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Crystal Growth and Studies of Dihydrogen Phosphates of Potassium and Ammonium complexes

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Abstract
A nonlinear optical (NLO) material Potassium dihydrogen phosphates (KDP) and Ammonium dihydrogen phosphates (ADP) are grown by slow evaporation solution growth technique. The FTIR studies confirm the presence of the functional group in the grown crystal. The optical transmittance studies show that the crystal has transparence in the entire visible and IR region. The thermal stability of the materials was assessed by TG/DTA analysis. The mechanical stability of the grown crystals was analyzed by Vicker's microhardness test. The dielectric behavior of the crystals was tested by dielectric analysis. The second harmonic generation (SHG) of KDP is confirmed by Kurtz and Perry powder technique using Nd: YAG laser.

Keywords: Crystal Growth; FTIR; UV; TG/DTA; Dielectric; Second harmonic generation

I. Introduction

The materials with high optical nonlinearities are the target to the researchers since their applications in optoelectronics, telecommunication industries, laser technology and optical storage devices are innumerable. Ammonium dihydrogen orthophosphate (ADP) and potassium dihydrogen orthophosphate (KDP) are two of the oldest crystals grown in large size for many applications and continue to be interesting materials both academically and industrially [1-6]. ADP crystals have a wide range of applications in integrated and nonlinear optics because of their piezoelectric (antiferroelectric at low temperature) and nonlinear optical property. Due to its interesting electrical and optical properties, structural phase transitions, and ease of crystallization, it has been the subject of a wide variety of investigations for several years [7, 8].

Ammonium dihydrogen Phosphate (ADP) is a representative of hydrogen-bonded materials that possesses excellent dielectric, piezoelectric, antiferroelectric, electro-optic and nonlinear optical properties. Growth and studies of ammonium dihydrogen phosphate are a center of attention to researchers because of its unique properties and wide applications. Single crystals of ADP are used for frequency doubling and frequency tripling of laser systems, optical switches in inertial confinement fusion and acousto-optical devices. ADP crystallizes in a body-centered tetragonal structure with the space group of I 4 2d and its unit cell parameters are a = b = 7.510 Å and c = 7.564 Å [9, 10].

Potassium dihydrogen phosphate (KDP) has been extensively studied due to its important applications such as second harmonic generation, Q-switch and quantum electronics [11, 12]. KDP is a nonlinear optical material that finds its application in optical modulators and frequency converters. The National Ignition Facility (NIF) at Lawrence Livermore National Laboratory (LLNL), requires single crystal plates of KDP and DKDP for Pockels cells and frequency converters as a part of its design [13]. For inertial confinement fusion, optical crystals with low impurity and higher damage threshold are required. KDP is one such transparent dielectric material best known for its optical and electro-optical properties. It has been incorporated into various laser systems for harmonic generation and opto electrical switching [14].

II. Experimental

Calculated amounts of the analar grade starting materials Potassium dihydrogen (KDP) phosphate and Ammonium dihydrogen phosphate (ADP) were dissolved separately in deionized (DI) water at room temperature. After 2 hours of the stirrer, the saturated homogeneous solution was prepared by using magnetic stirrer. The saturated solution was filtered twice with what man 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 within 30 days. The as grown KDP and ADP crystals are shown in the Fig. 1a and 1b.

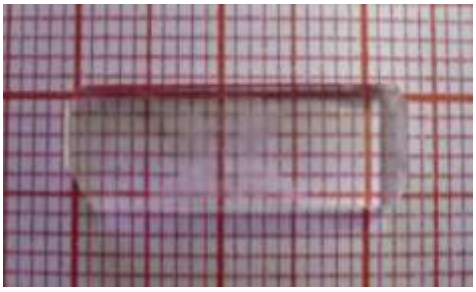

Fig. 1a As grown KDP crystal

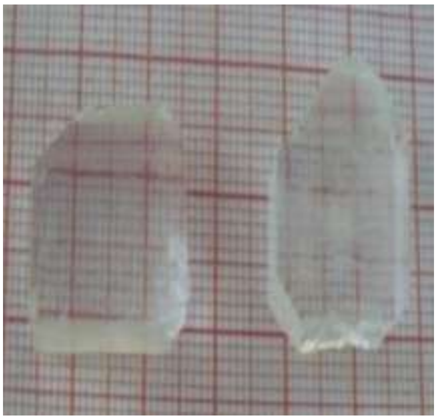

Fig. 1b As grown ADP crystal

III. Characterization analysis

3.1 Single crystal X-ray diffraction

The single crystal X-ray diffraction analysis was carried out using an ENRAF NONIOUS CAD-4 automatic X-ray diffractometer with MoKα radiations (λ= 0.717Å) to identify the structure and cell parameters of the grown single crystal . The cell parameter values are found to be a = 7.4401 Å, b = 7.4574Å, c = 6.9748 Å and α=β=γ=90°. The KDP crystal belongs to tetragonal system. The unit cell parameters of ADP crystal is a=b=7.90 Å, c=7.87 Å, α=β=γ= 90 ° Volume of the unit cell, V= 430.67 $Å^3$.

3.2 Fourier Transform Infrared Spectral analysis

Fourier transform spectroscopy is a very powerful technique for detection of very weak signals from the environmental noise. It is a simple mathematical technique to resolve a complex wave into frequency component. FTIR is rapidly becoming a common feature in modern spectroscopy laboratories with the advent of inexpensive microcomputers. The functional group and modes of vibration of KDP were carried out by using of Perkin Elmer Spectrum Two FTIR instrument scanning range is MIR 4000-450cm^{-1} with resolution 0.5 cm^{-1}**.** The broad band at the frequency 3703.29 cm^{-1} and 3318 cm^{-1} may represent 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 is shown in Fig. 2a and the absorption bands with the assignments are tabulated in table-1.

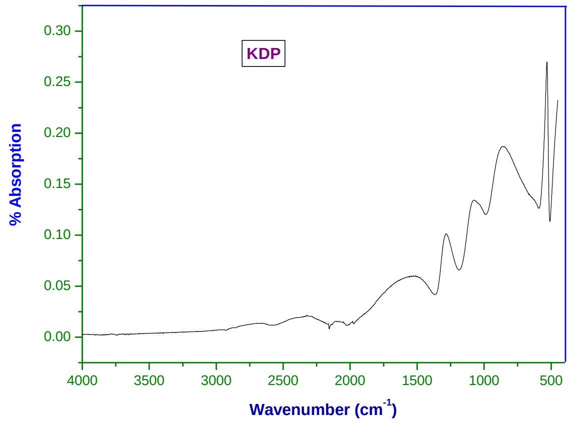

Fig. 2a FTIR spectrum of KDP crystal

Table-1 FTIR assignments of KDP crystal

Reference cm^{-1}	KDP cm^{-1}	Assignments
2429	2323	P-O-H asymmetric stretching
1509	1463	O-H stretching
1230	1283	CH_2 bending, P=O symmetric stretching
1142	1074	P-O-H stretching
866	859	O=P-OH bending
582	531	P-OH deformation/ K-O stretching

The grown ADP FTIR spectrum was taken between wave number 400 to 4000 cm^{-1}, shown in Fig. 2b and the assignments are tabulated in the table-2. The peaks between 485 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} indicate that the presence of O-H and N-H stretching vibration.

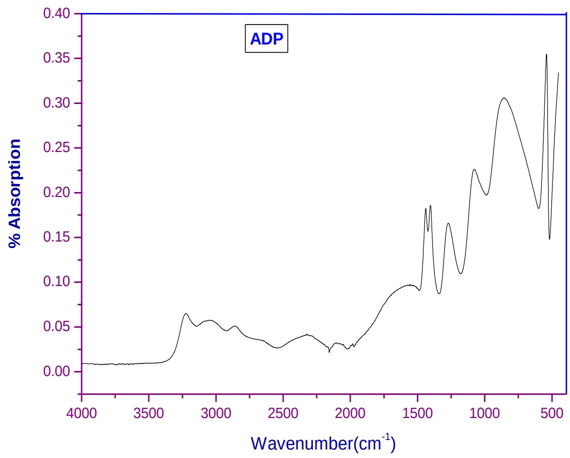

Fig. 2b FTIR spectrum of ADP crystal

Table-2 FTIR assignments of KDP crystal

Reference cm^{-1}	ADP cm^{-1}	Assignment
3249	3223	O-H stretching
2387	2323	Band due to hydrogen bond
1409	1404	Bending vibration of ammonium
1098	1078	P-O-H vibration
485-902	857	O-N=P and $-ONO_2$ vibration
545-439	540	PO_4 vibration

3.3 UV-Vis Spectral Studies

The UV-visible spectral of grown crystal was 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 are shown in Fig. 3a and 3b. The observed upper cut-off wavelength of the KDP and ADP crystal is 383 nm and 416 nm. Transparency in the entire visible region is one of the most desirable properties of a material to possess nonlinear optical property. 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 wavelength 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.

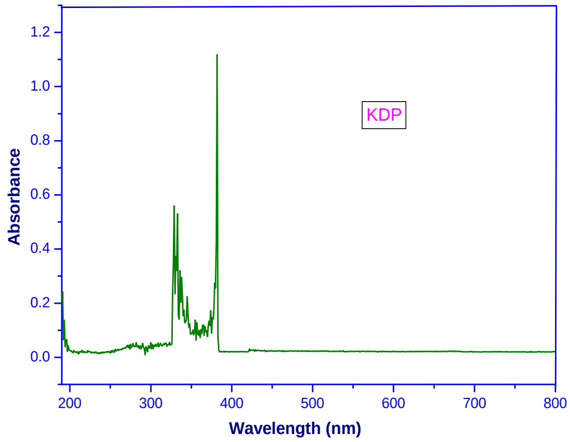

Fig. 3a Optical Absorption spectrum of KDP crystal

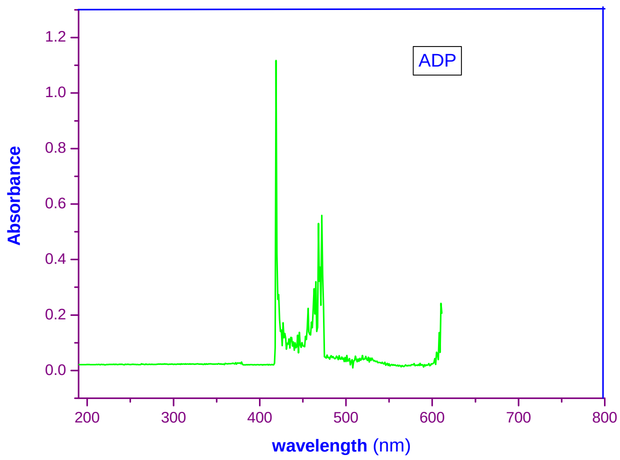

Fig. 3b Optical Absorption spectrum of ADP crystal

3.4 Measurement of Micro hardness Test

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 intended 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 a load. The graph was plotted between log P and hardness number (Hv) which is an almost straight line is shown in Fig. 4a. 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 Fig. 4b. The slope of the straight line gives the work hardening coefficient (n) value. The calculated work hardening coefficient 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.

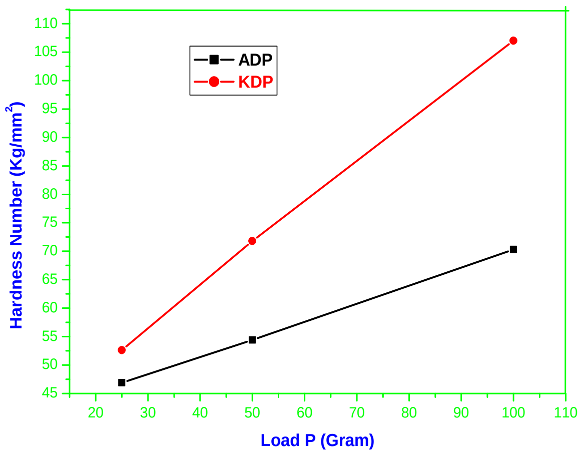

Fig. 4 a. Load P Vs Hardness Number for KDP and ADP single crystal

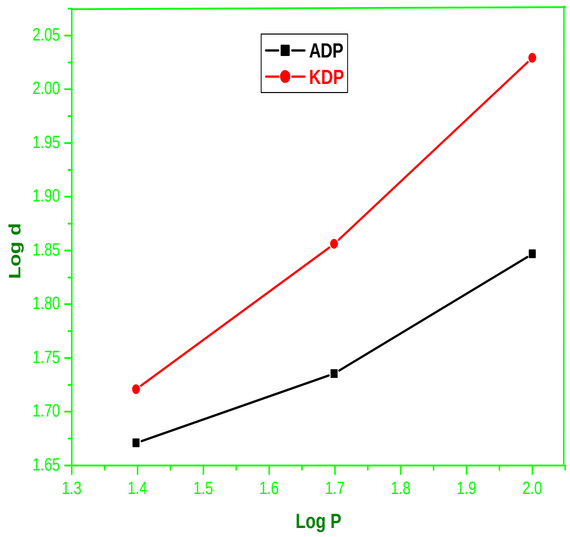

Fig. 4 b. Log P Vs Log d for KDP and ADP single crystal

3.5 Dielectric Studies

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 (Fig. 5a-b) and also between log f Vs dielectric loss (Fig. 5c-d) for KDP and ADP crystals. The dielectric constant decreases with increasing frequency and the dielectric loss of the material also decrease with increasing frequency with two different temperatures. The variation of dielectric constant is a function of frequency with two temperatures due to an attribution of an 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.

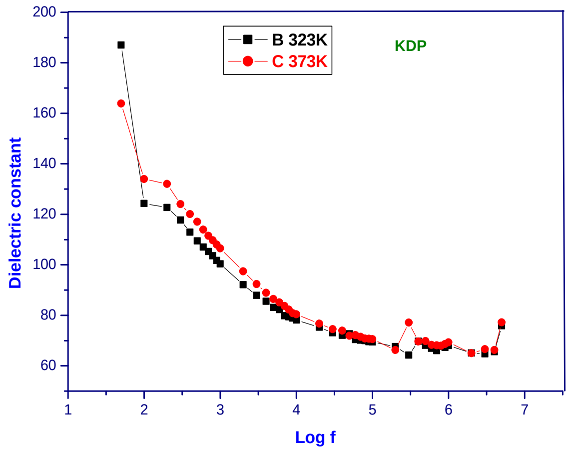

Fig. 5a Log f vs Dielectric constant of KDP crystals

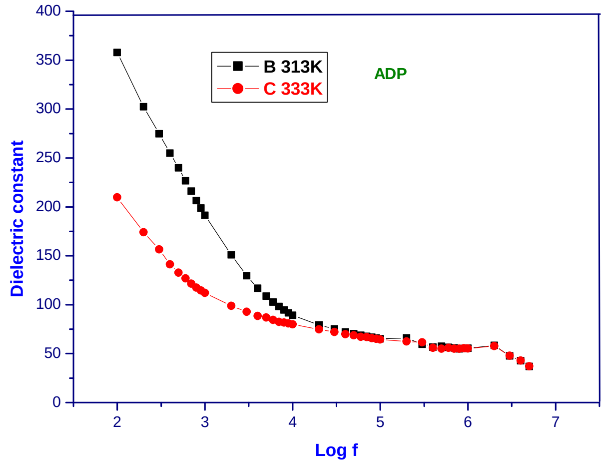

Fig. 5b Log f vs Dielectric constant of ADP crystals

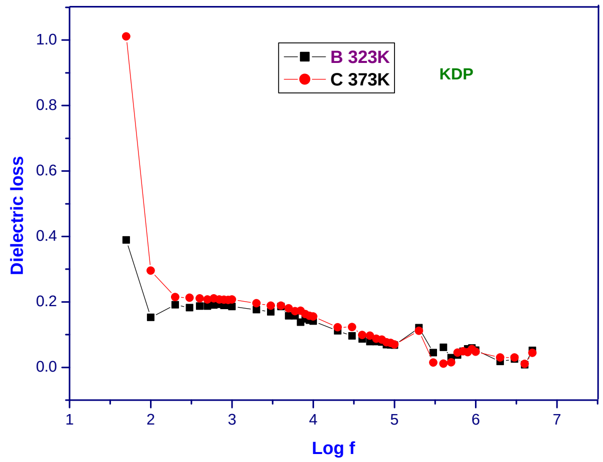

Fig. 5c Log f vs Dielectric loss of KDP crystals

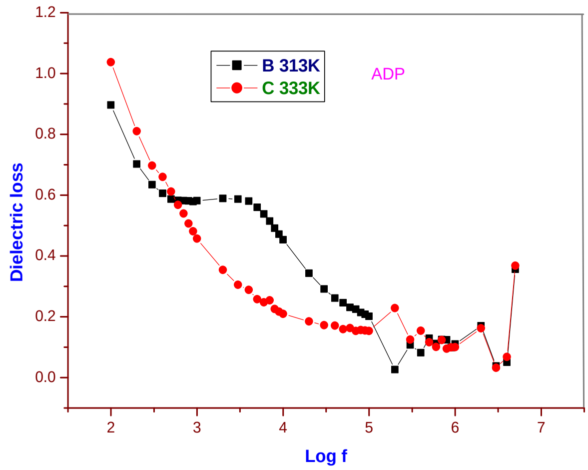

Fig. 5d Log f vs Dielectric loss of ADP crystals

3.6 Thermogravimetric Analysis

Thermogravimetric analysis of the grown KDP and ADP single crystals were carried out by using SDT-Q 600 analyzer with the temperature between 0^0C and 1100^0C at the heating rate 20^0C per minutes in nitrogen atmosphere. The grown KDP and ADP single crystals are thermally stable up to 192.4°C and 227.2°C (Fig. 6a). 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.

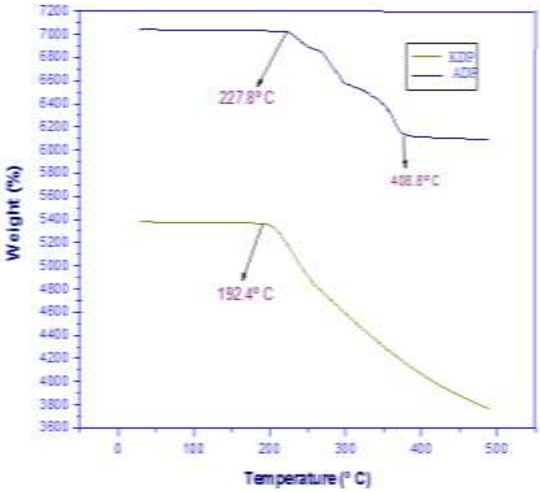

Fig. 6a TGA thermogram of KDP and ADP crystals

3.7 Differential Thermal Analysis

Differential thermal analysis is used to find out the melting point of grown crystal. 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 differential thermal analysis curve is shown in Fig. 6b.

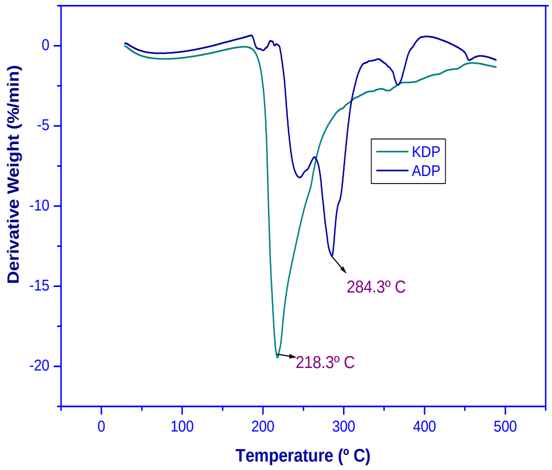

Fig. 6b DTA thermogram of KDP and ADP crystals

3.8 Measurement of SHG efficiency

The Nonlinear property of KDP and ADP crystal was studied by Kurtz and Perry. The crystal was grounded into a fine powder and densely packed in the capillary tube. A Q-switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm (pulse width 8 ns) was allowed to strike the sample. The second harmonic generation in the crystalline sample was confirmed by the emission of green radiation (532nm) emitted by the sample.

IV. Conclusion

Potassium dihydrogen phosphates (KDP) and Ammonium dihydrogen phosphates (ADP) single crystals were grown by conventional slow evaporation solution growth technique. The single crystal XRD analysis confirmed that KDP crystals belonged to the tetragonal system The grown crystals were subjected to various characterization analysis for testing the suitability of the materials in nonlinear optical device applications. The results suggest the potentiality of the materials are good in the fabrication of optical devices since the forbidden energy gap lies within 5 eV. Also, the thermal analysis suggests that both KDP and ADP are thermally stable till 218 °C and 284 °C respectively. The second harmonic generation in the crystalline sample was confirmed by the emission of green radiation (532nm) emitted by the sample.

V. Acknowledgements

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