}$$
(11)

If the solution composition does not change, R=const and the convective flow is constant ( $\delta = const$ ), then  $k_0 = c_0/C_{\infty} = const$ ,  $k^* = c^*/C_{\infty} = const$  and therefore,  $\alpha = const$ .

The generalized distribution coefficient

$$K(x) = \frac{(1 - c(x))C_{\infty}}{c(x)(1 - C_{\infty})} = \frac{(1 - c(x))}{c(x)p}; p = \frac{1 - C_{\infty}}{C_{\infty}} = \frac{C_{Ni}}{C_{Co}} = const,$$
(12)

Here, *p* is the mole fraction ratio of the KNSH ( $C_{Ni}$ ) and KCSH ( $C_{Co}$ ) in the bulk of the solution. Then:

$$c(x) = \frac{1}{1 + pK(x)} \text{ and } k(x) = \frac{1 - c(x)}{1 - C_{\infty}} \frac{1}{K(x)}.$$
 (13)

Taking into account Equations (12, 13), it is possible to obtain from Equation (10) the expression:

$$c(x) = \frac{1}{1 + pK^*} - \left(\frac{1}{1 + pK^*} - \frac{1}{1 + pK_0}\right)e^{-\alpha x}.$$
(14)

The diffusion coefficients in water for potassium-nickel and potassium-cobalt sulfates are unknown; however, one can determine parameter  $\alpha$  from the data presented in Figure 18. The approximation of the experimental data by the curves calculated by the Equation (14) at  $K_0 = 3.7$  [42] and  $K^* = 3.3$  [37] gives the values  $\alpha = 1.00$  for KCSH:KNSH = 1:2 and  $\alpha = 0.50$  for KCSH:KNSH = 1:1. The crystals with feeding were grown under the same conditions as those whose composition is shown in Figure 18.

The solution feeding must ensure a constant crystal composition, that is, in this case, it will be c(x) = const = c. At the same time, however, the solution composition  $C_{\infty}$  will change with time: this means that the different solution compositions will correspond to the different points along the crystal length, that is, it can be considered as a function of x. Then, Equation (10) should be written as follows:

$$k(x) = \frac{c}{C_{\infty}(x)} = k^* - (k^* - k_0(0))e^{-\alpha x}.$$
(15)

Assuming c(x) = const and conducting a reasoning similar to the previous one, it is possible to obtain the expression for the dependence of the KCSH concentration in the salt mass of the solution on the length of the grown crystal:

$$C_{\infty}(x) = 1/(1+p-p(1-K^*/K_0)e^{-\alpha x}).$$
(16)

Here, *p* is the ratio of the component concentrations in the bulk of the solution of the final composition. Respectively, the KNSH fraction change is equal to  $1 - C_{\infty}(x)$ .

Since feeding allows the component only to be added to the solution and not to be removed, this should be done with the solution of the component whose fraction in the solution should be increased. In our case, it was KNSH. The calculation results for the 5-L crystallizer with feeding solutions saturated at 20 °C (according to [42]) are shown in Figure 20a.



**Figure 20.** Curves: (**a**)—feeding by KNSH solutions saturated at 20 °C and (**b**)—condensate extraction in the non-stationary mode to maintain the constant composition of (110) oriented crystals growing from solutions with the component ratios KCSH:KNSH = 1:2 and KCSH:KNSH = 1:1 [41]. Reprinted from J. of Crystal Growth, vol. 500, Voloshin, A.E., Manomenova, V.L., Rudneva, E.B., Vasilyeva, N.A., Masalov, V.M., Zhokhov, A.A., Emelchenko, G.A. Growth of high-perfect mixed K2NixCo1-x(SO4)2·6H2O crystals for fabrication of high-efficiency UV optical filters, p. 98–103 © 2018 Elsevier B.V.

When an additional amount of KNSH is added to the solution, the total solubility of the salts decreases in accordance with the phase diagram [42]. This means that the solution supersaturation changes too. In order to conduct crystal growth at a constant rate, it is necessary to maintain constant supersaturation. For this, together with KNSH, it is also necessary to supply a strictly defined amount of water. In the case described, the volume of water in the feeding solution saturated at 20 °C was excessive, so its part was removed by the condensate extraction. This calculation was performed using the data on the joint solubility of the salts in water [42]; the results are shown in Figure 20b.

#### 3.3.2. Stationary Feeding Mode

The calculation described in Section 3.3.1 takes into account the change in the solution composition near the interface due to formation of the diffusion boundary layer, but does not take into account the change in the solution concentration due to the transition of the salt components from the solution into the crystal due to its growth. This change should be compensated for in order to keep constant both the supersaturation and the crystal composition, since the distribution coefficients of KNSH and KCSH are different. The calculation of the stationary feeding mode is very simple in the case of growing a cylindrical crystal with a constant growth rate; this can be seen in [41]. The solution feeding rate and the condensate extraction rate in this case are rather small, comprising 2.7–4.4 ml/day for KCSH feeding solution and 10.4–14.3 ml/day for KNSH feeding solution. Finally, the total volumes of the stationary and non-stationary feeding modes.

## 3.4. Characterization of the Grown KCNSH Crystals

The longitudinal Co distribution in two KCNSH mixed crystals grown with feeding from solutions with the ratio of the components KCSH:KNSH = 1:1 and 1:2 are presented in Figure 21. Taking into account the measurement accuracy, the crystal composition can be considered constant.



**Figure 21.** Co distribution along the growth direction of the KCNSH crystals grown from solutions with the ratio of the components KCSH:KNSH = 1:1 and 1:2 [41]. Reprinted from J. of Crystal Growth, vol. 500, Voloshin, A.E., Manomenova, V.L., Rudneva, E.B., Vasilyeva, N.A., Masalov, V.M., Zhokhov, A.A., Emelchenko, G.A. Growth of high-perfect mixed K2NixCo1-x(SO4)2·6H2O crystals for fabrication of high-efficiency UV optical filters, p. 98–103 © 2018 Elsevier B.V.

The X-ray topography of the KCNSH crystal grown from KCSH:KNSH = 1:1 solution is shown in Figure 22. It can be seen that there are no inclusions and dislocations at the seed-crystal boundary, and also that there are no areas of kinematic contrast, indicating the absence or an extremely low level of elastic stresses. Previously, inclusions and the dislocations generated by them were observed not only in KCSH/KNSH bicrystals [24], but also in the mixed crystals grown by the temperature difference method in the shapers, but without solution feeding [38].



**Figure 22.** X-ray topograph of the KCNSH crystal, grown from the solution with KCSH:KNSH = 1:1 [41]. Reprinted from J. of Crystal Growth, vol. 500, Voloshin, A.E., Manomenova, V.L., Rudneva, E.B., Vasilyeva, N.A., Masalov, V.M., Zhokhov, A.A., Emelchenko, G.A. Growth of high-perfect mixed  $K_2Ni_xCo_{1-x}(SO_4)_2$ ·6H<sub>2</sub>O crystals for fabrication of high-efficiency UV optical filters, p. 98–103 © 2018 Elsevier B.V.

The intensity variations on the topography correspond to weak (less than 1%) variations in the crystal composition in the radial direction because of the uneven structure of the solution flows inside the shaper. As the crystal grows, the flow structure improves, and there are practically no variations in the upper part of the crystal.

The optical filters with a diameter of 20 mm and a thickness of 10 mm were made from the grown crystals (Figure 23a). Their transmission spectra are shown in Figure 23b,c; for comparison, the transmission spectrum of the optical filter made of NSH crystal is given (Figure 23d). The KCNSH filters have a high transmittance in the UV range (85–87%), i.e., the same as the NSH filter. Also, unlike NSH, they have almost no peaks in the visible range, and in the IR range, peaks do not exceed 10%. The latter circumstance is not a significant drawback, since modern UV detectors are insensitive to radiation with wavelengths above 500 nm. So, all these advantages make possible the successful use of KCNSH crystals as bandpass optical filters.



**Figure 23.** The optical filters made from the grown KCNSH crystals (**a**) and the transmission spectra of 10 mm thick filters made from the KCNSH crystals grown from solutions with a ratio of KCSH:KNSH: (**b**)—1:1, (**c**)—1:2 [41] and of 10 mm thick NSH optical filter. Reprinted from J. of Crystal Growth, vol. 500, Voloshin, A.E., Manomenova, V.L., Rudneva, E.B., Vasilyeva, N.A., Masalov, V.M., Zhokhov, A.A., Emelchenko, G.A. Growth of high-perfect mixed K<sub>2</sub>Ni<sub>x</sub>Co<sub>1-x</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O crystals for fabrication of high-efficiency UV optical filters, p. 98–103 © 2018 Elsevier B.V.

It should be noted that the samples obtained show the same transmittance in the UV region as KNSH crystals (Figure 17c), that is, 12–15% higher than KCNSH crystals grown without feeding [38]. This indicates the absence of scattering centers therein, and therefore, a high level of structural perfection.

## 4. Conclusions

The results of the described studies may be summarized as follows.

1. The general mechanism of reaction, i.e., isomorphous replacement, was determined. The process of interaction of a crystal with a foreign solution of isomorphic component includes the following stages: primary crystal dissolution, the formation of a highly supersaturated solution of mixed composition in the subsurface layer, crystallization of new phase islands of the composition close

to equilibrium with the solution, and tangential growth of the islands. The possibility of island accretion is determined by the volume effect of the reaction  $\omega$ , which depends on the ratio of the volume solubilities of the initial salts. When  $\omega > 1$ , the islands grow together, forming a continuous epitaxial layer; when  $\omega < 1$ , there is no splicing, and simultaneously with the growth of the islands, the initial crystal dissolves in the spaces between them. Thus, the crystal surface turns into a mosaic of local areas where multidirectional processes (growth and dissolution) simultaneously proceed. This results in the formation of a mosaic microinhomogeneity, a new kind of composition inhomogeneity which is characteristic only of multicomponent crystals. It is shown that the primary dissolution of the substrate can be suppressed by creating a certain supercooling in the system. An analytical description of the process is given and expressions for the volume effect of reaction are obtained.

- 2. A new mechanism for the relaxation of elastic mismatch stresses in heterocompositions of brittle crystals growing from low-temperature solutions, when the formation of misfit dislocations is impossible, was discovered. In this case, the process of relaxation of the mismatch stresses is due to the formation of numerous inclusions at the heterointerface, which (by analogy) can be called mismatch inclusions. The probability of the formation of inclusions decreases with decreasing lattice mismatches.
- 3. According to the research results, the general concept of growing mixed crystals from solutions was formulated and implemented to ensure a high level of structural perfection:
  - crystal growth in the shapers to eliminate sectoral inhomogeneity;
  - feeding the solution according to a special law to eliminate the initial transient region;
  - growth at a constant temperature to reduce zonal inhomogeneity, the supercooling of the solution should be sufficient to suppress exchange reactions in the system.

The implementation of these principles in the growth of mixed KCNSH crystals yielded very perfect crystals with excellent optical characteristics. The crystals contain neither inclusions nor dislocations, and do not have noticeable internal stresses. The crystals demonstrate excellent optical characteristics: at a thickness of 1 cm, the transmission in the wavelength range of 200-300 nm is up to 87%, in the range of 400–600 nm, less than 1%, and in the range of 800–900 nm, less than 10%. Thus, taking into account the peculiarities of the growth of mixed crystals, and carrying out a set of measures aimed at increasing their homogeneity, it is possible to obtain mixed crystals of a good quality.

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Conflicts of Interest: The authors declare no conflict of interest.

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