Growth, Structural and Dielectric Properties of Gallium doped Potassium Dihydrogen Phosphate (KDP) Single Crystal by Shankarnarayan –Ramasamy Method

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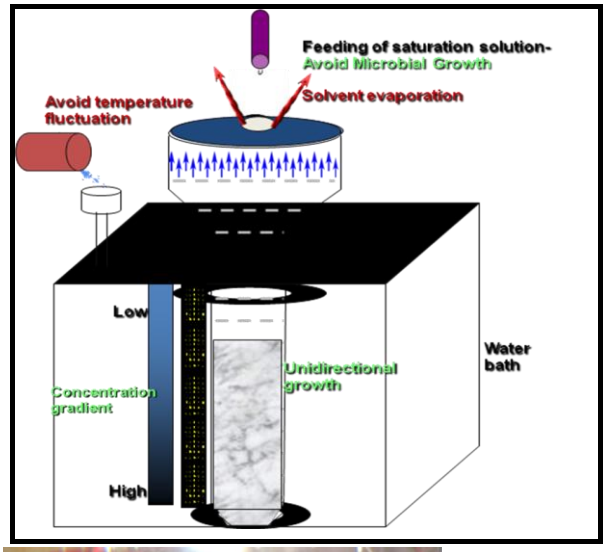
ABSTRACT
Gallium doped Potassium Dihydrogen Phosphate (KDP) single crystals are grown by Shankarnarayan –Ramasamy growth technique. Slow cooling method was adapted for the growth with variation in doping concentration, there is modification in growth habit, non linear optical properties of doped crystals. Powder XRD determines the parameters of unit cell of doped KDP crystals. EDAX study shows presence of gallium ion in appropriate sites in unit cell. The Fourier Transform Infra Red (FTIR) spectrum reveals strong absorption bands due to gallium 3+ ion. UV spectra show improvement in optical transmittance. TGA –DTA determines the composition of materials and to predict their thermal stability at temperatures.

Keywords
KDP, Solution Growth, XRD, FT-IR, EDAX,UV-VIS, TGA – DTA.

1. INTRODUCTION
Nonlinear optical (NLO) crystals, in particular, KDP are widely used for frequency conversion and optical switching in modern optoelectronics and photonics. Potassium dihydrogen phosphate (KDP) crystals have created considerable interest among researchers because of its Piezo-electric, nonlinear optical, and electro-optical properties, and also it is widely used in X-ray monochromators [1].

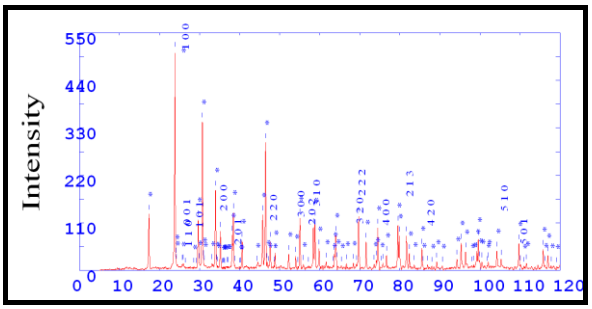
Aim of improving the quality of KDP crystals with better optical properties, an attempt has been made in the present work to grow the KDP crystals by doping it with Gallium ion with different concentration by weight % and to study the effect on the nucleation parameters and structural and optical properties[2].

2. EXPERIMENTAL
Saturated solution of KDP (KH_2PO_4) with specific concentration of Ga^{3+} was prepared which has been subjected to grow point seed by solution method . The crystals were grown from Shankarnarayan -Ramasamy with the Ph 4.0. The seed crystal placed at bottom of ampoule and allows growing with temperature gradient maintained by temperature controller[3]. The crystal growth rate 3mm per day was established as an average value equal to the ratio of crystal dimension to the growth time. The physical and characteristics of the crystal were investigated using 10mm X 10mm X 10mm same site sample obtained from the growth sector (100) with working surface subjected to grinding and optical properties. The crystal is shown in the photograph.



Photograph showing grown crystal KDP

3. Characterization
3.1. Powder crystal XRD analysis



KDP crystal belongs to the tetragonal scalerohedral symmetry with space group I42d having dimensions a = b = 7.5243A° and c =3.698A°. The sample was scanned in the range 10-90° at a scan rate 2° per min .The finely powered materials of the grown crystal were used for the analysis[4] .The powdered diffraction pattern with indices are shown in figure . The prominent well resolved Bragg's picks of specific 2θ angle reveal the high crystalline nature of the crystal . The XRD data is verified by KDP crystal *JCPDS* Card nos. 35- 0807[5] .

3.2. Fourier Transform Infrared spectroscopy

The Fourier transform infrared analysis of powered sample was carried out between 4000 and 400 cm-1 by recording the spectrum using Varian FTIR spectrometer by ATR technique in order to reveal the metal complex coordination[6]. The obtained result testifies that all the IR spectra are practically identical and agree with the available literature data [7]. The assignments confirm the presence of various functional groups present in the material, tabulated in Table.

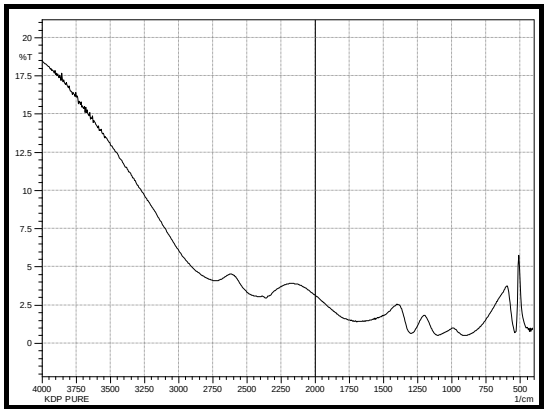
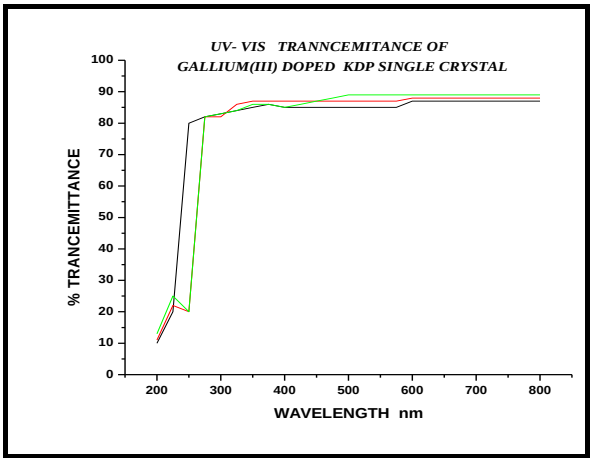


Table .

SN	Wave number	Wave number	Functional group
1	3605	3606	O-H
2	3333	3334	O-H
3	2919	2917	P-O-H
4	2839	2827	P-O-H
5	2461	2459	P-O-H
6	2358	2355	P-O=H
7	1650	1653	O=P-OH
8	1295	1293	P=O
9	1100	1123	P=O
10	904	911	P-OH
11	535	533	HO-P-OH

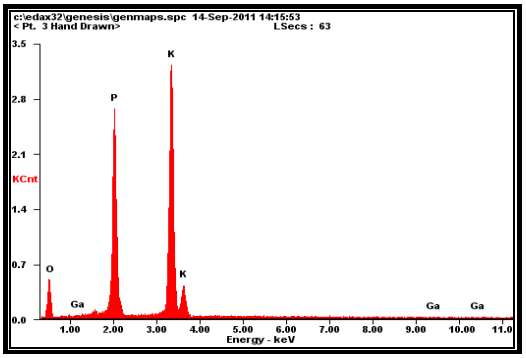
3.3. UV–VIS spectral analysis

The UV-Vis-NIR spectral transmittance was studied using a Shimadzu UV-1061 UV-Vis spectrophotometer with a single crystal of 6 mm thickness in the range of 200-1200 nm. The recorded spectrum is shown in figure. The crystal has sufficient transmission in the entire visible and IR region [8]. The lower cut off wavelength is around 250 nm; the transmission percentage of 2% Gallium added KDP crystal is around 93%, as compared to pure KDP, which is around 87% .



3.4. EDAX analysis

Energy dispersive X-ray analysis (EDAX) used in conjunction with all types of electron microscope has become an important tool for characterizing the elements present in the crystals[9]. In the present study, the crystal was analyzed by INCA 200 energy dispersive X-ray micro analyzer equipped with LEO – Steroscan 440 Scanning electron Microscope. The recorded EDAX spectrum is shown in figure . Presence of Gallium is confirmed from the EDAX spectrum[10].



3.5 TGA –DTA analysis

Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA) carried out simultaneously is very much useful in interpreting the melting point and thermal stability of a sample[11].

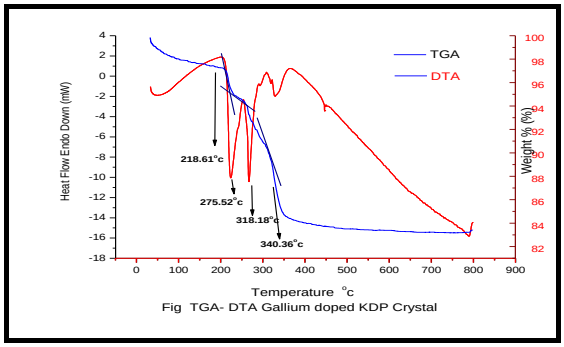


Fig TGA- DTA Gallium doped KDP Crystal

DTA and TGA of KDP were carried out with the help of an instrument (STA 409C) using KDP crystals as sample and alumina as reference[12]. KDP doped sample were decomposed at 340.36o c . The graphs show the peaks at 218.6 oc, 275.50 oc,318.18 oc and 340.36 oc reveal escape of oxygen atoms from the KDP crystal.

CONCLUSIONS

Pure and Trivalent Ga3+ ion added KDP crystals were grown by Shankarnarayan -Ramasamy method. The XRD spectrum shows the excellent crystalline nature of Gallium added KDP crystal. The transmission spectrum reveals that the crystal has sufficient transmission in the entire visible and IR region. All functional groups were present in crystals and are confirmed by FTIR spectrum.

Ga3+ ions are adsorbed on the crystal faces and create isolated centers. The presence of Gallium was confirmed by EDAX analysis. DTA, TGA analysis reveal that KDP is stable up to 340.36° C before it melts.

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