Semnan University

Progress in Physics of Applied Materials

journal homepage: https://ppam.semnan.ac.ir/

The fluctuations of Zn impurity Concentration Profile in KCl crystals growth by various pulling rate Czochralski method

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ARTICLE INFO

Article history:
Received: 17 June 2023
Revised: 12 August2023
Accepted: 21 August 2023

Keywords:
Impurities
Segregation
Growth from melt
Czochralski method
Alkali- Halides
Crystal structure

ABSTRACT

Single crystals of KCl(Zn) using different amounts of Zn impurity (0.5 and 1.0 mole percents) with and without rotating crucible were grown by Czochralski method. The speed of rotation and pulling rate of the seed crystal were adjusted at, 10 rpm and 12 mm per hour respectively. The crucible was rotated, in the opposite direction of crystal rotation, with 5 rpm. Crystals, with Zn impurity of 0.5 % grown by both rotating and fixed crucible, were found to be transparent and uniform. Since the KCl crystals with Zn impurity of 1% were not transparent, they were found not suitable for optics. Furthermore, it was observed that the upper and middle parts of the crystals grown with 1 mol% Zn impurity are more transplant but the lower part includes transplant and cloudy layers. The results show that a convenient rotation and pulling rate can improve the stability and uniformity of impurity distribution along the crystals.

1. Introduction

To grow a single crystal, the stoichiometric amounts of raw materials including both host and impurities are calculated and mixed together to produce congruent melt. In the conventional czochralski the impurity concentration in the grown crystal is not often equal to that of its melt. The impurity concentration ratio between the crystal and the liquid is known as the segregation coefficient K_0 [1,2].

$$K_0=\frac{C_s}{C_l} \tag{1}$$

C_s and C_l are the concentration of the impurities in the crystal and the melt (at the interface ofthe crystal-melt), respectively. By growing crystal, the amount of concentration impurities in the liquid varies [3]. In czochralski grow process, the effective segregation coefficient is obtained from the following equation [2,4].

$$K_e=\frac{K_0}{K_0+(1-K_0)e^{-(\frac{V}{D})\delta}} \tag{2}$$

Were, v is the crystal pulling speed, δ is the thickness of the liquid-crystal layer of the interface (more than the rest of the melt), and D is the impurity diffusion coefficients in the melt. Distribution of impurities in the crystal, tends toward a uniformed optimal state when ($K_e \rightarrow 1$), that is if $\frac{V}{D}\delta \rightarrow \infty$ then $e^{-\frac{V}{D}\delta}$ becomes zero. Therefore, assuming a constant, the values of v and δ should be large [5]. This means that the crystal pulling speed is increased and the rotation rate is decreased, as well.

There are limits in both rotation and crystal pulling rate, that if not observed will cause instability in growth [6].

Fig. 1 shows schematically the rotational motion of the crucible in the Czochralski system. The crucible rotates while moving vertically. Defining v_p as the speed of pulling crystal, v or crystal growth velocity, is derived from the following formula [4, 7].

$$v=\frac{\rho_m r_c^2}{\rho_m r_c^2-\rho_s r_s^2}v_p \tag{3}$$

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DOI: 10.22075/PPAM.2023.30941.1056

Where r_s and r_c are the radii of the crystal and the crucible respectively. In fact, this system can be used to control the crystal growth process.

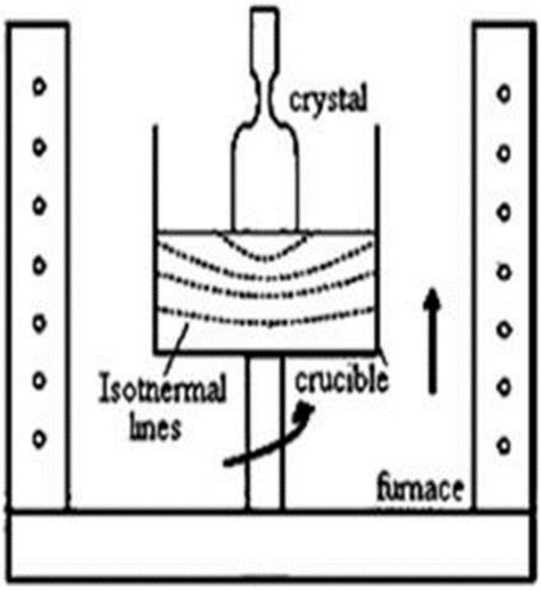

Fig. 1. Schematic diagram for Czochralski system with rotating crucible.


Fig. 2. Home-made Czochralski crystal growth system

2. Experimental

Single crystals of KCl(Zn) were grown by home-made Czochralski system, with and without using rotating system at our laboratory (Figure 2).

KCl(Zn) crystals were grown using KCl and $ZnCl_2$ pure powders having 99.9 percent purity purchased from Merck company. First, the proper amounts of $ZnCl_2$ and KCl raw material powders were weighed for both 0.5 and 1mole percent. The rotation and pulling rate of the seed crystal were set at 10 rpm and 12 mm per hour respectively. The rotation rate of the crucible, in the opposite direction of crystal rotation, was also set as 5 rpm [4,8].

It was observed that KCl crystals grown with 0.5 mole % Zn impurity with or without the rotation of crucible are having more uniform transparency. Whereas the crystals grown with 1.0 mole % Zn impurity are transparent at the top and middle parts but at the bottom part of the layers change form transparent to cloudy shape alternatively.

In case of rotation of crucible, these cloudy layers are pushed more to the end of the crystal. This means that rotation of crucible helps to have crystal grown with more transparent part [9].

Fig. 3, shows KCl single crystals grown with 0.5and 1.0 mole percent Zn impurities from left to right, respectively. It is seen that alternative cloudy layers finally cover bottom part of the crystal grown with 1.0 mole % Zn impurity.


Fig.3. KCl crystals grown with 1.0 (left) and 0.5 (right) mole % Zn impurities.

Since the KCl crystals grown with Zn impurity of 1.0 (left) and 0.5 (right) mole % were not transparent they are not suitable for making optics. Therefore, crystals grown with 0.5% impurity under both fixed and rotational crucible conditions. Were sliced perpendicular to the growth direction in thickness of 5 mm and prepared for analyses by chemical etching methods [10].

3. Results and discussion

Typical etch-pit density per unit area of the sample grown under the rotation of crucible condition is 2×10^5 pit/cm^3 and shown on Figure 4.


Fig.4. The etch-pits in the cleavage plane of KCl (Zn) crystals grown with 0.5 mole %impurity.

ICP measurement was carried out for all the KCl(Zn) crystals grown by 0.5 and 1.0 mole percentages of Zn impurity under both stationary and rotation so crucible. Results are shown in figures 5 and 6 respectively.

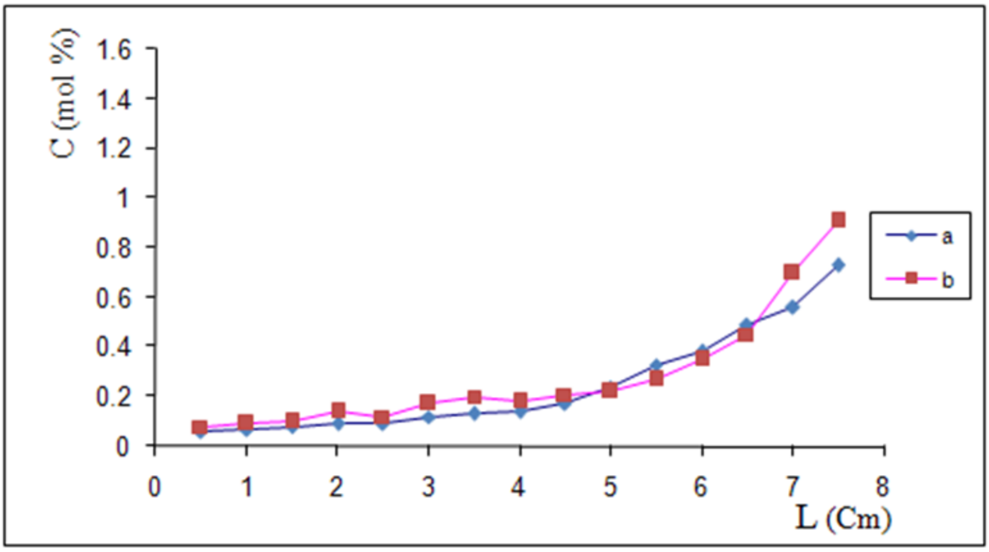

Fig. 5. Zn impurity concentration (0.5 mole %) along the KCl crystals grown in the rotating (a) and non-rotating (b) crucible conditions.

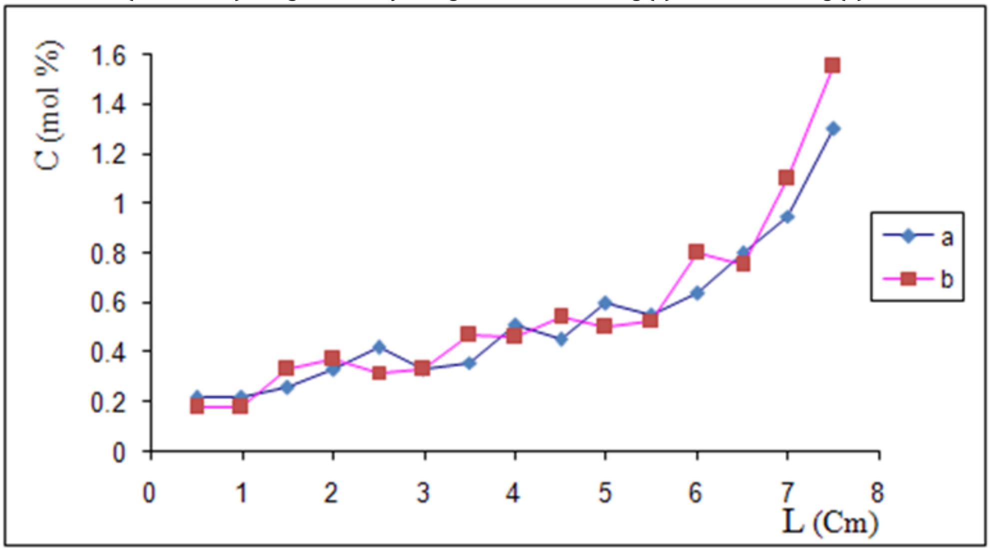

Fig. 6. Zn impurity concentration (1 mole %) along the KCl crystals grown in the rotating (a) and non-rotating (b) crucible conditions.

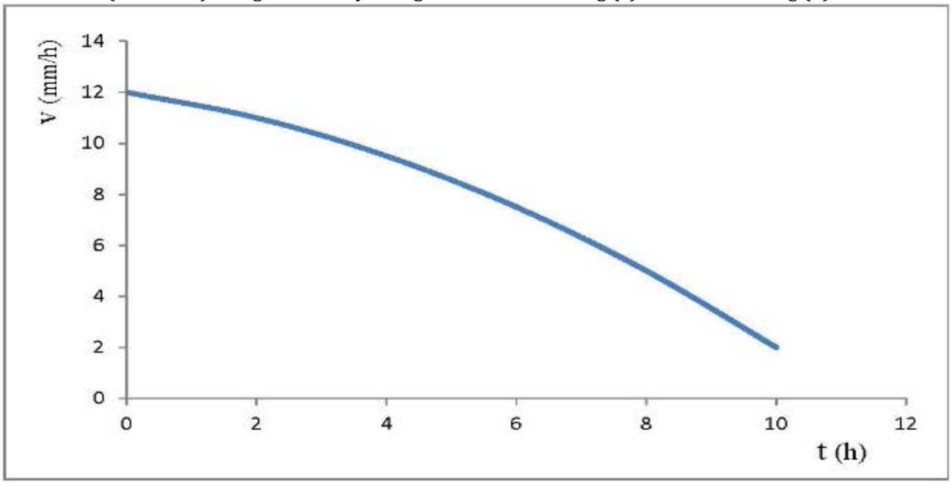

Fig. 7. The applied crystal pulling rate versus the time for growth of KCl crystals (with a concentration of 0.5 mol %).

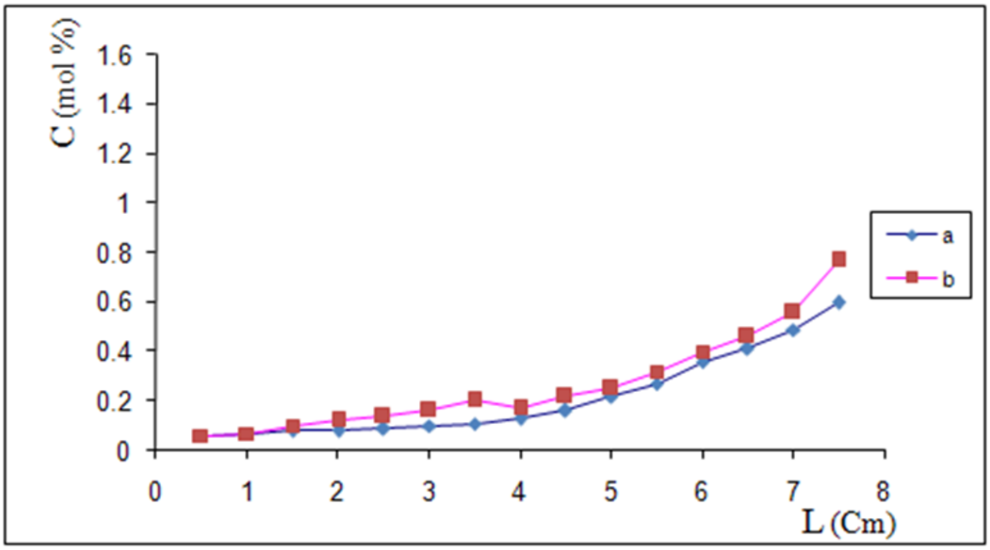

Fig. 8. Zn impurity concentration (0.5mol %) along the crystal with (a) and without (b) rotating crucible applying pulling rate showing in Fig.7.

A comparison between figures 5 and 6 show that grown with 0.5 mole %Zn has more uniformity in Zn concentration. Rotating crucible for both concentrations did not show significant change in this uniformity for both concentrations.

Figure 7 shows the applied change in speed of crystal growth pulling rate verse the time for the growth of KCl (Zn) crystals with a concentration of 0.5% to examine the effect of this growth factor on Zn impurity concentration. Figure8 shows the corresponding Zn impurity concentration in this case.

The crystal pulling rate and also the crystal and crucible rotation rate influence on the effective segregation in the crystal.

KCl crystals with 1.0 mole % Zn impurity in both conditions, with and without crucible rotation, due to the increased impurity content and high growth rate, are always unstable in their impurity distribution. However, the case of non- rotating crucible has greater stability of C_s compare to rotating one [l]. Of course, in the same conditions, in crystal with the concentration of 0.5 mole %, the molar concentration of impurities is more stable in the growth process.

Comparing Figures 5 and 6 one finds that the impurity gradients in KCl crystal with 1.0 mole % Zn is more than that with 0.5 mole % Zn and comparing Figures. 5a and 5b it is found that rotating crucible has insignificant fluctuations of the impurity concentration.

The crystal pulling speed seems to be an effective factor creating instability in the distribution of impurities in the crystal. It is better to decrease the pulling rate (for K_{eff} <1) to improve the impurity distribution. The crystal regime of pulling rate affects on the segregation coefficient (K_{eff}), and finally on the concentration distribution.

It is recommended that the crystal pulling rate begins from12 mm / h and ends at 2 mm/h during 10 hours (Figure 7). However, since the KCl(Zn) crystal segregation factor K_e <1 is defined as $K_0 = \frac{C_S}{C_l}$, it is expected that C_l versus time increases. Therefore, K_e is increased.

From the above equation it follows that for fixing the relative value of C_s, it is suggested to decrease K_e, as mentioned in formula (2), when v is diminished K_e is pursued. As indicated in fig. 8, to prevent the K_e increment, it is important to diminish the pulling rate.

4. Conclusions

In KCl crystal growth with relatively uniform Zn impurities in the crystal, the following conditions must be met:

1-Impurity content would not exceed than that in the host material.

2–For optimal control of distributed impurities, it is better to use rotating crucible during the growth to increase the thickness (δ) of the crystal-liquid interface layer.

3–It is necessary to improve the distribution of impurities in the crystal for which the crucible should be rotated. However, it is not enough due to the instability and lack of uniformity in the impurity distribution in the grown crystal.

4- Since Keff is less than unity for the KCl(Zn) crystal, Cl inevitably increases versus time and Cs follows this increment. Hence, the amount of Cs is chosen under the effect of the pulling rate.

References

[1] A. Jackson, A. Kenneth, Kenetic Processes, Wiley-VCH Verlay GmbH & Co. KGaA, Weinheim, 2004.

[2] F. Rosenberger, G. H. Westphal, "Low-Stress Physical Vapor Growth." Journal of Crystal Growth 43 (1978) 148-152.

[3] S. M. Pimputkar, S. Ostrach, "Convective Effects in Crystals Grown from Melt." Journal of Crystal Growth 55 (1981) 614-646.

[4] H. J. Scheel, T. Fukuda, crystal growth technology, 2003.

[5] J.J. Favier, L.O. Wilson, "A test of the boundary layer model in unsteady Czochralski growth." Journal of crystal growth 58 (1982)103-110.
[6] L.O. Wilson, "The Effect of Fluctuating Growth Rates on Segregation in Crystals Grown from the Melt." Journal of crystal growth 48(1980) 435-450.
[7] R. NOWAK, E. FORNALIK, J. GRONIAK, "Experimental analysis of velocity and temperature fields in a system similar to the Czochralski method of single crystal growth." archives of thermodynamics 29 (2008).
[8] K. Lal and A.R. Verma, "sophisticated equipment developed for growth and evaluation of perfection of nearly perfect crystals," Bulletin of Materials Science 6 (1984)129-149.
[9] R. Pereze –Salas,TM.Piters, "optical vibronic spectra of aggregates in Eudoped KCl and KBr crystals." Revista mexicana de fisica 49 (2003)102-106.
[10] K. Sangwal, Eching of Crystals, North Holland,1987.