



STRUCTURAL, XRD, FTIR STUDIES OF TITANIUM OXIDE DOPED KDP CRYSTALS GROWN BY GEL MEDIUM

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Cite This Article: M. P. Rameela, T. H. Freeda & T. Asaithambi, "Structural, XRD, FTIR Studies of Titanium Oxide Doped KDP Crystals Grown by Gel Medium", International Journal of Advanced Trends in Engineering and Technology, Volume 3, Issue 1, Page Number 54-58, 2018.

Abstract:

Potassium dihydrogen Phosphate (KDP) crystals are one of the most popular crystals for Non-linear Optical (NLO) applications. Optically good quality pure and metal doped KDP crystals have been grown by microbial free gel growth method at room temperature and their characterization have been studied. Gel method is a very simple method and can be utilized to synthesize crystals which are having low solubility. KDP is a representative of hydrogen bonded materials which possess very good electro – optic and nonlinear optical properties in addition to interesting electrical properties. Due to this interesting properties, we made an attempt to grow pure and Titanium Oxide doped KDP crystals in various concentrations (0.002, 0.004, 0.006) using gel method. The grown crystals were collected after 15 days. We get crystals with good quality and shaped. The dielectric constants of metal doped KDP crystals were slightly decreased compared to pure KDP crystals. FTIR, XRD and SEM analyses also done. Results were discussed in detail.

Key Words: Gel growth, KDP, FTIR, XRD & SEM

1. Introduction:

Potassium dihydrogen orthophosphate (KDP) is an excellent inorganic N L O material with different device applications. Single crystals of KDP and its isomorphs are representatives of hydrogen bonded materials which possess important piezoelectric, ferroelectric, electro-optic, mechanical and nonlinear optical properties. The demand for high quality large single crystals of KDP increase because of the application as frequency conversion crystal in inertial confinement fusion [1-2].

Therefore, it mostly used in various applications such as frequency conversion, laser fusion and electro-optical modulation. Lot of studies on the crystal growth and properties of KDP crystals in the presence of impurities have been reported [3-4]. Potassium dihydrogen phosphate (KDP) crystal attracts persistent attention of scientists due to its supreme quality and growing as large- size crystal possibility [5 - 6]. Microscopically, crystal growth includes growth rate, crystal morphology and crystal defects which are all related to the constituent growth units and their chemical bonding process [7 - 8]. DKDP, KDP and ADP are the only nonlinear crystal which are recently used for these applications because of its exclusive properties. The grown crystals were characterized using XRD, FTIR and SEM analyses.

2. Materials and Methods:

Pure and TiO₂ doped KDP single crystals are grown in gel medium using analytical grade KDP and TiO₂. Sodium meta silicate of 1.08 g/cm³ of 50 cc equally poured in a wide mouth test tube. KDP of 2.5 M of 50cc was prepared and 25 cc of above prepared KDP solution was mixed with sodium meta silicate. During the process pH was maintained at 5-6. Ethyl alcohol of equal volume is added over the cell surface without damaging the set of gel .When the alcohol diffuses in to the set gel, it reduces the solubility. This single crystal used to induce the nucleation and the nuclei process. The crystal growth was carried out at room temperature.

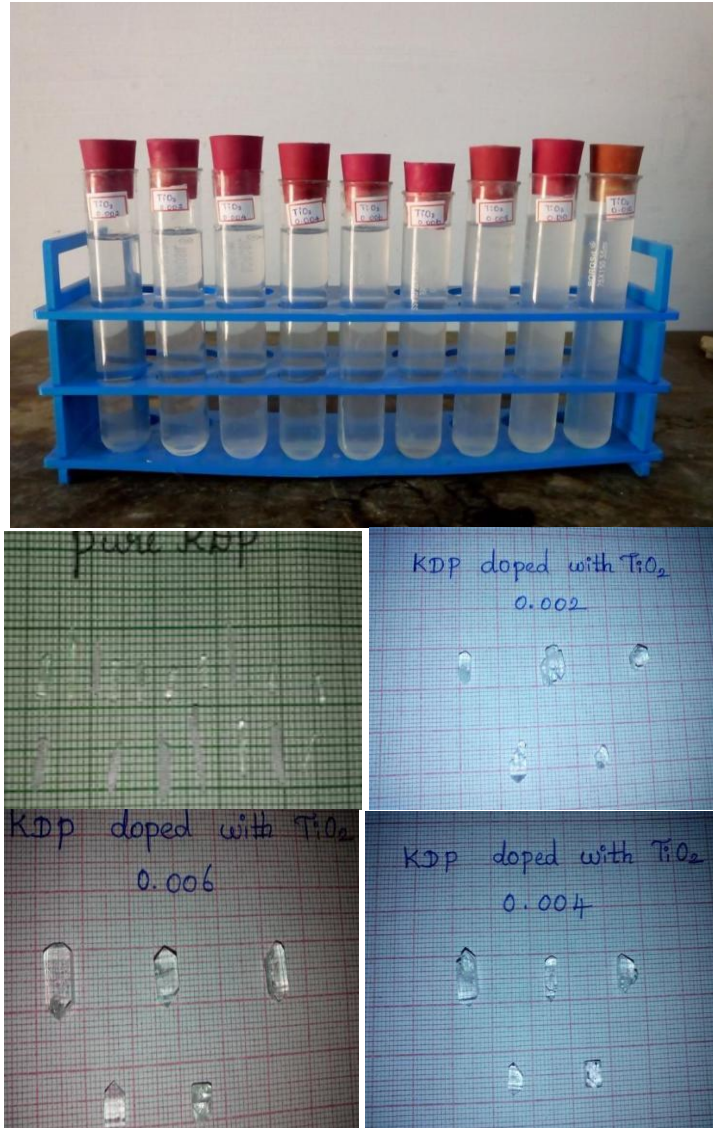
3. Doping:

Doping means adding impurity to the known pure crystal .To prepare a doped crystal a required amount of dopant solute is also mixed along with the pure solute.

Table 1: Doping Concentrations of Impurities

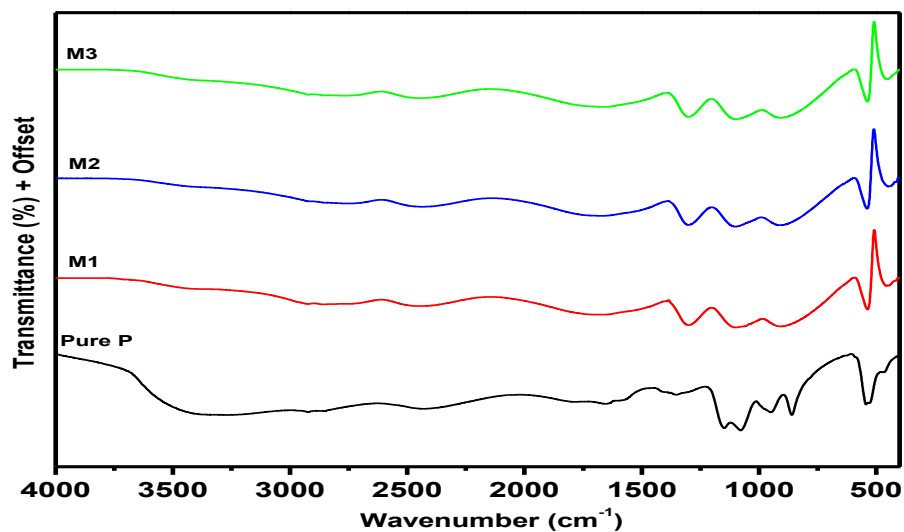
Doping Ratio	Mass of TiO ₂ added in mg
1:002	0.0715
1:004	0.1431
1:006	0.2147

An impurity can suppress, enhance or stop the growth of crystal completely. Usually it acts assure crystallographic faces. The effects depend on the pH, super saturation, impurity centralization, heat of the solution. The growth period was about 20 days. The photograph of the grown pure and TiO₂ doped KDP crystals were shown in the figures.



Photograph shown the grown pure KDP and TiO_2 doped KDP crystal

4. Results and Discussions:



FTIR spectra observed for the TiO_2 doped KDP crystals

The observed FT-IR spectra of pure and Titanium Oxide doped KDP crystals are shown in figure. From FT-IR spectra, the broad band which appears in the range 3261 to 2922 cm^{-1} is due to free O-H stretching of KDP [9]. It is seen that these are very weak bonds. The peak at 2922 cm^{-1} is due to P-O-H asymmetric

stretching. The strong intensity band at 2433cm^{-1} is due to one of the P-O-H bending of KDP. A sharp band in the spectral wavelengths of 1300 cm^{-1} is due to P=O stretching mode.. The sharp and strong intense bands appearing at 1147 cm^{-1} is due to P-O stretching. The spectrum shows an additional peak at 904 cm^{-1} .

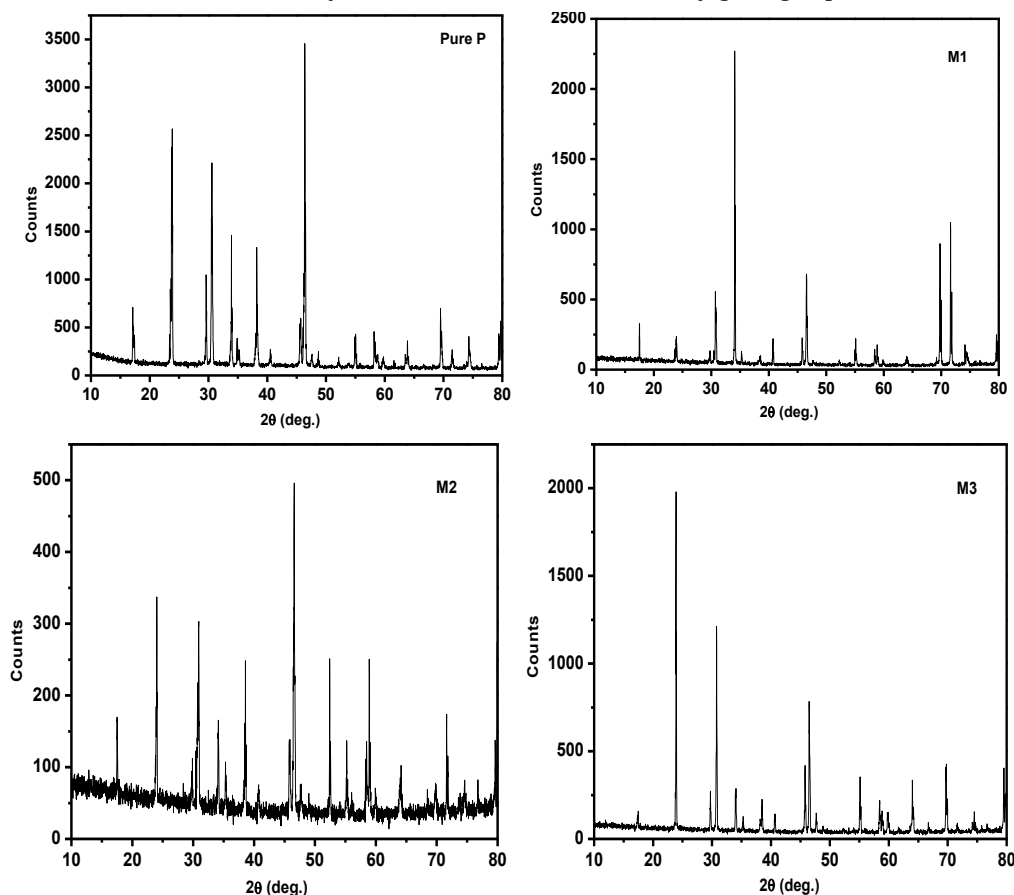
FTIR Assignments of (a) Pure KDP and (b) M1 (c) M2 (d) M3 are doped Titanium Oxide in different concentration.

.Pure KDP	(b) M1	(c) M2	(d) M3	Assignments
3261 vw	3422 vw	3419 vw	3408 vw	Free -O-H stretching
2922 s	2925 s	2924 s	2854 s	P-O-H symmetric stretching
1147 vs	1300 vs	1300 vs	1299 vs	P=O stretching of KDP
948 vs	1098 vs	1097 vs	1097 vs	P-O stretching
859 s	904 s	911 s	1098 s	P-O-H stretching of KDP
543 sh	457 sh	448 sh	450 sh	HO-P-OH bending

vs –very strong s- strong vw –very weak sh- sharp

Powder X-Ray Diffraction Characterization:

The grown crystals of KDP + Titanium oxide were subjected to powder X-ray diffraction analysis. RD patterns of TiO_2 doped with 0.002, 0.004 and .006 of KDP respectively. In all samples we can clearly see that both TiO_2 peaks as well as KDP peaks are visible. In 0.002 samples, the intensities of TiO_2 peaks are more dominant compared to KDP peaks but this pattern changes as we increase the doping concentration of KDP. As we increase the KDP concentration from 0.002, 0.004 the intensity of TiO_2 peaks decreases gradually while the intensity of KDP increases. This clearly indicates that KDP is successfully getting doped in TiO_2 .



XRD Pattern of TiO_2 doped KDP crystals

At maximum intensity the various structure parameters like the crystalline size, micro strain and dislocation density has been calculated by Debye – Scherer's formula and tabulated.[10,11]

$$D = 0.9 \lambda / \beta \cos \theta$$

Where λ is wavelength of the X-ray radiation, β is full width at half maximum (FWHM) of diffraction peak (in rad), and θ is scattering angle. Further, the dislocation density (δ) and micro strain (ϵ) was estimated by the relation

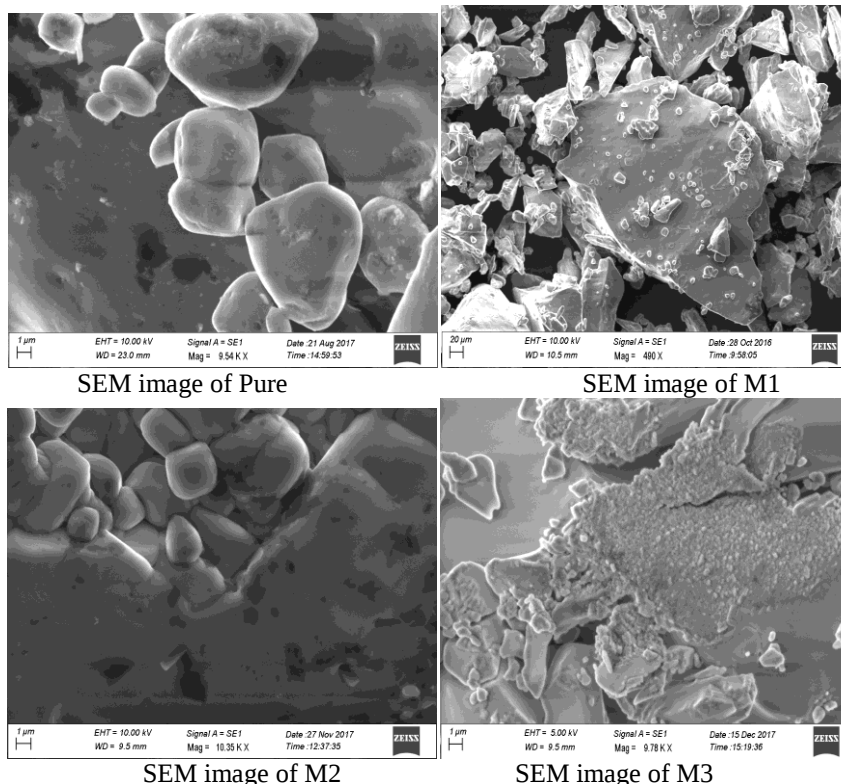
$$\delta = 1/D^2 \quad \text{and} \quad \epsilon = \beta \cos \theta / 4$$

X-Ray Diffraction data (crystalline size, micro strain and dislocation) for KDP doped with M1- 0.002, M2- 0.004, M3- 0.006, concentration of Titanium Oxide

Samples	d-spacing	2 θ	FWHM β	Crystalline size $\times 10^{-9}$ m	Dislocation $\times 10^{14}$ l/m	Microstrain $\times 10^{-4}$
Pure KDP	3.73804	23.784	0.0047	30.1478	11.0024	11.4978
Pure KDP+M1	3.71667	23.9432	0.00233	60.8312	2.7023	5.6983
Pure KDP+M2	3.70555	24.0161	0.00116	85.3950	1.3713	4.0591
Pure KDP+M3	3.72563	23.8847	0.00145	97.7388	1.0468	3.5465

Scanning Electron Microscopy (SEM):

Scanning Electron Microscopy is a method for high resolution surface imaging. SEM micrograph is representative of the surface topography and the material properties like morphology, shape and size of the grains can be clearly studied. It is a two dimensional image generated over a selected area of the surface of the sample for analysis. In the present study, the surface morphological features of all the samples have been observed .



Conclusions:

The gel technique of growing crystals is very slow process, but this process yields good quality of crystals. In the preparation of gel, PH of the solution plays a vital role. For good quality of gel, PH between 5 and 6 is desirable. Addition of Titanium Oxide with KDP gives some changes in its basic character. Here the characteristic properties of pure KDP and Titanium Oxide with KDP crystal has been investigated through FTIR, XRD and SEM analysis the results obtained from FTIR spectroscopy confirmed the presence of Titanium oxide in pure KDP. The presence of additional peaks in the XRD spectrum of doped KDP crystals shows the presence of additional phases due to doping. The SEM images of all the concentration are lead to the formation of spherical patterns which are good agreement

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