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Invited Paper

Segregation of impurities in crystal growth from solutions

H. V. ALEXANDRU
University of Bucharest, Romania

Impurities have a great influence on the growth kinetic, particularly at small supersaturations. We have performed fractional recrystallization and chemical analysis of the pure and impurified KDP substance, which lead some unexpected results. Large atomic radius elements, like Ba and Sr, has segregation coefficient much higher than one and are real "poison" impurities in single crystal growth. They produce crystal lattice distortion in the first stages of growth, after seed regeneration and heavily disturb the long run growth process. The concentration of these impurities in successive fractions of recrystallized KDP from solution was measured and analysed. The concentration dependence of Ba and Sr, versus recrystallized fraction, X fit an equation similar to the distribution of impurities (or dopant) during normal, unidirectional solidification, in purification of electronic materials. It is emphasised that impurities, having segregation coefficient K>1, are "dangerous" in single crystal growth from solutions.

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1. Introduction

Solution growth method prevail versus rapid melt growth (Czochralski, Bridgman) methods, when the substance decomposes before reaching the melting point, or single crystal has a destructive crystallographic transition, returning from the melting point to the room temperature. Recently, a major interest appeared in growth of very large KDP (KH_2PO_4) crystals for laser fusion experiments. Large single crystal plates of ~40x40 cm, free of defects or impurities are needed for the third harmonic generation of glass:Nd high power lasers (e.g. National Ignition Facilities–NIF project, under construction in Lawrence-Livermore, USA) [1-3]. The laser damage threshold of solution grown KDP crystal, which is of at least several Gw/cm^2, in nanosecond laser pulses, is about one order of magnitude higher than for usual melt grown crystals (e.g. $LiNbO_3$) [4]. Besides, crystals of large dimensions would be quite unusual and very expensive to produce on a large scale.

Usually, Me^{3+} impurities have been considered the only harmful impurities in KDP crystal growth, particularly for prismatic faces [3-10]. Very little is known about the segregation of Me^{2+} impurities in KDP type crystals (e.g. Ba and Sr), in relation with the supersaturation and the pH of solution. Segregation coefficient and the distribution of these impurities in several recrystallized fractions of KDP crystal shall be considered in this paper.

The segregation coefficient (SC) defined $K = C_{solid} / C_{liquid}$, was not considered as a real constant in solution growth. As previously shown [5,12], the SC depends on supersaturation, the pH of the solution, the crystallographic direction of growth and the mechanism of crystallisation. Impurities having K>1 are more dangerous than those having K<1. Large quantities of such impurities enter in the first layers, during the regeneration process of the seed and heavily disturb the crystal lattice during subsequent growth process. Besides, Ba^{2+} and Sr^{2+}, increases the electrical conductivity of the crystal [13]

2. Experimental

The solubility of KDP crystal increases considerably with the pH increase, similar to ADP [14]. Solutions of several pH values, saturated at ~60 ^oC were prepared from row materials containing Ba and Sr sulphate as major impurities. Several recrystallized fractions were obtained sequentially by temperature decrease of solution and than by solution concentration under the solvent evaporation control. The amount of recrystallized fractions was roughly estimated "in situ", counting the solute balance and the temperature decrease. Then, several properly weight fractions were chemically analysed as previously shown [15,16], by standard emission and absorption spectroscopy.

Experimental data were fitted with the equation:

$$C_S (X) = C_{S\,0}\, 10^{\alpha X} \qquad (1)$$

as $\log C_S(X)$ versus the recrystallized fraction X. As shown in Fig.1, there is not a well defined linear dependence of Ba and Sr concentrations in experiments C 5^o and C 7^o. Besides, α parameter has not a real physical support. Some other interpretation procedure shall be further considered.

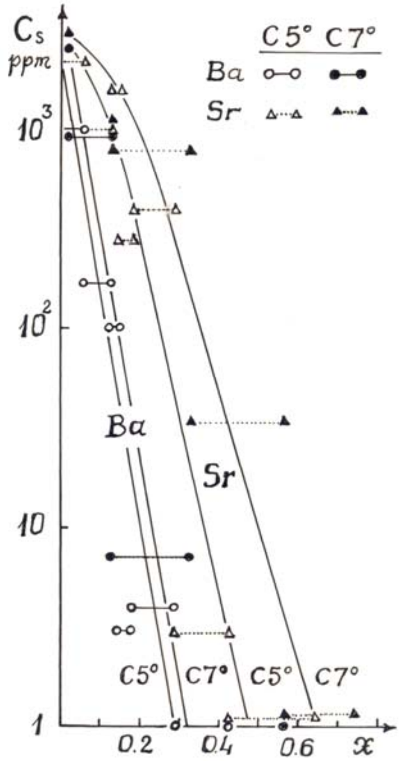

Fig. 1. Distribution of Ba and Sr impurities versus X the crystallized fraction in experiments C 5^o and C 7^o.

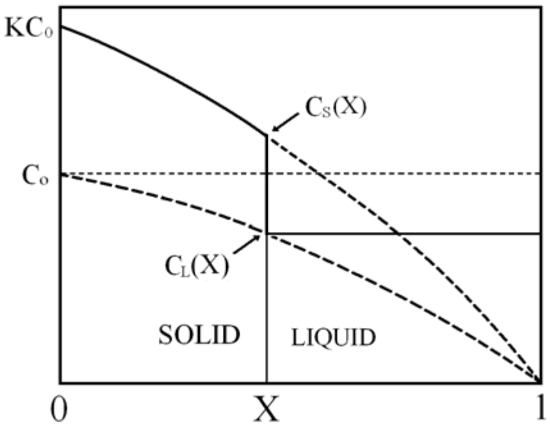

Fig. 2. Distribution of impurities for K>1, in normal, unidirectional solidification [16].

3. Normal distribution of impurities

Impurity distribution in unidirectional solidification of the melt, during the purification procedure in electronic materials, was applied [17]. The balance of the impurity content, at any moment in partly solidified ingot can be written (see Fig.2):

$$\int_0^X C_S(X)\,dX + (1-X)\,C_L(X) = C_o \qquad (2)$$

Here, $C_S(X)$ and $C_L(X)$ are the impurity concentration in solid and liquid (solution), when X fraction of the ingot was solidified and C_o is the initial, uniform concentration in the melt. The segregation coefficient $K = C_S(X)/C_L(X)$ was considered constant, throughout the recrystallization process.

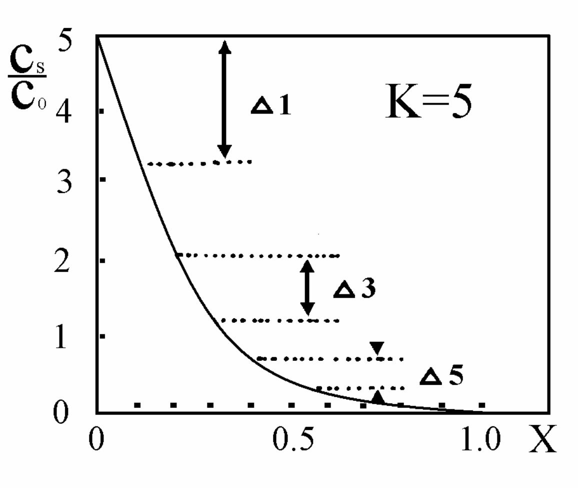

Fig. 3. Impurity distribution in the solid phase for K=5. The quantities Δ1-Δ5 show the concentration extension for several X/10 fraction intervals.

Taking the differential of the equation (2), after the separation of variable and integration, we find the distribution of impurity concentration in the solid:

$$C_S(X) = K\,C_o\,(1-X)^{K-1} \qquad (3)$$

The normal distribution, eq. (3) is presented in Fig. 3, for K = 5. Fractional recrystallization has specific features. The distribution with X/10 fraction interval shows much larger concentration variation of the first fractions. The ultimate recrystallized fractions have more uniform concentrations and may cover larger concentration intervals.

Normal distribution for several K values is presented in Fig. 4. The relative concentration distribution C_S/C_L is linear with the recrystallized fraction for K = 2 and the purification procedure become more efficient for higher K values (section 5).

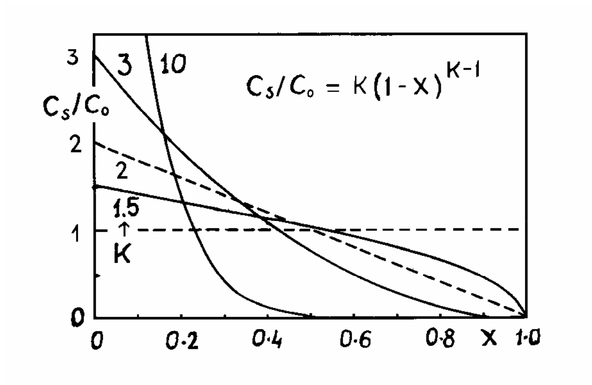

Fig. 4. The distribution of the relative concentration in solid for several values of the segregation coefficient.

4. Results

Experimental data of fractional crystallization distribution of Ba and Sr impurities in double-log scale representation of eq. (3) is presented in Fig.5. The solution pH ≈ 4.2 in C5 experiment was close to the natural value of KDP solute, in double distilled water.

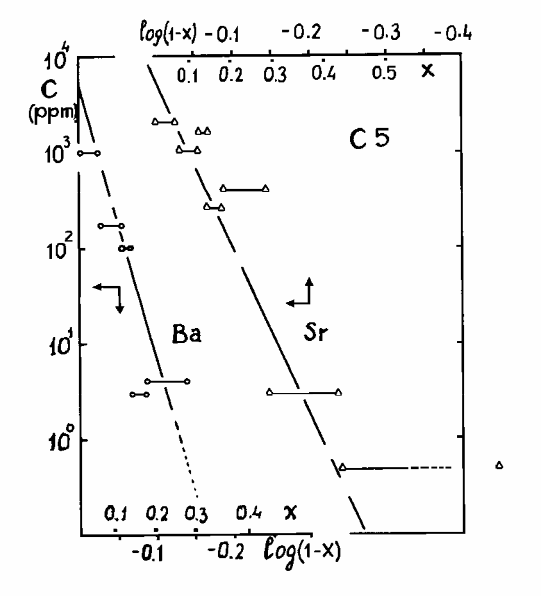

Fig. 5. Normal distribution of Ba and Sr impurities according to eq. (3) in double log scale. The solution pH was close to neutral value of KDP. The recrystallized fraction X in a nonlinear scale is given on the inside part of the picture.

For KDP (KH_2PO_4) recrystallization, we have introduced instead of pH, the mole fraction Z of the secondary phosphate (K_2HPO_4), which is a precise experimental parameter. At higher pH values, the overall composition of the solute in solution can be written $K_{1+Z}H_{2-Z}PO_4$ (pH > 3.8). A correlation of the following parameters we have found from our data [16] and from the literature data [18], at 30 °C:

$$pH = 2.9_1 + 1.9_0 \log Z \; ; \; Z < 0.5 \tag{4}$$

The segregation coefficient of Ba and Sr at several values of Z parameter (related to pH by eq. 4) is presented in Fig. 6. Up to Z = 0.5 (i.e. pH ≈ 6) the SC of Ba decreases slowly, while the SC of Sr increases. Barium SC values we have found are larger than overall SC found by Belouet [12]. The SC values of 20-30 we have found on a much larger concentration range (up to 10^3 ppm), while Belouet values of 10-15 for SC were found for concentrations smaller than 2 ppm [19]. However, a similar slight decrease can be also noticed in the pH dependence of SC measured in ref. [12].

The SC found by Zaitseva at normal pH, for pyramidal faces of KDP single crystal [20], was approximately 12 and 6 for Ba and Sr respectively. The concentration of impurities in the starting materials again was very small, i.e. less than 1 ppm.

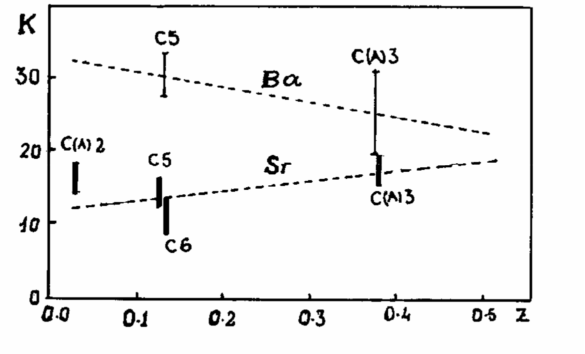

Fig. 6. Segregation coefficient versus Z ratio, related to solution pH (see text).

Some preliminary data we have found for the SC of Fe^{3+}. The SC value K ≅ 6 at Z= 0.2 (pH~5.7) is also higher than Belouet's data [12], K ≈ 1-2. This disagreement might be due also to supersaturation dependence of the SC. Indeed, for the SC of Fe^{3+}, we have estimated from ref [12] the dependence $K^{Fe} = 24.7 - 4.0\,\sigma(\%)$, on the supersaturation range $3 < \sigma(\%) < 6$ and this roughly agree with our previous data [5].

5. Discussions I

The impurity concentration distribution has not an exponential dependence (eq.1), on crystallized fraction X, see Fig. 1. Much more suitable representation appears to be the dependence similar to the normal unidirectional solidification, in crystal growth purification from melt [15-17]. Deriving the eq.3 for purification from solution, the basic hypothesis is quite similar to melt purification [17]. The uniform distribution of impurities in solution under the continuous stirring is more efficient than in the melt. Although, the solid-liquid interface phenomena in crystal growth from solutions is quite different versus melt growth, this does not affect the normal distribution. However, every recrystallized fraction (processed in small grains), has a mean value of impurities concentration, not a "frozen" distribution as in melt solidification, where diffusion of impurities along the solid ingot is inefficient.

In solution crystallization analysis, first fractions have to be taken on narrow concentration intervals. The "head" fraction $\Delta 1$, on the first 10% X interval in Fig.3, for K = 5, cover almost 40% of the ratio C_S/C_o. Less sensitive to X intervals are "middle" and "tail" fractions in such distributions (see figs.3 and 5). The purification efficiency increases if SC is higher. As seen in Fig. 4, about 30% "head" has to be drawn out if K=10, in order to decrease substantially the impurity concentration in the remained basic substance.

The pH dependence of the SC in Fig. 6 shows slight variations. The decreases of the SC for Ba agree with Belouet estimation [12], but his values are about half versus our data, on the same pH domain. Recent data, we have found (not published yet), shows indeed a substantial decrease of the SC at very small impurity concentrations. No details about pH variation of SC for Sr could be found in the literature, except the SC value given in ref. [20].

6. Discussion II

The experience we got in fractional recrystallization, allowed to elaborate an adequate recrystallization scheme of purification for both K>1 and K<1 impurities in KDP, see Fig. 6. Circles in this figure represent solutions in several stages, which contain fractions of the initial solute (START 1.00, in the first column). The "head" fraction 10% (or larger), has to be drawn first, in order to eliminate K>1 impurity. Anyway, this small fraction has to be always eliminated, as a caution step. The "tail" and "recovery" fractions in successive stages of crystallisation, contain increasing concentration of K<1 impurities. Some links has been made between equivalent stages of about the same fraction purity, e.g. TAIL I (0.18) and TAIL II (0.30) in Fig. 7. If, K>1 impurity has been eliminated as "head", in the first or in the first and second crystallisation, the most pure substance, to be used in crystal growth, is MIDDLE III (0,43) from the third crystallization step. The fraction TAIL III (0.20) has to tested for some K<1 impurities.

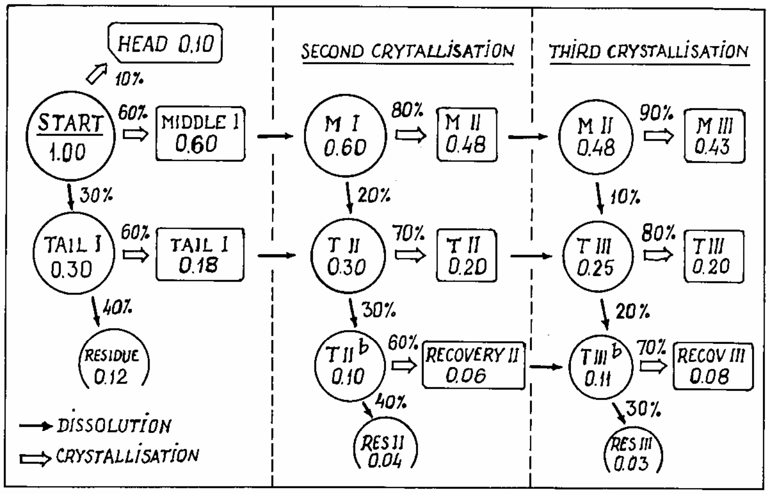

Fig. 7. Purification by sequential recrystallization in three steps. Circles show solutions containing several fractions of solute versus the "START 1.00" quantity. Rectangular boxes show fraction of the grain substance in several stages of purity.

We can estimate how large has to be the "head" fraction, which must be drawn out, in order to eliminate a known K>1 impurity. In fact, we need to decrease N times the ratio C(X)/Co, i.e. the eq.3 can be written:

$$C_S\left(X_N\right)/C_o = K\left(1-X_N\right)^{(K-1)} = 1/N \qquad (5)$$

and we find the limit of the fraction we need to stop at:

$$X_N = 1-\left[K\ N\right]^{\frac{1}{1-K}} \qquad (6)$$

The mean value of the remained impurity concentration in solution, versus C_o - the starting concentration, counted between fraction X_N and 1 can be estimated as:

$$\left[\frac{C_S(X)}{C_o}\right]_{X_N\to 1}=\frac{K}{1-X_N}\int_{X_N}^{1}(1-X)^{K-1}dX=\left[K\cdot N\right]^{-1} \qquad (7)$$

If we need this mean value to be C_o/p, than $p=K\cdot N$ and we find the corresponding fraction:

$$X_N=1-p^{\frac{1}{1-K}} \qquad (8)$$

For example, if we need to decrease the Ba concentration (K=30) in the p.a. basic substance, from 15-20 ppm to equal or less than 1 ppm, e.g. $p\approx 20$, we have to cut crystallisation process at the fraction $X_N=0.098_1\approx 10\%$. Than the "head" fraction has to be minimum 10%, like in Fig.7. For smaller SC values, for example K=10 or K=5, the "head" fraction has to be ~30% and ~50% respectively. For smaller K values, e.g. K=3, the "head" fraction has to be ~78% and the purification process become completely inefficient. In this situation, it has to be searched for some higher SC value of the impurity, at higher or lower pH values of the solution.

7. Conclusions

Fractional recrystallization of impurified KDP solutions was performed and analysed by standard emission and absorption spectroscopy. The concentration of Ba and Sr impurities, which were carefully analysed, show a distribution similar to the normal unidirectional solidification in semiconductor purification [17]. An exponential distribution type of impurities does not fit properly our experimental data.

Specific features appear due to the uniform distribution of impurity, during processing of every crystallized fraction. For higher SC values, the first fraction covers a much larger range of concentrations (see Fig. 3). However, the purification becomes useless if the SC is smaller than about five (section 6 and Fig. 4).

There are slight variations of SC for Ba and Sr at higher pH values of solution. The SC, we have measured at higher impurity concentrations of about 10^3 ppm, are about two times higher than those measured in the literature [12,19,20] at much smaller concentrations of a few ppm.

We have proposed a diagram model of KDP purification, for both K>1 and K<1 impurities. The "head" fraction that has to be removed from solution can be estimated, if the segregation coefficient is known. In our opinion, the impurities having segregation coefficient K>1 are more dangerous in solution growth. Such impurities enter in large quantities in the first stages of growth, disturb the crystal lattice and make difficult the long run growth processes.

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*Corresponding author: horia@infim.ro