Effect on Doping of EDTA on Structural, Optical and Mechanical Properties of KDP Crystal

A M Dholariya\textsuperscript{a} and K G Raval\textsuperscript{b}

Narmada College of Science and Commerce, Bharuch, Gujarat, India-392011.
\textsuperscript{a}) Corresponding author: ankitadholoriya26293@gmail.com
\textsuperscript{b}) kamleshraval@hotmail.com

Abstract Single crystal of Potassium Dihydrogen Orthophosphate (KDP, KH\textsubscript{2}PO\textsubscript{4}) pure and doped with EDTA (Ethylenediaminetetraacetic acid, [CH\textsubscript{2}N(CH\textsubscript{2}CO\textsubscript{2}H)]\textsubscript{2}\textsubscript{2}) have been successfully grown by slow evaporation method at room temperature with deionized water as a solvent with a aim to improve the properties of KDP crystal. The concentration of EDTA was 0.1mol\%. The Energy Dispersive X-ray Analysis (EDAX) confirms the presence of EDTA in grown crystals. A tetragonal structure of crystals was confirmed and the value of lattice parameter was calculated by X-Ray diffraction (XRD) analysis. Optical energy band gap was determined by UV-VIS Spectroscopy. Raman Spectroscopy studies structural mode of bond in pure and EDTA doped KDP crystal. Microhardness of the crystals was measured with different dwell time and different load using Vicker microhardness tester.

Keyword KDP crystal, EDTA, EDAX, XRD, UV-Vis spectroscopy, Raman Spectroscopy, Microhardness

1. Introduction
Potassium Dihydrogen Phosphate (KH\textsubscript{2}PO\textsubscript{4}, KDP) single crystal is known as a nonlinear optical crystal. The KDP crystal have been of huge interest to researchers because of their unique combination properties like electro-optical, piezoelectric effect, big range of transparency, ferroelectric and relative high magnitude of quadratic nonlinear susceptibility [1-3] and also their wide spread applications like photonic laser, optical disk data storage, frequency conversation, telecommunication, high speed information processing, photonic laser, microelectronics and non-linear optics such as Second Harmonic Generation (SHG) [4-7]. Literature review shows that KDP single crystal doped with some impurities has been shown improvement in material’s characteristics. For the past few years, Synthesis and Characterisation of Pure and impurities doped KDP single crystal have been reported and the various dopants used like p- dinitroaniline [6], Phenylalanine [7], L-Lysine, L-Arginine, L-Alanine [8], Cadmium sulphide (CdS)[9], Sacrosine [10], Urea, Thiourea [11], glysine [12] and many more. In the present research paper, we have grown pure and 0.1 mol\% EDTA doped KDP single crystal by slow evaporation technique at room temperature and also studied Energy Dispersive X-ray Analysis, Powder X-Ray Diffraction (XRD), Ultraviolet Visible (UV-Vis) spectroscopy, Raman Spectroscopy and Vicker Microhardness

2. Experimental
The single crystal of pure and 0.1 mol\% EDTA doped KDP were synthesized by slow evaporation method in solution growth method at room temperature using DI water as a solvent. For the Synthesis of KDP seed crystal, homogeneous and super saturated solution of AR grade KDP was prepared with DI water which was first filtered by whatman filter paper and after than kept in a
petri dish and covered to ensure the slow evaporation. After three weeks, KDP seed crystal was harvested as shown in figure 1.

For a synthesis of Pure and EDTA doped KDP single crystal, super saturated solution of potassium dihydrogen phosphate (200 ml) prepared with DI water and after than it was filtered by whatman filter paper. Two similar beakers which have 100ml homogeneous and super saturated potassium dihydrogen phosphate (KDP)’s solution; the first beaker contains pure KDP solution, and the second beaker contains doped with 0.1mol% EDTA were stirred using temperature controlled magnetic stirrer for 2 hours for homogeneous solution. Two seed crystals were tied with a nylon thread and suspended into a beaker filled with two different solutions. Both solutions were covered kept undisturbed place to for four weeks. After four weeks, transparent and colourless pure KDP single crystal and 0.1mol% EDTA doped KDP single crystal were harvested as shown in figure 2 and figure 3.

3. Result and Discussion

3.1. Energy Dispersive X-Ray analysis (EDAX)

EDAX was done by using a Philips XL30 ESEM model in the range of 0.2kv to 30kv. The element confirmations for both single crystals were done by EDAX. EDAX spectrum observed, presence of element Oxygen, Phosphors, sodium and potassium in pure KDP single crystal and Carbon, Oxygen, Phosphors and potassium in 0.1mol% EDTA doped KDP single crystal as shown in Figure 4 and figure 5 and also observed that C of EDTA is present in 0.1 mol% EDTA doped KDP single crystal. The stoichiometric ratio of every element in pure and 0.1 mol% EDTA doped KDP single crystals are shown in Table 1.
Table 1. Stoichiometric ratio of element of pure KDP single crystal and 0.1 mol% EDTA doped KDP single crystal

| Elements | Pure KDP single crystal | 0.1 mol% EDTA doped single crystal |
|----------|-------------------------|-----------------------------------|
| C        | 6.55                    | 11.66                             |
| O        | 45.98                   | 69.93                             |
| Na       | 1.03                    | 1.02                              |
| P        | 22.65                   | 16.52                             |
| K        | 30.34                   | 17.53                             |
| Total    | 100                     | 100                               |

3.2. Powder X-Ray Diffraction (XRD)
The powder X-Ray Diffraction patterns for the both single crystals were taken using a Rigaku Miniflex X-Ray powder diffractometer with monochromatic CuKα radiation $\lambda = 1.54$ Å in the 2θ range in 0° to 80°. Lattice parameters were determined from the data using the equation 1, equation 2 and Xpowder software.

$$n\lambda = 2d\sin\theta$$

(1)

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

(2)

Where, h, k and l are miller indices [13].

Lattice parameters for both single crystals are in good agreement with JCPDS card no. 350807 as shown in Table 2 and XRD spectra for both single crystals are shown in figure 6.

Table 2. Comparison of lattice parameters of pure and 0.1 mol% EDTA doped KDP single crystal

| Parameters | Pure KDP crystal | 0.1 mol% EDTA doped KDP crystal | JCPDS Card data 350807 |
|------------|------------------|---------------------------------|------------------------|
| a (Å)      | 7.416            | 7.4185                          | 7.453                  |
| b (Å)      | 7.416            | 7.4185                          | 7.453                  |
| c (Å)      | 6.9855           | 6.9858                          | 6.974                  |
| v (Å³)     | 384.182          | 385.45                          | 385.54                 |
| $\alpha = \beta = \gamma$ | 90°   | 90°                             | 90°                    |
| Structure  | Tetragonal       | Tetragonal                      | tetragonal             |
3.3 Ultra Violet Visible Spectroscopy (UV-VIS)
In Optoelectronic devices, the optical behavior of material is very important. The absorption spectrums for both single crystals were accomplish by using carry 5000 UV – Vis spectrometer at room temperature in the range of 200nm to 800nm and crystals were optically transparent in the visible range and hence indicates the suitability of the crystals for optical devices. For optical energy band gap in both single crystals were determine from the UV-Vis absorption spectra and using the using equation 3.

$$E_g = \frac{hc}{\lambda}$$  \hspace{1cm} (3)

Where, $E_g$ = optical energy band gap, $\lambda$ = intercept of straight line, $c$ = velocity of light = 3 x 10^8 m/s, $h$ = Planck’s constant = 4.135 x 10^{-15} ev.s [14].

UV-VIS spectra for both single crystals are shown in figure 7, the intercept of straight line on the wavelength $\lambda$ and optical energy band gap $E_g$ for both crystals are shown in Table 3.
Table 3. Intercept of straight line on the wavelength $\lambda$ and optical energy band gap $E_g$.

| Sr. no | Single Crystal                              | The intercept wavelength $\lambda$(nm) | Optical energy band gap $E_g$ (ev) |
|--------|---------------------------------------------|---------------------------------------|----------------------------------|
| 1      | Pure KDP single crystal                     | 301                                   | 4.11                             |
| 2      | 0.1 mol% EDTA doped KDP single crystal      | 324                                   | 3.83                             |

3.4. Raman Spectroscopy

Raman Spectroscopy for both single crystals are take relevant optical modes to considered using ranishaw spectrometer in the Raman shift range of 0 cm$^{-1}$ to 3000 cm$^{-1}$ at room temperature. Raman spectra of pure and 0.1mol% EDTA doped KDP single crystals are shown in figure 8 and figure 9. Raman spectra shows that pure and 0.1mol% EDTA doped KDP single crystals have peak in Raman shift 912cm$^{-1}$ and 362cm$^{-1}$. Raman shift 912cm$^{-1}$ indicates the very strong bond of PO$_4$ and Raman shift 362cm$^{-1}$ indicates the strong bond of PO$_4$ [15].

![Figure 8. Raman spectra for Pure KDP single crystal](image)

![Figure 9. Raman spectra for 0.1mol% EDTA doped KDP single crystal](image)

3.5. Vicker Micro hardness

The experimental values of vicker microhardness of pure and 0.1mol% EDTA doped KDP single crystal shown in table 4. Figure 10 and figure 11 shows the variation of Vicker Microhardness number with different dwell time and applied load.

Table 4. Comparison of vicker Microhardness of pure and 0.1mol% EDTA doped KDP single crystal with different dwell time and load

| Load | Pure KDP single crystal | 0.1 mol% EDTA doped KDP single crystal | Pure KDP single crystal | 0.1 mol% EDTA doped KDP single crystal |
|------|-------------------------|---------------------------------------|-------------------------|---------------------------------------|
| 10   | 256.6                   | 228.51                                | 316.8                   | 219.045                               |
| 25   | 225.084                 | 201.94                                | 241.629                 | 186.84                                |
| 50   | 267.95                  | 229.44                                | 322.65                  | 202.41                                |
4. Conclusion

Pure Potassium Dihydrogen phosphate and doped with 0.1mol% EDTA single crystal were successfully grown by slow evaporation method. As a result, the effect of EDTA in KDP crystals was shown in all the characteristics. The presence of all elements and the EDTA dopant were confirmed by Energy Dispersive X-Ray Analysis. The presence of carbon is indicating that EDTA are including in doped KDP crystal. According to Powder XRD, lattice parameters are found to be fairly matching with both single crystals and also fairly matched with JCPS card No. 38507 and also tetragonal structure was confirmed. According to UV- VIS spectroscopy, both crystals having ~ 4ev optical energy band gap and it’s indicate that both crystals are insulating material. According to Raman spectroscopy, KDP having a very strong bond of PO4 and EDTA was not effect in this bond. In a 0.1mol% EDTA doped KDP single crystals have less Vicker microhardness than the pure KDP single crystal and also both belongs to the soft categories nature.

5. References

[1] K. G. Raval and A. M. Dholariya 2020 AIP Conference Proceedings. 2220, 060015 (2020) 1-6
[2] Dr.M.Selvapandian and R.Arivuselvi 2014 Asian Journal of Engineering and Applied Technology (AJEAT). 2(1) 1-7
[3] R.Raja, D.Vedhavalli, P.Kurinji Nathan and R. Kanimozhi 2017 International Journal of Materials Science. 12(2) 273-281
[4] VinhTrungPhan, AnhQuynh Le and DatThanh Huynh 2017 American Journal of Physics and Applications. 6(1) 11-17
[5] T H Freeda and C Mahadevan 2001 Journal of physics. 57(4) 829-836
[6] Shaikh Kalim, A.B Lad and B.H Pawar 2014 Arch. Phy. Res. 5(6) 36-42
[7] Sandhya Ravi, S.Chenthamarai and R.Jayavel 2015 IOSR Journal of Applied Physics (IOSR-JAP). 7(2) 39-44
[8] K. D. Parikh, B. B. Parekh, D. J. Dave and M. J. Joshi 2013 Journal of Crystallization Process and Technology. 3(3) 92-96
[9] O V Mary Sheeja and C K Mahadevan 2013 International Journal of Research in Engineering and Technology. 2 (12) 738-748
[10] K.Manimekalai and R.Rajasekaran 2018 International Journal of Engineering Sciences & Research Technology. 7(1) 383-392
[11] T. Prasanyaa, M. Haris, V. Mathivanan, M.Senthilkumar, T. Mahalingam and V. Jayaramkrishnan 2014 Materials Chemistry and Physics. 147(3) 433-438
[12] N. Pattanaboonmeeaa, P. Ramasamyb and P. Manyunc 2012 Procedia Engineering. 32 1019 – 1025
[13] D. Voronstov, S. Filonenko, A. Kanak, G. Orkepka and Y. Khatavaka 2017 CrstEngcomm. 19(45) 6804-6810
[14] Jayant Dharma, AniruddhaPisal and PerkinElmer.Application note, Simple Method of Measuring the Band Gap Energy Value of TiO2 in the Powder Form using a UV/Vis/NIR Spectrometer.
[15] Houda Ettoumi, Youping Gao, Mohamed Toumi and Tahar Mhiri 2013 Internation Journal of ionics. 19(7) 1067-1075