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## **GROWTH VELOCITIES AND SECTORIAL AND ZONAL DISTRIBUTIONS OF IMPURITIES IN CRYSTALS**

*Formulae for relative impurity content in various parts of a crystal have been derived and analysis of sectorial and zonal distributions of impurities conducted. Contribution of volume diffusion controlled crystal growth for sectorial and zonal distributions of impurities in lopezite crystals has been evaluated as small in comparison with surface diffusion.*

**Keywords:** Crystal growth, impurities, lopezite crystals, defects.

### **1. INTRODUCTION**

Impurities in crystals are incorporated either uniformly or nonuniformly [1-4]. Sectorial and zonal distributions of foreign atoms are common in minerals and synthetic crystals. Various elemental processes occurring during crystal growth and various physical and chemical parameters decide on the type and final distribution of impurities. Sectorial and zonal distributions of various types of defects: inclusions, dislocations, point defect clusters, growth bands in synthetic lopezite (KBC,  $K_2Cr_2O_7$ , potassium bichromate) crystals grown from aqueous crystals have been revealed and described in our previous papers [5-12]. Since point defects affect many physical properties of crystals our recent interest focused mainly on point defect clusters distributions, that have been revealed on crystals surfaces as flat-bottomed etch pits [12]. Both sectorial and zonal distributions of these defects have been recently revealed by etch topography and analysed [11,12].

The aim of the paper was to derive formulae describing effects of variation of growth velocities and anisotropy of growth velocities on incorporation of impurities in crystals basing on Burton-Prim-Slichter equation [13, 1-4].

Examples of calculations for sectorial and zonal variations of impurity content contributed by volume diffusion controlled crystal growth of lopezite crystals are presented and discussed.

## 2. RESULTS AND DISCUSSION

Figure 1 presents EDX and EDXRF spectra of a  $K_2Cr_2O_7$  crystal. EDX reveals only K, Cr and O elements indicating that it is a pure crystal, but EDXRF shows that foreign atoms are also present in a host crystal. They are impurities in lopezite structure. Impurities from the growth environment are adsorbed and captured by particular faces of lopezite and other crystals giving rise to zonal and sectorial distributions (Fig. 2).

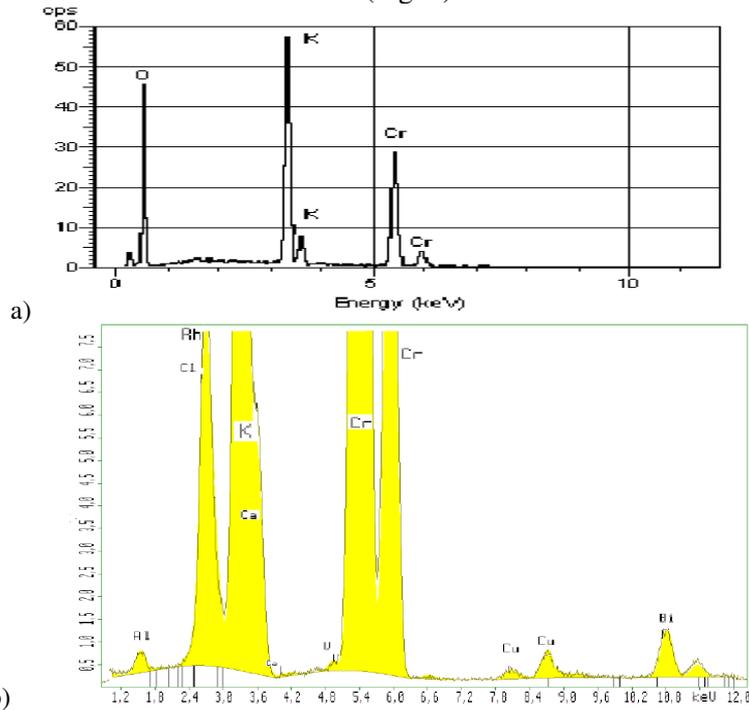


Fig. 1. (a) EDX spectrum, (b) EDXRF spectrum of a  $K_2Cr_2O_7$  crystal

Changes in impurity content in various sectors, and in one and the same sector will be analyzed by the effective distribution coefficient. Burton-Prim-Slichter (BPS) equation for the volume diffusion model will be used [13, 1-4] for explaining the origin and quantitative evaluation of local impurity content

leading to sectorial and zonal inhomogeneities, especially the sectorial and zonal distribution of point-defect clusters in lopezite crystals.

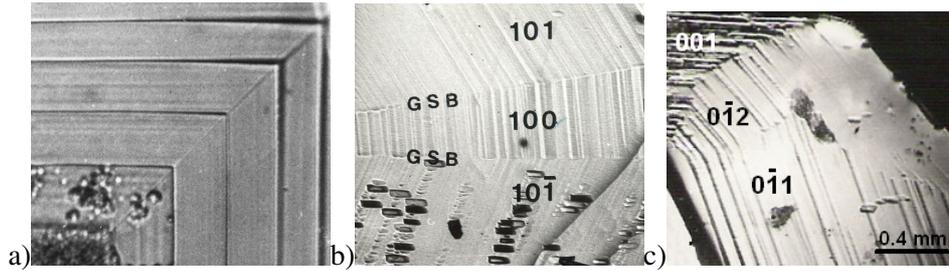


Fig. 2. Etch topographs revealing sectorial and zonal structure of crystals. (a)  $\text{NH}_4\text{Cl}$  crystal, (b,c)  $\text{K}_2\text{Cr}_2\text{O}_7$  crystals. Plane of observation: a) (001), b)  $(0\bar{1}0)$ , c)  $(\bar{1}00)$

## 2.1. Growth rate anisotropy and sectorial distribution of impurities in crystals

Volume diffusion and surface diffusion approaches are applied for describing impurity content in crystals. This paper will use volume diffusion Burton-Prim-Slichter approach, the others will be only discussed.

(i) According to Burton, Prim and Slichter the effective distribution coefficient  $k_{\text{eff}}$  is given by the expression

$$k_{\text{eff}} = k_0 / [k_0 + (1 - k_0) \exp - (R \delta / D)], \quad (1)$$

where  $k_0$  is the equilibrium distribution coefficient,  $R$  is the growth rate,  $\delta$  is the boundary layer thickness, and  $D$  is the diffusion coefficient [13, 1-4].

The effective distribution coefficient  $k_{\text{eff}}$  is defined as

$$k_{\text{eff}} = C_{s(\text{act})} / C_{l(\text{act})}, \quad (2)$$

where  $C_{s(\text{act})}$  and  $C_{l(\text{act})}$  are the actual concentrations in the solid and in the liquid, and the equilibrium distribution coefficient  $k_0$  is defined as

$$k_0 = C_{s(\text{eq})} / C_{l(\text{eq})}, \quad (3)$$

where  $C_{s(\text{eq})}$  and  $C_{l(\text{eq})}$  are the equilibrium concentrations in the solid and in the liquid.

When  $k_0 \ll 1$ , equation (1) can be written in the form

$$k_{\text{eff}} = k_0 \exp (R \delta / D), \quad (4)$$

and when  $R \delta/D \ll 1$ , eq. (4) simplifies to [1]

$$k_{\text{eff}} = k_0 + k_0 (R \delta)/D. \quad (5)$$

The three forms of the BPS equation, i.e. eqs (1), (4), and (5), show that the inhomogenities are produced when any of the parameters  $k_0$ ,  $R$ ,  $\delta$ , and  $D$  depends on the orientation of crystal face or changes during crystallization. The enrichment or depletion impurities in the solution during growth affect  $k_0$ , which is also function of the temperature [3]. The growth rate  $R$  of crystals is strongly dependent on growth conditions, supersaturation and temperature, in particular (e.g. [14] for lopezite). According to eq. (4)  $k_{\text{eff}}$  increases exponentially, and according to eq. (5) increases linearly with the increase in growth rate  $R$  [1].

Dependencies of  $k_{\text{eff}}$  on growth rate  $R$ , and on supersaturation  $\sigma$ , and on other growth parameters have been derived by various researchers and analyzed using four approaches: i) volume diffusion approach (BPS eqs), (ii) diffusional relaxation approach, (iii) statistical selection approach, and (iv) surface adsorption approach [1]. Since  $R$  depends also on adsorption on specific faces or on the crystallographic direction, the orientation-dependent impurity incorporation is expected [1], and both sectorial and zonal distribution of point-defect clusters in lopezite crystals shown in our recent papers [11,12], and sectorial and zonal distributions of inclusions reported in these crystals in our earlier papers [5,6], are the natural consequence of these dependencies.

To explain and evaluate the expected changes in impurity content in various sectors of lopezite crystals the growth rate anisotropy of these crystals has been taken into considerations. The order of relative growth velocities  $R_{\text{rel}}(\text{hkl})$  for two lopezite crystals grown at low temperature range ( $T_{\text{Growth}} < 40^\circ\text{C}$ ), at relative supersaturation about 2%, and 4% is as follows [15]

$$\begin{aligned} R_{\text{rel}}(001)_{1,0} < R_{\text{rel}}(\bar{1}01)_{2,0} < R_{\text{rel}}(100)_{2,0} < R_{\text{rel}}(012)_{2,1} < R_{\text{rel}}(101)_{2,2} < R_{\text{rel}}(\bar{0}11)_{2,8} < R_{\text{rel}}(010)_{2,9} \approx R_{\text{rel}}(011)_{2,9} < R_{\text{rel}}(\bar{1}11)_{3,0} < R_{\text{rel}}(\bar{1}11)_{3,2} < R_{\text{rel}}(111)_{3,3} < R_{\text{rel}}(\bar{1}\bar{1}0)_{3,4} < R_{\text{rel}}(110)_{3,5}, \end{aligned} \quad (6)$$

$$R_{\text{rel}}(001)_{1,0} < R_{\text{rel}}(\bar{1}11)_{2,0} < R_{\text{rel}}(012)_{2,2} < R_{\text{rel}}(011)_{2,4} < R_{\text{rel}}(010)_{2,5}, \quad (7)$$

respectively. The values of relative growth velocity  $R_{\text{rel}}(\text{hkl})$  of a given pair of faces (hkl) used here and defined as

$$R_{\text{rel}}(\text{hkl}) = R(\text{hkl})/R(001), \quad (8)$$

have been given by small figures. It is seen from inequalities (6) and (7) that growth velocities of (11k) and ( $\bar{1}\bar{1}k$ ) corner faces ( $k = 0, \pm 1$ ) are the largest, and

those of (001) faces are the smallest ones. That is why, relative growth velocity  $R_{rel}(hkl)$  defined as a ratio of growth velocity of particular, given pair of faces to the growth velocity of the largest in the habit, but the slowest growing (001) faces has been used to express the growth anisotropy of lopezite crystals. The  $R_{rel}(hkl)$  of the fastest corner faces is usually equal to or somewhat greater than 3 (2.5-3.5), and those of middle-size faces such as  $(\bar{1}01)$ ,  $(0\bar{1}1)$ ,  $(101)$ , and sometimes  $(012)$ ,  $(011)$ ,  $(100)$  and  $(010)$  [16,14], have usually  $R_{rel}(hkl)$  in the range between 1.7 and 2.5. In addition, lopezite (KBC) crystals exhibit pronounced growth polarity of  $\{100\}$  and  $\{001\}$  faces (e.g.[16,5]).  $(100)$  and  $(00\bar{1})$  faces of KBC crystals at low temperatures and at low supersaturation exhibit close to zero growth velocity [14,6]. Due to significant growth anisotropy the various growth sectors of KBC crystals can capture different amount of impurities under given growth conditions, according to equations (1), (4) and (5). The sectorial distribution of point defect clusters in lopezite crystals can be thus explained.

The changes in growth conditions, such as changes in growth temperature, and supersaturation, and in stirring rate should result in changes in distribution of point defects and other growth defects, what it has been observed [5,6,10-12]. The order of relative growth velocities  $R_{rel}(hkl)$  of one of KBC crystals grown at high temperature range, at the boiling temperature (104.5°C) is as follows

$$\begin{aligned} R_{rel}(001)_{1.0} < R_{rel}(0\bar{1}2)_{1.6} < R_{rel}(\bar{1}01)_{1.80} < R_{rel}(0\bar{1}1)_{2.0} < R_{rel}(101)_{2.1} < R_{rel}(100)_{2.2} < \\ < R_{rel}(1\bar{1}1)_{2.3} < R_{rel}(1\bar{1}\bar{1})_{2.6} \approx R_{rel}(010)_{2.6} \approx R_{rel}(011)_{2.6} < R_{rel}(111)_{2.7} \approx \\ R_{rel}(110)_{2.7}. \end{aligned} \quad (9)$$

Comparison of inequalities (9), (6) and (7) shows that growth rate anisotropy of the high temperature crystal differs from the growth anisotropy of KBC crystals grown at low temperature range. (001) faces still have the smallest growth rate equal to  $R_{(001)} = 28 \cdot 10^{-6}$  cm/s for this crystal, i.e. about ten times larger than growth rate of low temperature crystals, but differences between growth rates of various faces of high temperature crystals are smaller.

To compare impurity content in various growth sectors the relative effective distribution coefficient  $k_{eff\ rel}$  may be considered, which is defined as the ratio of the effective distribution coefficient of (hkl) face  $k_{eff(hkl)}$  and (001) face  $k_{eff(001)}$

$$k_{eff\ rel} = k_{eff(hkl)} / k_{eff(001)} = C_{s(act)(hkl)} / C_{s(act)(001)}, \quad (10)$$

where  $C_{s(act)(hkl)}$  and  $C_{s(act)(001)}$  are concentrations of impurities in sectors (hkl), and (001), respectively.

According to the BPS equation, assuming that  $k_o \ll 1$ , and both variable  $k_o$  and  $\delta$  are the same for various faces, the relative effective distribution coefficient can be written in the form

$$k_{\text{eff rel}} = \exp[(R_{(\text{hkl})} - R_{(001)}) \cdot (\delta/D)] = \exp[(R_{(001)} \delta/D) \cdot (R_{\text{rel}(\text{hkl})} - 1)]. \quad (11)$$

To analyze eq. (11) let us assume that  $\delta/D = 100$  s/cm, and supersaturation is equal to 4% at which at low temperature range  $R_{(001)} = 2.5 \cdot 10^{-6}$  cm/s. For these values factor  $R_{(001)} \cdot \delta/D = 2.5 \cdot 10^{-4}$ .

Since  $[(R_{(001)} \cdot \delta/D) \cdot (R_{\text{rel}(\text{hkl})} - 1)] \ll 1$  equation (11) simplifies to

$$k_{\text{eff rel}} = 1 + [(R_{(001)} \cdot \delta/D) \cdot (R_{\text{rel}(\text{hkl})} - 1)]. \quad (12)$$

Substitution of  $R_{(001)} \cdot \delta/D = 2.5 \cdot 10^{-4}$  into equation (12) gives

$$k_{\text{eff rel}} = 1 + [2.5 \cdot 10^{-4} (R_{\text{rel}(\text{hkl})} - 1)]. \quad (13)$$

According to the definition of  $k_{\text{eff}}$  given by equation (2),  $k_{\text{eff rel}}$  expresses ratio of actual concentration of impurities captured by (hkl) face and concentration of impurities captured by (001) face.

To analyze the relative changes in concentration of impurities in various sectors of crystals the second dimensionless coefficient assigned as  $\Omega_{\text{sec}}$  may be used, which is defined by

$$\Omega_{\text{sec}} = (C_{\text{s(act)(hkl)}} - C_{\text{s(act)(001)}}) / C_{\text{s(act)(001)}}. \quad (14)$$

Coefficient  $\Omega_{\text{sec}}$  represents relative intersectorial impurity change. Coefficient  $\Omega_{\text{sec}}$  may be expressed by  $k_{\text{eff rel}}$

$$\Omega_{\text{sec}} = k_{\text{eff rel}} - 1. \quad (15)$$

Substituting equations (12) and (13) into equation (15) gives

$$\Omega_{\text{sec}} = (R_{(001)} \cdot \delta/D) \cdot (R_{\text{rel}(\text{hkl})} - 1), \quad (16)$$

and

$$\Omega_{\text{sec}} = 2.5 \cdot 10^{-4} (R_{\text{rel}(\text{hkl})} - 1), \quad (17)$$

for lopezite crystals.

Equation (17) and inequality (7) show that  $\Omega_{\text{sec}} = 0.00025 = 0.025\%$  for sector (011), 0.030% for sector (012), 0.035% for sector (011), and 0.037% for sector (010). When  $\delta/D$  is larger, and equals to 1000 s/cm, which is also a reasonable value, we obtain  $\Omega_{\text{sec}} = 0.25\%$  for sector (011), face, and 0.37% for sector (010) of lopezite crystals.

The presented evaluation based on the BPS equation shows differences between the impurity content in (001) sectors and impurity content present in other sectors of lopezite crystals. Relative intersectorial changes in concentration of impurities in low temperature KBC crystals, expressed by  $\Omega_{\text{sec}}$  are of the order of 0.01% and 0.1%. Our assumption that  $k_0$  and  $\delta$  are the same for various faces may be oversimplified, but if these parameters are different for various faces, what seems to be probable, the differences in impurity content, expressed by coefficients  $k_{\text{eff rel}}$  and  $\Omega_{\text{sec}}$ , for various sectors of lopezite crystals are expected to be larger. Even these predicted differences are large enough to be detected by various experimental techniques.

Since sector (001) is always present in lopezite crystals obtained in various growth conditions, the growth anisotropy of lopezite crystals has been expressed by the relative growth velocity  $R_{\text{rel}}(\text{hkl})$  of a given pair of faces (hkl) with respect to (001) faces, as it was defined by equation (8).

To compare growth velocities of another pair of faces, e.g.  $(h_1k_1l_1)$  and  $(h_2k_2l_2)$  faces, the relative growth velocity  $R_{\text{rel}}^*$  should be used which is defined as

$$R_{\text{rel}}^* = R(h_1k_1l_1) / R(h_2k_2l_2), \quad (18)$$

where  $R(h_1k_1l_1)$  and  $R(h_2k_2l_2)$  are growth rates of  $(h_1k_1l_1)$  and  $(h_2k_2l_2)$  faces.

$R_{\text{rel}}^*$  can be expressed by  $R_{\text{rel}}(\text{hkl})$

$$R_{\text{rel}}^* = (R(h_1k_1l_1) / R(001)) / (R(h_2k_2l_2) / R(001)) = R_{\text{rel}}(h_1k_1l_1) / R_{\text{rel}}(h_2k_2l_2). \quad (19)$$

Let us determine, for example,  $R_{\text{rel}}(100) / R_{\text{rel}}(\bar{1}01)$ , using data from inequality (9). Substituting values  $R_{\text{rel}}(100) = 2.2$ , and  $R_{\text{rel}}(\bar{1}01) = 1.8$  into eq. (18) we have  $R_{\text{rel}}(100) / R_{\text{rel}}(\bar{1}01) = 1.22$ .

Generalizing equation (14) for any pair of faces  $(h_1k_1l_1)$  and  $(h_2k_2l_2)$  we introduce coefficient  $\Omega_{\text{sec}}^*$  defined as

$$\Omega_{\text{sec}}^* = (C_{s(\text{act})(h_1k_1l_1)} - C_{s(\text{act})(h_2k_2l_2)}) / C_{s(\text{act})(h_1k_1l_1)}, \quad (20)$$

and generalizing equation (10) we introduce coefficient  $k_{\text{eff rel}}^*$  defined as

$$k_{\text{eff rel}}^* = k_{\text{eff}(h_1k_1l_1)} / k_{\text{eff}(h_2k_2l_2)} = C_{s(\text{act})(h_1k_1l_1)} / C_{s(\text{act})(h_2k_2l_2)}, \quad (21)$$

where  $C_{s(\text{act})(h_1k_1l_1)}$  and  $C_{s(\text{act})(h_2k_2l_2)}$  are concentrations of impurities in sectors  $(h_1k_1l_1)$ , and  $(h_2k_2l_2)$ , respectively.

Generalized equations (12), (15), and (16) take the form

$$k_{\text{eff rel}}^* = 1 + [(R_{(h_1k_1l_1)} \cdot \delta / D) \cdot (R_{\text{rel}}^* - 1)], \quad (22)$$

$$\Omega_{\text{sec}}^* = k_{\text{eff}}^* - 1, \quad (23)$$

$$\Omega_{\text{sec}}^* = (R_{(h_1k_1l_1)} \cdot \delta/D) \cdot (R_{\text{rel}}^* - 1), \quad (24)$$

where indices  $(h_1k_1l_1)$  and  $(h_2k_2l_2)$  are assigned to both faces.

(ii) Diffusional relaxation approach based on the presence of an adsorption layer at crystal-medium interface give also possibility to determine effective distribution coefficient and to explain the nonuniform distribution of impurities in various sectors of crystals [1]. When  $k_o \ll 1$  the effective distribution coefficient may be expressed by the equation

$$k_{\text{eff}} = k_{\text{ads}} \exp(-R_i/R), \quad (25)$$

and when  $R_i/R \ll 1$ , eq. (14) simplifies to [1]

$$k_{\text{eff}} = k_{\text{ads}} + k_{\text{ads}} \cdot (-R_i/R), \quad (26)$$

where  $R$  is growth rate, and  $R_i = h/\tau = D/h$ .  $D$  is diffusion coefficient of the impurity,  $h$  is the thickness of the deposited layer,  $\tau$  is a time during which a new growth layer is deposited, and  $k_{\text{ads}}$  is the adsorption layer constant [1]. According to these relations (eqs. (25) and (26))  $k_{\text{eff}}$  decreases exponentially or linearly with the inverse of growth rate  $R$  [1]. Equations (25) and (26) show that growth rate anisotropy, i.e. dependence of  $R$  on the crystallographic direction shown in inequalities (6), (7) and (9) will lead to sectorial distribution of impurities in lopezite crystals. Apart from  $R$  also  $k_{\text{ads}}$  will contribute to sectorial capture of impurities.

(iii) To discuss the supersaturation dependence of  $k_{\text{eff}}(\sigma)$ , the statistical selection approach developed by Voronkov and Chernov, and Chernov will be shortly discussed. In this approach the process of incorporation of the impurity in the crystal is a statistical selection process of impurity particles by kinks, and is determined by the probability of attachment and detachment of impurity particles [1,2]. The effective distribution coefficient may be expressed by the equation

$$k_{\text{eff}} = k_{\text{st0}} / [1 + \sigma / \sigma^*], \quad (27)$$

where  $\sigma$  is the actual supersaturation at the surface,  $k_{\text{st0}}$  is the equilibrium distribution coefficient at the step corresponding to the equilibrium concentration in the surface, and  $\sigma^*$  is some constant depending on the elementary frequencies of attachment and detachment of host and impurity particles [1,2].

For  $\sigma / \sigma^* \ll 1$  the equation for  $k_{\text{eff}}$  can be written in the linear form [1,2]

$$k_{\text{eff}} = k_{\text{st0}} - k_{\text{st0}} \sigma / \sigma^*. \quad (28)$$

Equations (27) and (28) predict that with increasing  $\sigma$ ,  $k_{\text{eff}}$  decreases [1]. Experimental data on supersaturation dependence of  $k_{\text{eff}}(\sigma)$  have shown that for different faces of crystals, for (110) and (031) faces of  $\text{K}_2\text{SO}_4$  crystals, and for (001) and (110) faces of  $\text{ZnK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  crystals grown from aqueous solution differences between values of  $k_{\text{eff}}$  for the analysed impurities incorporated by these faces are of the order of 10-20% at various supersaturations [1]. This means that  $k_{\text{eff}}$  can strongly depend on the orientation of the face, caused mainly by orientation dependence of  $k_{\text{st0}}$  [1]. This type results can be explained. Impurity particles enter into the step not only directly from the solution bulk, but also from the adsorption impurity layer on the surface [2]. At sufficiently low lifetimes of impurity particles on the surface, compared with  $h/R$ , where  $R$  is normal growth rate, and  $h$  is the step height, it is this adsorption layer that will be the mother medium from which the selection is made [2]. The value of  $k_{\text{st0}}$  corresponds to the concentration of a two-dimensional surface solid solution and differ by several times from the equilibrium concentration of three-dimensional solution [2]. The values of  $k_{\text{st0}}$  are different for faces of different crystallographic indices, and therefore the amounts of impurity trapped by these faces will be different, and sectorial structure of the crystal will arise according to Chernov explanation. The sectorial distribution of impurities in crystals can be changed in various ranges of supersaturations [2].

The orientation-dependent impurity incorporation in all presented approaches shows that growth rate anisotropy will lead to the sectorial distribution of impurities in crystals, which is unavoidable for polygonal crystals, and different for various growth conditions. In our previous paper we have stated that the anisotropy in the distribution of defects in lopezite crystals is directly related with the anisotropy in growth rates, and that with a decrease in growth anisotropy, the anisotropy in the distribution of defects decreases [6]. Distributions of clusters of point defects in lopezite confirm this feature [12].

## 2.2. Variation of growth velocities and zonal distribution of impurities in crystals

To analyze the zonal incorporation of impurities in crystals in various sectors and in various growth conditions the relative change in growth velocity  $R_{\text{rel}}(\text{hkl})^*$  of a given face  $(h_1k_1l_1)$  will be used, which is defined as

$$R_{\text{rel}}^{**} = R^{*}(\text{hkl}) / R^{**}(\text{hkl}), \quad (29)$$

where  $R^{*}(\text{hkl})$  is the linear growth velocity of the face at instant 1, and  $R^{**}(\text{hkl})$  is the linear growth velocity of the same face at instant 2. Each of

the velocities is conditioned by various growth parameters, supersaturation, temperature, velocity of movement of the mother solution from which the crystal grow, type and concentration of impurities. Changes in a growth parameter or its variations will affect growth velocity, and as a result changes in the incorporation of impurities at a given instant. This leads to zonal distributions of impurities, known as impurity striations and revealed by chemical etching (Fig. 1) [5-9, 11,12,17], X-ray topography [10,18], cathodoluminescence or another technique.

To express relative changes in concentration of impurities in one and the same sector ((hkl) sector) of the crystal dimensionless coefficient assigned as  $\Omega_{\text{intrasec}}$  may be used, which is defined by

$$\Omega_{\text{intrasec}} = (C_{s(\text{act})(\text{hkl})^*} - C_{s(\text{act})(\text{hkl})^{**}}) / C_{s(\text{act})(\text{hkl})^*}. \quad (30)$$

where  $C_{s(\text{act})(\text{hkl})^*}$  and  $C_{s(\text{act})(\text{hkl})^{**}}$  are concentrations of impurities in various parts of the (hkl) sector grown at instant 1 and 2, respectively.

Coefficient  $\Omega_{\text{intrasec}}$  can be called the relative intrasectorial impurity change.

Using the same procedure as in case eqs. (16) and (24) coefficient  $\Omega_{\text{intrasec}}$  may be expressed by

$$\Omega_{\text{intrasec}} = (R^*(\text{hkl}) \delta/D) \cdot (R_{\text{rel}}^{**} - 1). \quad (31)$$

Taking previous values  $R^*_{(001)} = R_{(001)} = 2.5 \cdot 10^{-6} \text{ cm/s}$  (at supersaturation 4% and high stirring rate of the solution), and  $\delta/D = 100 \text{ s/cm}$  we have for lopezite  $R^*_{(001)} \cdot \delta/D = 2.5 \cdot 10^{-4}$ . Since the ratio of growth velocity of (001) face of lopezite crystal in regime of forced convection can be 1.5 times larger than growth velocity of the same face in regime of free convection [11], we can substitute value  $R_{\text{rel}}^{**} = 1.5$  into equation (31). In this case  $\Omega_{\text{intrasec}} = 1.9 \cdot 10^{-4} = 0.019\%$ . Assuming  $\delta/D = 100 \text{ s/cm}$  we get  $\Omega_{\text{intrasec}} = 1.9 \cdot 10^{-3} = 0.19\%$ . For (011) face we have  $R_{\text{rel}}^{**} = 5$  [11],  $R^*_{(0-11)} = R_{(0-11)} = 0.9 \cdot 10^{-6} \text{ cm/s}$  (ineq. (6)) and  $\Omega_{\text{intrasec}}$  between 0.04 and 0.4%.

This means that in various parts of (001) and (011) sectors impurity striations of the zonal structure are caused by the relative changes in impurity content comparable with the relative changes in impurity content in various sectors due to growth rate anisotropy. However, for one and the same sector value of  $\delta/D$  is exactly the same, and for various sectors  $\delta/D$  has been only assumed, in our approach, to be the same.

### 3. CONCLUSIONS

1. Formulae for relative impurity content in various parts of a crystal have been derived (eqs. (24) and (31)).
2. They enable one to evaluate the contribution of volume diffusion controlled crystal growth for sectorial and zonal distributions of impurities in crystals.
3. The formulae predict that the variation of impurity content in various sectors of lopezite crystals due to growth rate anisotropy, and/or variations due to changes in growth velocities caused by fluctuations or deliberately induced changes in growth conditions, are of the same order of magnitude (between 0.01 and 0.4%).
4. Predicted values of relative impurity content are one to two orders of magnitude less than differences in density of point defect clusters in various sectors of lopezite crystals [12], and in density of clusters in regions of impurity striations [11,12]. This means that the volume diffusion contribution to impurity content is small in comparison with the surface diffusion and/or that density of flat-bottomed etch pits localizing clusters of point defects is not proportional to impurity content.

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## **PRĘDKOŚCI WZROSTU I SEKTORALNE ORAZ ZONALNE ROZKŁADY ZANIECZYSZCZEŃ W KRYSZTAŁACH**

### **Streszczenie**

Analizowano rozkład zanieczyszczeń w kryształach, wprowadzając nowe zależności na zawartość zanieczyszczeń w różnych częściach kryształów, które wprowadzono wykorzystując równanie Burtona-Prima-Slichtera. Porównanie zawartości domieszek określonych teoretycznie z danymi eksperymentalnymi gęstości klasterów defektów punktowych w różnych sektorach i prążkach domieszkowych kryształów lopezytu pokazuje, że dla lopezytu wkład dyfuzji objętościowej jest mały i uwzględnienie procesów dyfuzji powierzchniowej jest konieczne.