Influence of $\text{Ca}^{2+}$ ions on the habit of KDP crystals

S. Javidi, R. Enayati, M. Iraj, N. Aliakbari
Crystal Growth Lab., Metallurgy Group, Material Research School, NSTRI, P.O. Box 14395-836, Tehran, Iran
Corresponding author e-mail: sjavidi@aeoi.org.ir

Abstract. A few KDP ($\text{KH}_2\text{PO}_4$) and KDP:Ca$^{2+}$ ($\text{CaCl}_2$) single crystals were grown based on the temperature reduction method. Investigations show that the presence of bivalent ions like Ca$^{2+}$ could be a cause of retarded growth rate and induced crystalline lattice defects. Here the pure KDP crystals are compared with KDP:CaCl$_2$. Crystals of both types were also studied in aspect of other structural and optical properties.

Keywords: KDP compounds, impurities, optical and structural properties.

Manuscript received 17.03.10; accepted for publication 16.03.11; published online 30.06.11.

1. Introduction

Incorporation of impurity ions into crystalline network will affect the shape of the nearest lattice. So, chemical potential in this deformed region will be increased. Consequently, the affected region will act as a growth process inhibitor. In fact, impurity ions with a small distribution coefficient do not incorporated to the crystal network but act as foreign particles. These foreign particles will be easily adsorbed on the surface of growing crystal. The prismatic faces of KDP are alternatively composed of positive $\text{K}^+$ ions and negative $\text{H}_2\text{PO}_4^-$ ions, while the pyramidal faces are ended by $\text{K}^+$ in the growing crystal. The Ca$^{2+}$ ions are easily adsorbed on the prismatic faces of the crystal. As a result, the growth rate of prismatic faces might be decreased, while the growth rate of pyramidal faces will remain unchanged. They reduce the growth rate and, in some cases, inhibit the growth process. On the other hand, thermodynamic effects of some impurities are the cause of increasing the growth rate. In the previous work done by our group, KDP single crystals were grown by the temperature reduction method using point seeds [1]. Studying the effect of impurities on the habit of crystals has been the subject of many researches in recent years [2-11]. In this research, the influence of Ca$^{2+}$ in crystal growth has been studied when adding it to KDP solution in various concentrations.

2. Experimental

The crystal growth system consists of a crystallizer and water bath. The crystallizer was a 1000 cm$^3$ Pyrex cylinder installed inside the glass water bath for thermal stability control. The heating system was supplied by electrical heating elements that were installed inside the water bath adjacent to the walls. A Jumo PID with Pt100 probe was used for temperature control of the growth unit. The $z$-cut crystal seed with $6 \times 7 \times 8$ mm dimensions was glued on the lower plate of the holder. The seed holder shaft could rotate continuously in adjustable periods clockwise, pause and then counterclockwise directions based on accelerated crystal rotation technique (ACRT). The required power for the seed holder and stirrer was supplied by a DC electromotor.

Our crystallization experiment was performed within the temperature range 64-58 °C. Super-saturated solution was prepared by mixing KDP powder in distilled water. The solution was then filtered under vacuum and overheated, above the saturation point, to endure the solution stability. A small amount of CaCl$_2$ (about 6 ppm) was initially added to the solution. The solution then was overheated to 80 °C for 48 h. After two days, a KDP single crystal of $1.7 \times 1.8 \times 1.9$ mm sizes was created. Afterward, the experiment was repeated for 8 ppm of CaCl$_2$. The CaCl$_2$ doped crystals with two different amounts of additives are shown in Fig. 1.

3. Optical transmission studies

Well polished (001) plane of single crystalline KDP samples was used for optical transmission studies. Optical transmission spectra were recorded for samples obtained from pure crystals as well as from those with planned impurities and grown using the slow cooling method. Pure KDP crystals grown show about 86% transmissions in the visible region as indicated by the curve in Fig. 2a. But in KDP:Ca$^{2+}$ crystals, it has been
Fig. 1. Photos of: a) KDP crystal doped with 6 ppm of CaCl$_2$, b) two KDP crystals doped with 8 ppm of CaCl$_2$, c) two KDP crystals doped with 8 ppm of CaCl$_2$ grown on the horizontal seed.

Fig. 2. UV-VIS transmission spectra of (001) face for pure KDP (a) and KDP:Ca$^{2+}$ crystals (b).

decreased drastically (Fig. 2b). Comparison between spectra of pure and non-doped samples shows that the presence of impurity ions decreases the transmission percent in KDP:Ca$^{2+}$ crystals considerably. The spectra have been generated by Cary 17DX spectrophotometer at room temperature.

4. X-ray diffraction studies

The well ground powders of pure KDP and KDP:Ca$^{2+}$ crystals were used to identify the crystal phase and structure. X-ray powder diffraction patterns of doped crystals (KDP:CaCl$_2$) indicate that these samples are structurally similar to pure samples. Nevertheless, the slight differences in the intensities of a few selected peaks reveal that the impurity distribution may be anisotropic and concentrated on prismatic faces of the crystal. As the amount of doped impurity in the initial solution was in a very low concentration about 6-8 ppm, so this insignificant value of the matter could not shift the main X-ray peaks of curve. X-ray patterns are shown in Fig. 3. These analyses performed with Philips Pw1130/90 analyzer using a tube voltage and current of 40 kV and 100 mA, respectively.

Fig. 3. X-ray powder diffraction patterns for pure KDP (a) and KDP:Ca$^{2+}$ crystals (b).
5. EDAX analysis

The presence of Ca\(^{2+}\) ions is confirmed by EDAX analysis in KDP crystal lattice. KDP crystal is fragile and hygroscopic, so, samples were coated with gold plates of 20-nm thickness before being analyzed using a Philips XL30 scanning electron microscope. EDAX spectrum is shown in Fig. 4.

![Fig. 4. EDAX data of KDP:Ca\(^{2+}\) crystals.](image)

6. SEM studies

Scanning electron microscopy (SEM) investigations of the grown samples of pure KDP, and those of doped with CaCl\(_2\) on the (100) plane of the crystals (Fig. 5) show formation of a layer on the surface of the crystal due to impurities. SEM photos exhibit the effectiveness of the impurity in changing the surface morphology of KDP crystals.

![Fig. 5. SEM photos of pure KDP crystal (a) and CaCl\(_2\)-doped KDP crystal (b).](image)

7. Conclusion

Crystals of pure KDP and those of CaCl\(_2\) doped KDP have been grown and studied for their optical properties, X-ray diffraction, EDAX and SEM analyses. Incorporation of impurity ions in KDP crystals affect on the habit and surface morphology of the grown crystals depending on the distribution coefficient of impurity. EDAX data confirm the presence of calcium impurity in the KDP crystalline lattice. Comparison of transmission spectra of the pure KDP and CaCl\(_2\) doped crystals show that the percent of transmission will be decreased by presence of Ca\(^{2+}\) ion impurity.

Acknowledgement

Appreciate to Material Research school colleagues for their assistance in measurement jobs.

References


