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CRYSTAL GROWTH AND CHARACTERIZATION OF KDP AND ADP SINGLE CRYSTALS

[1]Dr.M.SELVAPANDIYAN and [2]R.ARIVUSELVI
[1,2]PG and Research Department of Physics
[1,2]Sri Vidya Mandir Arts & Science College
[1,2]Uthangarai, India-636 902
Tel: +91-9976493935; Fax: +91-04341-243362
Email: mselvapandiyan@rediffmail.com[1]

ABSTRACT

The nonlinear optical crystals have been given much importance because of their potential applications such as telecommunication, optical information process, frequency conversion and optical disk data storage. KDP and ADP is a well known nonlinear optical (NLO) materials. Single crystal of potassium dihydrogen phosphate and ammonium dihydrogen phosphate were grown by using slow evaporation method at ambient temperature water as a solvent. The grown single crystals have been analyzed with Fourier infrared spectrometer, Ultra violet and visible spectrometer, Vickers micro hardness test, dielectric studies, thermo grave metric analyses and differential thermal analysis. The presence of functional groups and modes of vibration of the grown crystals was confirmed by FTIR studies. The cut off wavelength of the grown KDP and ADP single crystals were obtained to be 383 nm and 416 nm. Vickers micro hardness studies recorded that the grown both KDP and ADP belong to the categories of the soft in nature. The thermal behaviour of the materials was analyzed by thermo gravimetric and differential thermal analysis (TGA/DTA). The grown materials are thermally stable up to 192° C and 227° C. The dielectric constant and loss of the materials is low at high frequency with different temperature.

Keywords: NLO single crystals; slow evaporation; FTIR; TGA/DSC;UV-vis spectroscopy; Dielectric properties

1. INTRODUCTION

Potassium dihydrogen phosphate single crystal is widely used and well studied nonlinear optical materials. The unique combination properties like wide range of transparency, relative high magnitude of quadratic nonlinear susceptibility, electrooptical and piezoelectric effect, as well as the possibility of wide range aperture crystals make KDP single crystals to have special attentation of the researchers. KDP single crystals are used in industrial laser facilities of frequency multipliers, parametric amplifiers, electrooptical shutter. Many attempt have the growth conditions or by adding different impurities [1-4]. In the present Investigation, the growth of single crystal ADP and KDP was subjected to various characterizations such as Vickers micro hardness studies, Ultraviolet visible (UV-Vis) spectroscopy, Dielectric studies, and TGA/DTA. Also the results of the work are reported in this paper.

2. EXPERIMENTAL WORK

The calculated amounts of the analar grade starting materials Potassium dihydrogen phosphate (KDP) and Ammonium dihydrogen phosphate (ADP) were dissolved separately in deionised (DI) water at room temperature[5-6]. After 2 hours of stirrer, the saturated homogeneous solution was prepared by using magnetic stirrer. The saturated solution was filtered twice with whattman filter paper before it was subjected to evaporation. The solution was covered to avoid dust and kept undisturbed for days together. Crystal of appreciable size was obtained at the end of 30th day. The as grown KDP and ADP crystals are shown in the figures 1 and 2.

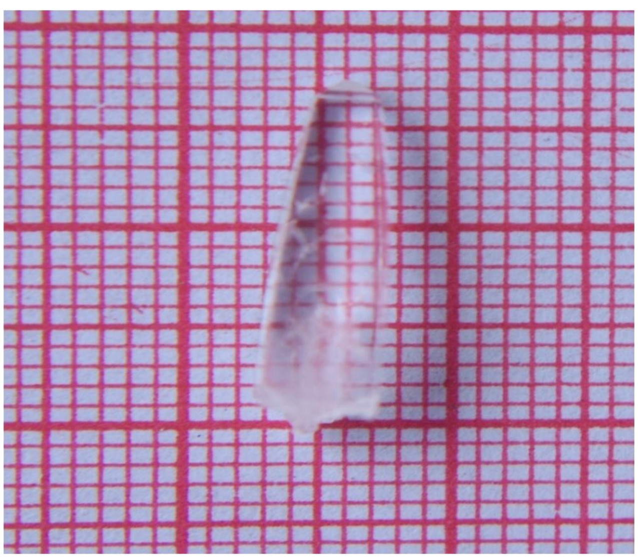

Figure 1 As grown KDP single crystal

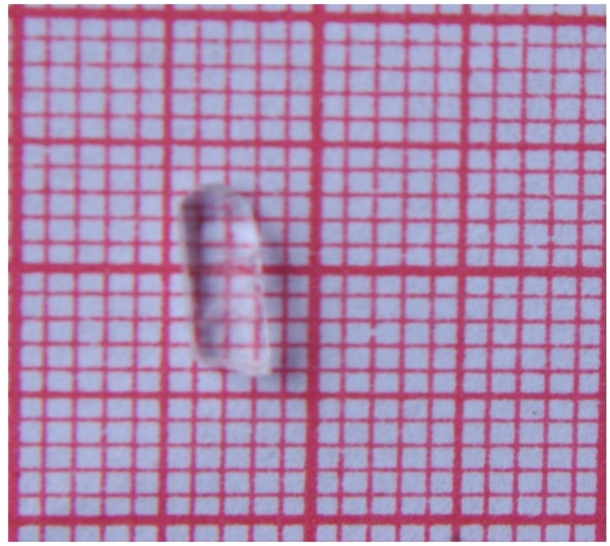

Figure 2 As grown ADP single crystal

3. RESULT AND DISCUSSIONS

3.1. FTIR analysis

The functional group and modes of vibration of the grown crystals were carried out by using of Perkin Elmer Spectrum Two FTIR instrument scanning range is MIR 4000 cm^{-1} - 450 cm^{-1} with resolution 0.5 cm^{-1}**.** The broad band at the frequency 3703.29 cm^{-1} and 3318 cm^{-1} may represents the OH stretching of unchanged COOH group of the amino acid. An absorption in FTIR spectra of KDP crystal at 1761.32 cm^{-1} is assigned to stretching vibration. The involvement of NH^{3+} in hydrogen bonding is evident by the fine structure of the band at lower energy region. The FTIR spectrum of both KDP and ADP are shown in figures 3 and 4. The peaks between 485 cm^{-1} and 902 cm^{-1} are due to the O-N=P and –ONO_2 bond vibration in ADP crystal. The band at 1076 cm^{-1} and 1544 cm^{-1} are assigned to be P=O and O-H stretching vibration. The frequencies of 2400 cm^{-1} and 3371 cm^{-1} are indicates that the presence of O-H and N-H stretching vibration.

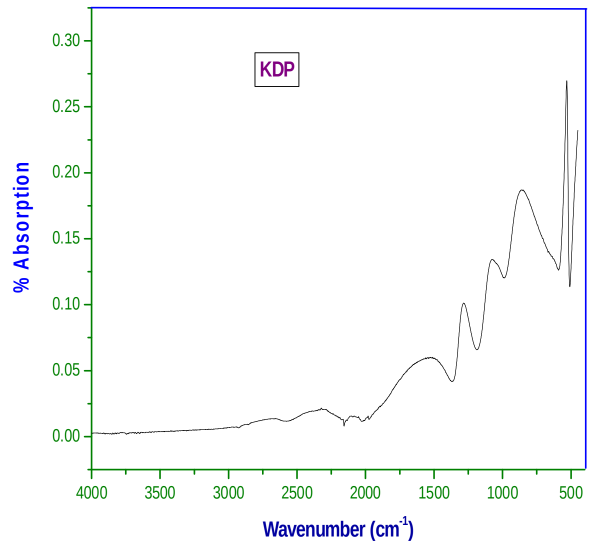

Figure 3 FTIR spectrum of grown KDP single crystal

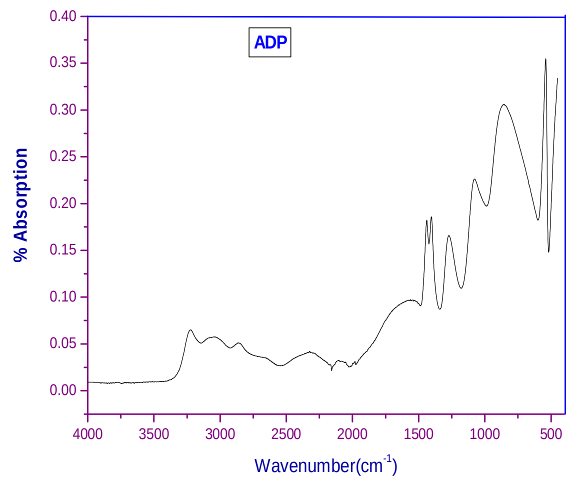

Figure 4 FTIR spectrum of grown ADP single crystal

3.2 Ultraviolet and Visible Spectroscopy Analysis

The UV visible spectral studies of grown crystals were carried out using lambda 35 model UV- visible spectrometer in the spectral range 190 nm-1100 nm. The absorption spectra of KDP and ADP crystals have shown in figures 5 and 6. The observed cut off wavelength of the KDP and ADP crystal is 383 nm and 416 nm. The forbidden band gap for the grown crystal was calculated by using the relation

$$E_g = hc/\lambda$$

Where,

h is the plank's constant

c is the velocity of the light and

λ is the lower cut off wave length of the material the material.

The calculated forbidden energy band gap of KDP and ADP crystal is 3.24 eV and 2.98 eV respectively. These results suggest that the grown materials belong to the typical insulating material and are suitable for fabricating optoelectronic devices.

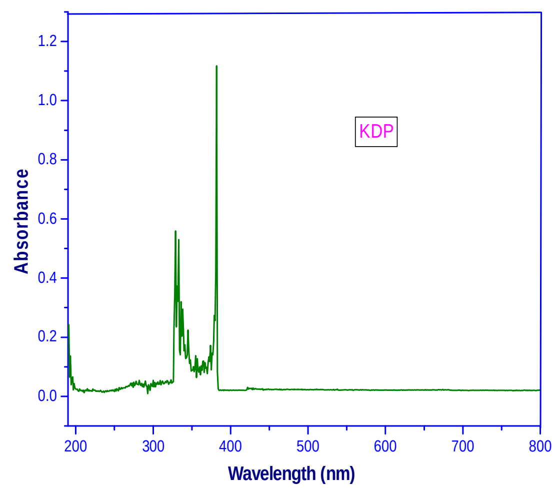

Figure 5 UV spectrum of grown KDP single crystal

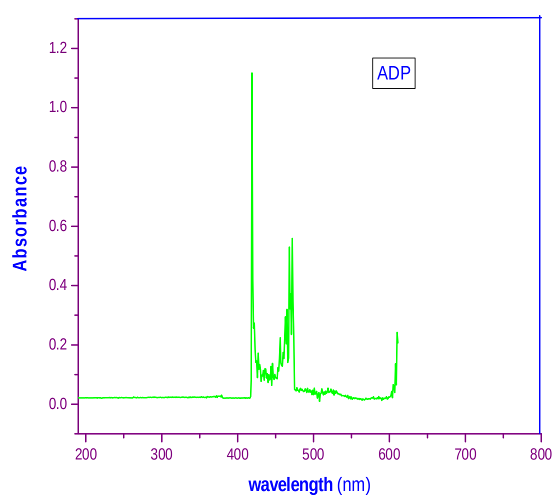

Figure 6 UV spectrum of grown ADP single crystal

3.3 Vickers Micro Hardness Test Analysis

The mechanical behaviours of the grown KDP and ADP crystals were analysed by using Vickers micro hardness tester HMV-2T model. The selected surface of grown crystal polished, washed and dried. Then the crystals were monitored as the platform of the micro hardness tester, the tester diamond intender tip in used. The hardness values of grown crystals were measured by applying different loads like 25 gm, 50 gm, and 100 gm. This shows that the hardness values of grown crystal are increased with increasing of load. The graph was plotted between log P and hardness number (Hv) which is a almost straight line is shown in figure 7. If we increase the load beyond 100 gm the crystal will be broken. The graph is also plotted between load P and log d and is also a straight line is shown in figure 8. The slope of the straight line gives the work hardening co-efficient (n) value. The calculated work hardening co-efficient of KDP and ADP crystals are 2.9 and 2.6. The obtained values of n confirmed that the grown both KDP and ADP crystals belong to the categories of soft in nature.

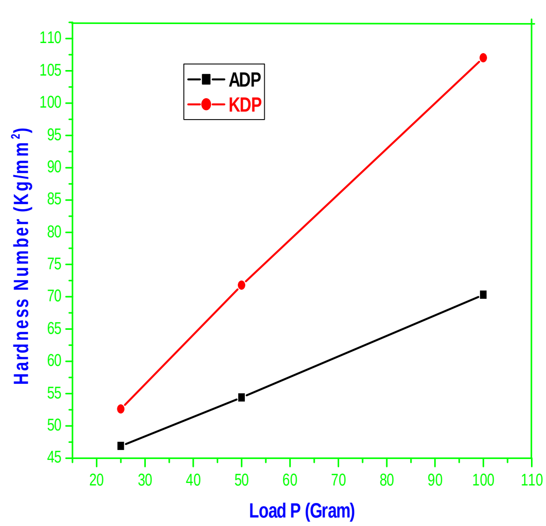

Figure 7 Load P Vs Hardness Number for KDP and ADP single crystal

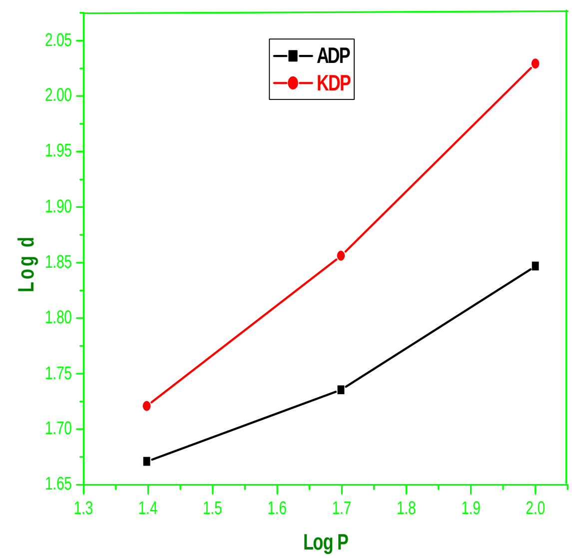

Figure 8 Log P Vs Log d for KDP and ADP single crystal

3.4 Dielectric Analysis

The dielectric studies of the KDP and ADP single crystals carried out using LCR HIOKI 3532 HI tester with the frequency range between 50 Hz to 5 MHz at the temperature 323 K and 373 K for KDP single crystal and 313 K to 333 K for ADP single crystal. The dielectric constant and dielectric loss were calculated. The graph plotted between log f Vs dielectric constant and also between log f Vs dielectric loss. The dielectric constant decreases with increasing frequency and the dielectric loss of the material also decreases with increasing of frequency with two different temperatures. The variation of dielectric constant is a function of frequency with two temperatures due to attribution of electronic and ionic orientation of polarization. The grown materials are well suited to apply the optoelectronics device applications, because the dielectric loss of material very low at high frequency. A graph plotted between Log f Vs dielectric constant, Log f Vs dielectric loss of both KDP and ADP are shown in figures 9 – 12.

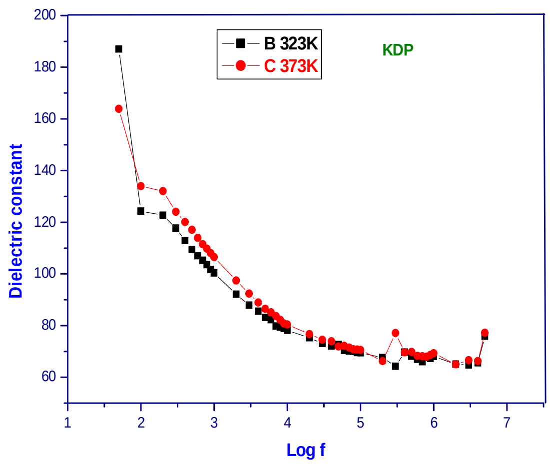

Figure 9 Log f Vs dielectric constant of KDP single crystal

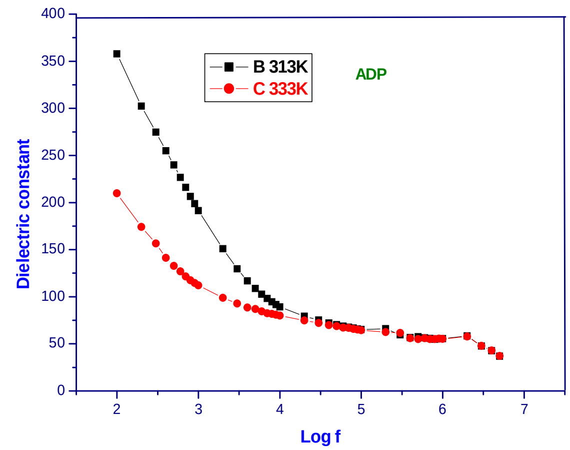

Figure 11 Log f Vs dielectric constant of ADP single crystal

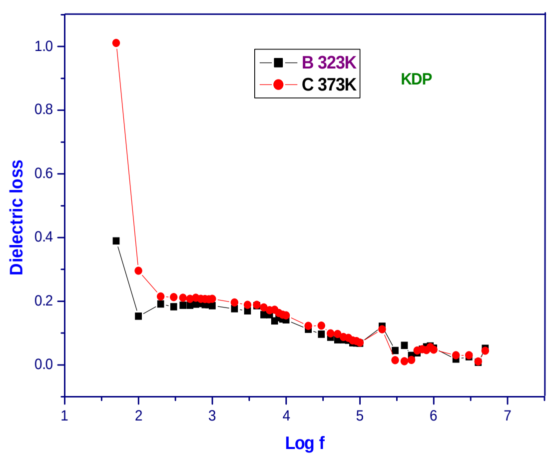

Figure 10 Log f Vs dielectric loss of KDP single crystal

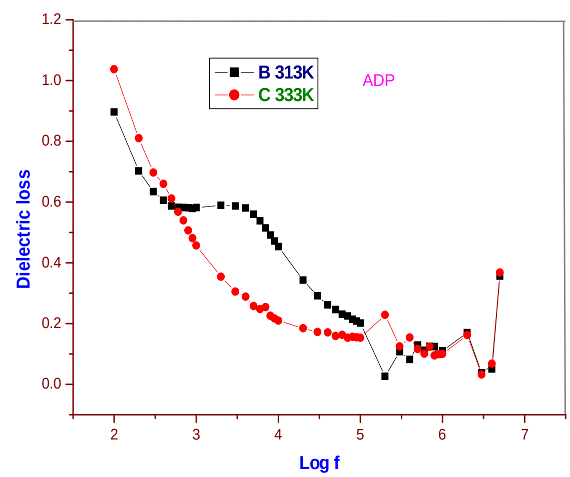

Figure 12 Log f Vs dielectric loss of ADP single crystal

3.5 Thermo Gravimetric and Differential Thermal Analysis

Thermo gravimetric and differential thermal analysis of the grown KDP and ADP single crystals were carried out by using SDT-Q 600 analyzer with the temperature between 0^o C and 1100^o C at the heating rate 20^o C per minutes in nitrogen atmosphere. The grown KDP and ADP single crystals are thermally stable up to 192.4^oC and 2272^oC. The major weight losses of ADP and KDP crystals are 12.9% and 28.8% takes place between the temperatures 227.8°C - 408.8°C and 192°C – 473.1°C respectively. The number of sharp peaks of differential thermal analysis curves shows that the grown materials having high crystalline nature. The sharp endothermic peaks of differential thermal analysis curves are 218.3°C and 284.3°C which represents the melting point of the grown KDP and ADP single crystals. The TGA and DSC curves are shown figures 13 and 14.

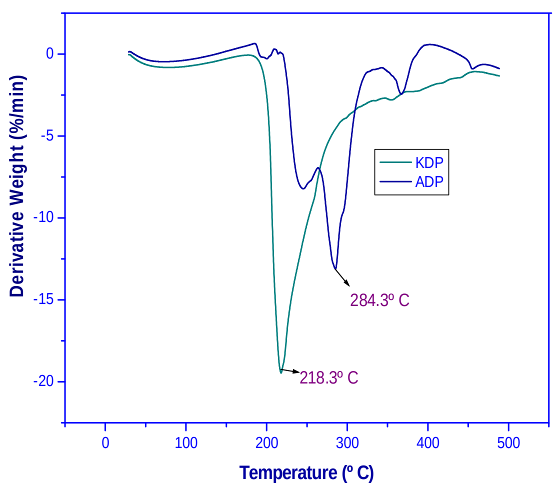

Figure 13 DTA curves of KDP and ADP single crystals

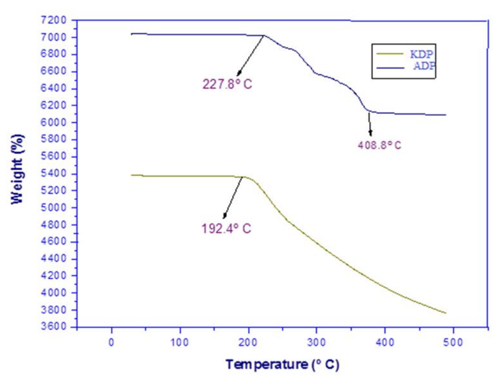

Figure 14 TGA curves of KDP and ADP single crystals

3.6 CONCLUSION

The nonlinear optical crystal of KDP and ADP were grown by using slow evaporation technique at room temperature. The grown crystals carried out various characterization studies viz., The broad band at the frequency 3703 cm^{-1} and 3318 cm^{-1} represents the OH stretching. An absorption of KDP crystal at 1761.32 cm^{-1} is assigned to stretching vibration. . The peaks between 485cm^{-1} to 902 cm^{-1} are due to the O-N=P. The UV visible spectral of grown crystal was carried out using lambda 35 model UV- visible spectrometer. The observed upper cut off wave length of the KDP and ADP crystal is 383 nm and 416 nm. Forbidden energy band gap of KDP and ADP crystal is 3.24eV and 2.98 eV respectively. These results suggest that the grown materials belong to the typical insulating material and are suitable for fabricating optoelectronic devices. Work hardening co-efficient of KDP and ADP crystals are 2.9 and 2.6. The obtained values confirmed that the grown both KDP and ADP crystals belong to the categories of soft in nature. Dielectric constant of material decreases with increasing frequency. The dielectric loss of material also decreases with increasing of frequency. The grown materials are well suited to apply the optoelectronics device applications, because the dielectric loss of material very low at high frequency. TGA/DTA studies shows that grown KDP and ADP single crystals are thermally stable up to 192.4°C and 227.8°C.The melting point of the grown KDP and ADP single crystals are 218.3° C and 284.3° C.

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