Semiconductor Physics, Quantum Electronics & Optoelectronics, 2008. V. 11, N 4. P. 342-344.

PACS 42.70.-a, 61.72.Ss, 61.80.Ed, 77.84.Fa

Effect of La^{3+} ions on the habit of KDP crystals

S. Javidi, M. Esmaeil Nia, N. Aliakbari, F. Taheri
Crystal Growth Lab., Metallurgy Group, Material Research School,
NSTRI, P.O. Box 14395-836, Tehran, Iran
Corresponding author e-mail: sjavidi@yahoo.com

Abstract. A few KDP (KH_2PO_4) and KDP: La^{3+} ($LaCl_3$) single crystals were grown being based on the temperature reduction method. Investigations show that the presence of three valent ions like La^{3+} could be a cause of retarded growth rate and induced crystalline lattice defects. Here the pure KDP crystals are compared with KDP: $LaCl_3$ before and after their exposure to gamma irradiation. Both types of crystals also were studied in aspect of other structural and optical properties.

Keywords: KDP compounds, impurities, γ-ray effects, optical and structural properties.

Manuscript received 29.07.08; accepted for publication 20.10.08; published online 11.11.08.

1. Introduction

An impurity ion in the crystalline lattice acts as a foreign particle, chemical composition which of differs from the main crystal morphology. In many crystallizing procedures, the presence of impurities even in the ppm range substantially affects the growth parameters and habit of crystals. Even though ion impurities exert their influences in any stage of crystal growth, their specific action induces changes in the growth rate and growth kinetics. When the impurity ion is incorporated into the crystalline lattice, decreasing the rate of crystal growth is a cause of retarded growth processing and created considerable changes in the physical parameters. Therefore selective impurities could be applied to modify the physical properties of crystals for the special purposes. Selective additives have been applied vastly in crystal growth industry in order to change the appearance shape of crystals and modify their qualities [1]. Study of influence of impurities on the crystal growth procedure has been the subject of many researches in recent years [2-7].

The different faces of KDP crystal alternatively have negative and positive ions. The last charged face attracts the ion impurity with the opposite charge and subsequently influences on the crystal lattice shape. The KDP crystals grown in the presence of La^{3+} are elongated along the *b*-axis, and predominant faces are (101). Incorporation of foreign particles into the surface layer of the crystal retards the growth procedure due to weak network stresses.

In the growth from solution, due to high supersaturation and nucleation the situation inside the growth solution is very unstable. Therefore, to avoid nucleation in the growth procedure is very important. Low amount of additives, particularly organic ones as a solution stabilizer could be utilized to grow crystals in large scales and high purity [8-9].

2. Experimental

2.1. Crystal growth

To investigate influence of impurity in the growth procedure of KDP crystal, pure and doped KDP crystals with lanthanum chloride of 4 wt% as an impurity were grown in a system based on the temperature reduction method described earlier [10]. Seed dimensions were about 5×3×3 mm, and pH of solution growth was determined as 3.5. Although the lanthanum chloride has been lowered the solubility of solution, the filtered solution after 24 h overheating at 65 °C was poured into the crystallizer. The initial temperature was 58 °C and gradually decreased by the rate of 1 °C per day. After start of the growth procedure, there were still some insoluble particles in the stirring solution might be related to lanthanum chloride molecules. A PID system with pt100 sensor was installed as a thermo controller in the water bath. The concentration of solution growth was measured 40 g/cm^3. The pure crystals of KDP are colorless but the color of doped crystals was found to be milky (Fig. 1).

Semiconductor Physics, Quantum Electronics & Optoelectronics, 2008. V. 11, N 4. P. 342-344.

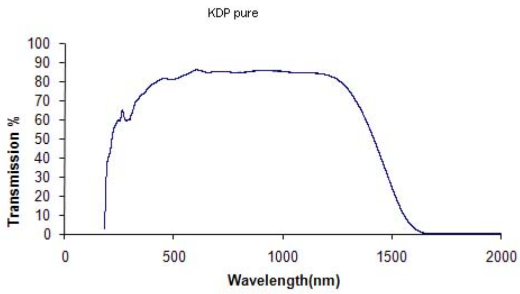
Fig. 1. Photo of the grown KDP:La^{3+} crystals.

2.2. Irradiation arrangement

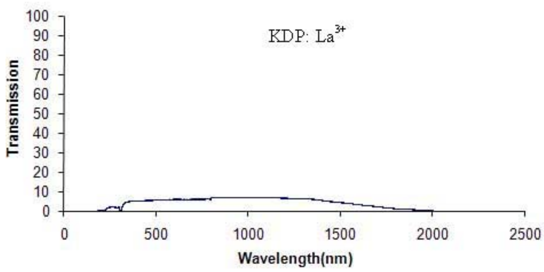
The grown crystals were exposed to gamma irradiation using ^{60}Co source in three steps by a dosage of respectively 10, 20, and 30 Gray. In order to characterize samples, the following experiments were performed on both pure and doped crystals.

3. Optical transmission studies

Transmission spectra of the polished (001) plane of all samples were provided for the 200-2500 nm wavelengths. The spectra have been obtained by Cary 17DX Spectrophotometer and immediately after polishing. The transmission of the grown pure KDP crystals as indicated by the curve in Fig. 2a are about 90 % in the visible region, but in KDP:La^{3+} crystals it has been decreased drastically (Fig. 2b). Comparison of the spectrum of pure and non-doped samples show that the presence of ion impurity considerably decreases the transmission percent in KDP:La^{3+} crystals. Fig. 3 shows a weak increase in transmission of doped samples after any stage of gamma irradiation.



a



b

Fig. 2. UV-VIS transmission spectra of (001) face of: (a) pure KDP; (b) KDP:La^{3+}.

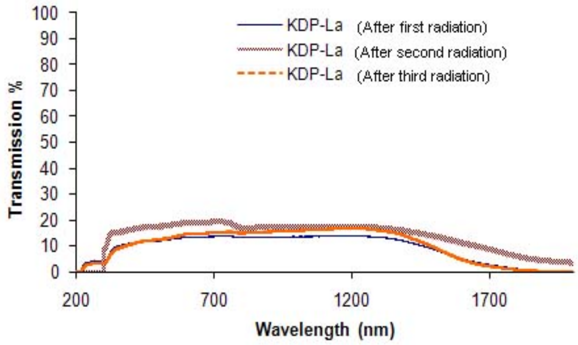
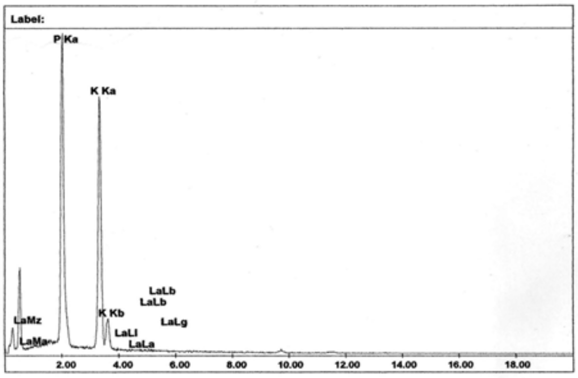


Fig. 3. Comparison of the UV-VIS transmission spectra of gamma irradiated samples.

4. EDAX analysis

The presence of La^{3+} ions is confirmed by EDAX analysis in KDP crystal lattice. The grown crystals were analyzed by a Philips XL30 scanning electron microscope. EDAX spectrum is shown in Fig. 4.



Element	Wt %	At %
P K	42.24	48.36
K K	56.63	51.35
LaL	1.13	0.29
Total	100.00	100.00

Fig. 4. EDAX data of KDP:La^{3+} crystals.

5. Microardness test

Microhardness is a good testing to determine the firmness degree of matters. The respective tests were performed on KDP crystals: pure, doped, and irradiated ones. Measurements were carried out using Leitz MM6 microhardness tester fixed to a Vickers diamond pyramidal indenter attached to a microscope. Tests were made on the 100 face of crystals with 25 g load for 10 s. The related numbers for all kinds of samples in Table show that the degree of hardness in pure KDP crystals is higher than that in doped crystals. It could be concluded that the presence of ion impurity weakens the KDP crystalline lattice. The obtained data also show the degree of crystal hardness will be increased any time after irradiation.

Table. Hardness degree of all the samples in comparison with each other.

Sample type	KDP pure	KDP:La^{3+}	KDP:La^{3+} after first irradiation	KDP:La^{3+} after second irradiation	KDP:La^{3+} after third irradiation
Measure of hardness	206	116	122	154	170

6. Conductometry

At low temperatures, electrical conductivity in dielectrics is controlled by impurities but at high temperatures due to defects created in crystalline lattice it will be increased with temperature increasing [11]. To study the influence of lanthanum ions on conductivity of crystals, their conductivity were measured by a SIGNATONE Four Point Probe system at the room temperature. Measurements show that the crystals exposed to gamma rays have larger conductivity than non-irradiated ones as well as pure crystals.

7. Conclusion

Pure KDP crystals and those doped by lanthanum chloride were grown by the temperature reduction method. Then grown crystals were subjected to gamma irradiation in three steps to study the effect of irradiation on them.

EDAX data confirm the presence of lanthanum impurity in the KDP crystalline lattice. Transmission spectra of the samples and comparison of them show that the percent of transmission would be decreased in the presence of ion impurity. Conductivity measurements of pure KDP crystals and doped samples indicate the increase in conductivity after irradiation. Microhardnees test show the increase in degree of crystal hardness after any stage of gamma irradiation. In general our observations agree with earlier theoretical studies.

Acknowledgement

We thank the staff of Material Research School for their valuable assistance during these measurements.

References

1. D.T.J. Hurle, *Handbook of Crystal Growth*, vol. **2**. Elsevier Science B. V., 1994.
2. N. Zaitseva, L. Carman, I. Smolsky, R. Torres, M. Yan, The effect of impurities and supersaturation on the rapid growth of KDP crystals // *J. Cryst. Growth* **204,** p. 512-514 (1999).
3. K.B.R. Varma, K.V.R. Prasad, The effect of Cr_4^{-2} ions on the electro-optic properties of KDP single crystals // *J. Phys. D: Appl. Phys*. **23**, p. 1723-1726 (1990)
4. K. Srinivasan, K. Meera, P. Ramasamy, A novel method to enhance metastable zone width for crystal growth from solution // *Cryst. Res. Technol*. **35** (3), p. 291-297 (2000).
5. M. Rak, N.N. Eremin, T.A. Eremina, V.A. Kuzentsov, T.M. Okhrimenko, N.G. Furmanova, E.P. Efermova, On the mechanism of impurity influence on growth kinetics and surface morphology of KDP crystals-I:defect centers formed by bivalent and trivalent impurity ions incorporated in KDP structure-theoretical study // *J. Cryst. Growth* **273,** p. 577-585 (2005).
6. K. Maeda, R. Tabuchi, Y. Asakuma, K. Fukui, Distribution of metallic ions in a single KDP crystal grown from aqueous solution // *Cryst. Res. Technol.* **41** (10), p. 955-960 (2006).
7. V. Kannan, R.B. Ganesh, R. Sathyalakshmi, N.P. Rajesh, P. Ramasamy, Influence of La^{3+} ions on growth and NLO properties of KDP single crystals // *Cryst. Res. Technol.* **41** (7), p. 678-682 (2006).
8. W. Shengali, G. Zhangshou, F. Youjun, S. Xun, Z. Jieguo, Z. Hong, L. Yiping, Scattering centers caused by adding metaphosphate into KDP crystals // *J. Cryst. Growth* **223,** p. 415-419 (2001).
9. C. Jianzhong, L. Sukun, Y. Fengtu, W. Jiahe, L. Jianming, Effect of alcoholic additives on the nucleation of KDP and DKDP crystals // *J. Cryst. Growth* **179,** p. 226-230 (1997).
10. S. Javidi, H. Faripour, M. Esmaeil Nia, K.F. Sepehri, N. Ali Akbari, Development of a KDP crystal growth system based on TRM and characterization of the grown crystals // to be published in *Semiconductor Physics, Quantum Electronics and Optoelectronics* Vol. **11**, No.3 (2008).
11. R.A. Kumari, R. Chandramani, Ion transport in Au^+ doped/undoped KDP crystals with KI/NaI as additives // *Bull. Mater. Sci.* **26**, No. 2, p. 255-259 (2003).