Peculiar aspects in crystal growth from solutions

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Crystal growth from solutions is the unique method of single crystal growth, if the basic substance does not melt congruently, or if the crystal has a destructive crystallographic transition coming from the melting point to the room temperature. In the lower or high temperature solutions, the growing process is fundamentally related to the phase diagram of the components. Liquidus line represent the solubility curve of the component intended to be grown. However, impurities have a great influence on the growth kinetic, and on the crystal properties, particularly at small supersaturations [1-3]. Special purification procedures has to be used if the basic substance is not of high purity (i.e. higher than pro analysis), which usually is quite expensive. Fractional recrystallization is an efficient purification procedure if it is properly used [3, 4].
If the nature of impurities and theirs segregation coefficients is not known, only "middle" fraction of crystallisation might be used. If the concentration of impurities in the basic substance was estimated (measured) and theirs segregation coefficient was determined, or could be found in the literature, than the exact fraction, having a predicted degree of purity can be estimated [3]. In KDP we have found the Ba and Sr impurities concentration in the recrystallized substance follow the rule of normal, unidirectional solidification encountered in purification of electronic materials.: $C_S(X)=KC_o(1-X)^{K-1}$ (X-recrystallized fraction, K-segregation coefficient, C_o-initial concentration), [3, 5, 6].
Using, as "purified", the "head" fraction of recrystallization process might be very dangerous. Such impurities might be real "poison" impurities in single crystal growth, if they were present in the initial basic crystal. Such impurities enter in large quantities in the crystal lattice during the period of seed regeneration, disturb the crystal lattice and can make very difficult or impossible further crystal growth. Impurities having $K<1$, or $K<<1$ are less dangerous, as they remain in the "tail" fractions, or in the residual solution. The influence of some other impurities, like Me^{3+} in KDP, in relation with solution pH shall be presented.
A review of the kinetic and mechanism of growth for prismatic and pyramidal faces of KDP and ADP shall be presented, along with literature data, to compare with. Laser interferometry [7] and AFM [8] studies have shown dislocation and nucleation mechanism of growth compete at supersaturations $\sigma \sim (6\text{-}8)$ %. A retarding effect due to Me^{3+} impurities was reveled at smaller supersaturations [9]. At higher supersaturations a 2D nucleation mechanism of growth was proved, according to Chernov's theory [7]. Pyramidal faces of KDP are much less sensitive to impurities and show a large dispersion of the growth rates at $\sigma \approx 1\text{-}5$ %. Our data show a coherent increase of efficiencies towards the smaller σ and were represented as $1/\varepsilon_R = 1/m + (2/19)(L/ma)(\gamma/KT)^{-1}\,\sigma$. There are distinct BCF curves, fitting the experimental data on this σ range,

corresponding to efficiencies of growth as large as ε_R =1-16, [10]. All experimental data, including some literature data, fall in the area limited by the BCF equations: $R^{(101)} = C\sigma$ and $R^{(101)} = C(\sigma^2/\sigma_1)\cdot\tanh(\sigma_1/\sigma)$, suggesting the dislocation mechanism of growth is dominant at σ<8 %. Burgers vector and the linear dimension of the dominant centers of dislocations involved during growth shall be discussed. Pyramidal faces of ADP crystals show even a larger dispersion. A macroscopic switching effect of growth efficiencies was revealed around $\sigma \approx 0.5$ %, correlated with the competition of the dominating center of dislocations. The eq. $R = A\ \sigma^{5/6} \exp(-B/\sigma)$ was used to fit the experimental data at supersaturations higher than ~8 %. The edge free energy ratio γ/kT was estimated, in agreement with some other literature data.

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