GROWTH AND DIELECTRIC PROPERTIES OF GALLIUM(III) DOPED KDPSINGLE CRYSTAL BY SHANKARNARAYAN- RAMASAMY METHOD

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ABSTRACT

Potassium Dihydrogen Phosphate (KDP) is newly developed ideal nonlinear optical crystal used for high-energy laser technologyand optical electronic devices. Gallium ion doped KPD single crystal grown by Shankarnarayan-Ramasamy method. Good and transparent qualities of crystals have been harvested with dimension 11x10x13 cm .The crystal structure and perfection has been determined using powder XRD and High resolution XRD. Presence of Gallium was confirmed by EDAX in the crystals.Functional groups were present in the crystal by FTIR.Thermal properties of the crystal have been studied by using Thermogravimetric (TGA) and Differtial thermal analysis (DTA). Optical transparency has been studied by UV-VIS spectrum. Dielectric properties were studied with varying frequency at different temperature.

KEYWORD:- single crystal growth, KDP, Powder XRD,FTIR,TGA-DTA, Dielectric properties,EDAX

INTRODUCTION

KH_2PO_4 (KDP) and KD_2PO_4 (DKDP) crystals are currently the only nonlinear materials suitable for frequency converters and Pockels cells in high-power large-aperture laser systems. These crystals often suffer from laser damage, which adversely affects the quality of the downstream beam. The observed damage thresholds of KDP/DKDP crystals are much lower than the intrinsic thresholds, due to the nano-scale impurities, which are difficult to identify due to their sizes. Laser-induced bulk damage resistance of KDP/DKDP crystals strongly depends on the laser wavelength. The laser damage threshold at 1064nm is much higher than that at 355 nm.[1]

Trivalent impurities like Fe $^{3+}$,Cr^{3+}, Al^{3+} have effect growth rate of the crystal. Due to there comparable ionic size with potassium ion and probably substitutedtrivalent impurities. Ga $^{3+}$ ion is optically active material and no study has been made to investigate the effect of Ga(III) ion on growth and optical properties of KDP crystal.Present work is based on effect of trivalent on growth and dielectric properties of crystal. SR method is most suitable method for unidirectional growth with 100% solute conversion efficiency[2].

SHAKARNARAYAN RAMASAMY METHODFOR CRYSTAL GROWTH

S-R method is the unidirectional crystal growth method by slow evaporation of solution. Seed crystals were prepared by convectional recrystallization slow evaporation method. KDP of Merck AR grade was used to prepared seed crystal. Very good and transparent qualities of seed crystals were selected having perfect external morphology. <100> crystal plane was selected for unidirectional growth in S-R method. Seed crystal was cut carefully and polished portion along <100> plane. The processed seed crystal has been placed at the bottom of ampule, which is special designed for S-R method[3,4].

Solution was prepared at 30 ^{o}C according to solubility curve. 27.8 gm/ 100 of KDP solute Merck AR grade has been dissolved in (Millipore 18.2 MΩ.cm resistance) triple filter deionized water. Solution was kept three hours on magnetic stirrer at 30^{o}C temperature for homogeneity in the solution. Solution was kept slightly under saturated for S-R method. Clean filtered solution was carefully filled in ampoule without disturbing the position of seed crystal inside the ampoule.

The ampule has been rested in S-R set up for two hour. Initially, temperatures are kept 30 ^{o}C at upper and lower ring heater. The solution has been settled inside the ampule and concentration gradient maintain along the ampule. Concentration gradient was maintained minimum at top and maximum at the bottom of the ampoule. Upper ring heater temperature slightly was increased 35 °C for rising evaporation rate at top of the ampoule. The top ring heater controls the spurious nucleation near the surface region of the solution during crystal growth process. Upper part of ampule has been covered with transparency sheet and the small hole at the center is reduced nucleation at upper part of ampule.

A transparent KDP crystal growth has been observed at the bottom of ampule under optimizing condition in week. The KDP growth rate is approximately 1 mm per day was observed. A good transparent quality of crystal was harvested. KDP Crystal growth has been carried out for different doping concentration in S-R method[5].

Fig1. SR set up for growth crystal

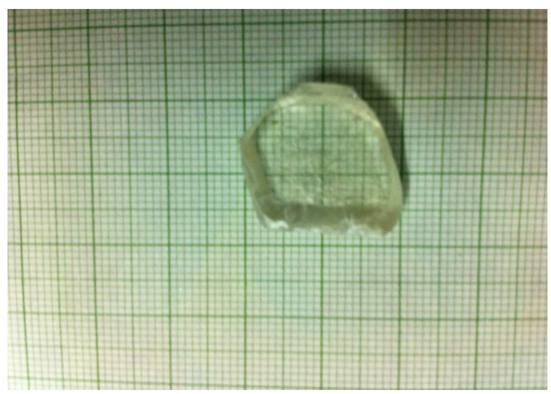


Fig 2 Grown KDP crystals by SR method

Characterization

Good quality and transparent KDP crystals were ground in pestle mortar to determine different characterization. Some KDP crystals were cut in dimension 10mm x 10mm square area for optical transmission studies.

1. **Powder XRD and single crystal XRD analysis**

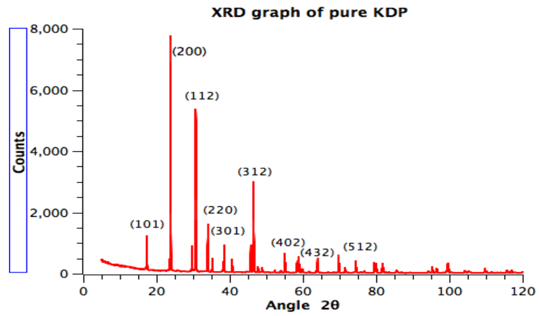


Fig 3 powder XRD of KDP crystal

The crystalline phase characterization of the samples is carried out by a computer interfaced X-ray Diffractometer (Philips, Xpert - MPD) operating at 40 kV and 30 mA with CuKα radiation where =1.54056 Å. It is observed that the powder XRD diffracted peaks are same in the pure and doped KDP crystal. The prominent peak of pure and doped KDP (101), (200), (112), (202), (310), (312) are observed. The sharp peak indicated that the crystalline natures of grown crystal are fine quality. The XRD data matched with the JCPDF data file no 035-0807 and result shows that gallium has entered into the KDP lattice. It shows that the crystal structure of KDP remains same by doping gallium[6]

2. **FTIR spectral analysis**

An FTIR spectrum of pure and doped KDP crystal has been recorded on VARIAN resolution pro FTIR spectrometer in the range 400- 6000 cm $^{-1}$ by KBR pallet technique.

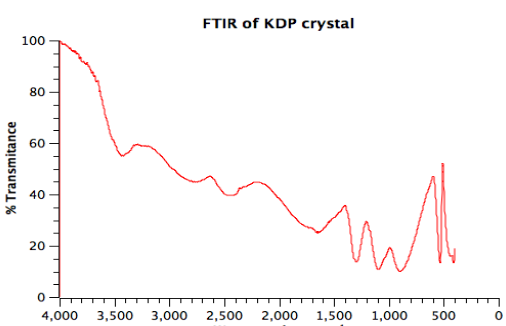
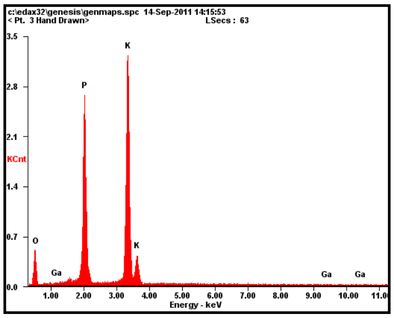


Fig 4 FTIR of KDP crystal

The assignments confirm the presence of various functional groups present in the material. The wave number 3065,3334 cm $^{-1}$is presence of O-H bond, 2919,2839,2461 cm^{-1} presence of P-O-H bonding, 2358 cm $^{-1}$ represent P-O=H bond, 1295,1100 cm $^{-1}$ presence of P=O bond, 904 and 543 cm $^{-1}$ is represent of P-O-H bond [7,8].



3. **EDAX studies**

Fig5 EDAX of Gallium doped KDP crystal 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[8]. In the present research module study, INCA 200 energy dispersive X-ray micro analyzer equipped with LEO – Steroscan 440 Scanning electron Microscope, analyzed the crystal. The recorded EDAX spectrum is shown in figure 6. Presence of Gallium is confirmed from the EDAX spectrum[9,10].

4. **TGA -DTA Studies**

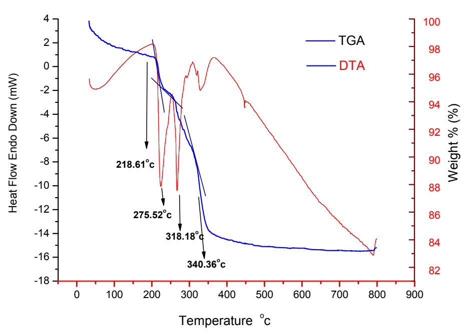


Fig TGA- DTA Gallium doped KDP Crystal

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 [11]. As shown in figure 7, KDP doped sample were decomposed at 320.3℃. The graphs show the peaks at 261.6 ℃, 213.5 ℃, 261.6℃

reveal exothermic reaction due to escape of oxygen atoms from the KDP crystal. As shown in figure , TGA curve sharply decrease at temperature at 230 ℃ and 356 ℃ is most probable melting point of KDP crystal . TGA curve shows that crystals are thermally stable below 230℃ [12,13]

5. **Dielectric studies**

KDP has dielectric nature was measured by Wynne Kerr 6500B (UK) impedance analyzer. At low frequency, it was observed that the dielectric constant increases with increase temperature. Also, it is observed that the dielectric loss reduces with increase in doing concentration. At high frequency the dielectric constant decreases to large extent. This peculiarbehavior appears because of dopant Ga^{+3} ions in the crystal lattice [14].

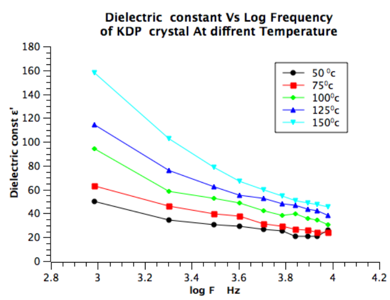


Fig 7 Dielectric constant vs. log frequency

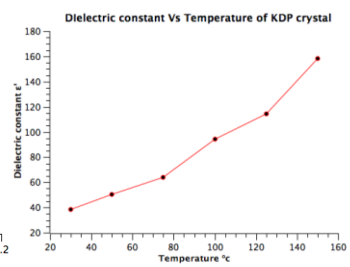


Fig 8 Dielectric constant vs. Temperature

Result and discussion

Pure and Trivalent Ga^{3+} ion added KDP crystals were grown by Shankarnarayan -Ramasamy method. The XRD spectrum shows the excellent crystalline nature of Gallium added KDP crystal. All functional groups were present in crystals and are confirmed by FTIR spectrum.

Ga^{3+} ions are adsorbed on the crystal faces and create isolated centers. The presence of Gallium was confirmed by EDAX analysis. DTA, TGA analysis revealsthat KDP is stable up to 240.36℃ before it melts. Gallium ion enhances the conductivity in crystal and

Dielectric constant. Dielectricconstant is decreases with increase in frequency as temperature increases.

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