STUDY ON OPTICAL AND ELECTRICAL PROPERTIES OF L-TARTARIC ACID DOPED AMMONIUM DIHYDROGEN PHOSPHATE (ADP) SINGLE CRYSTAL A NONLINEAR OPTICAL APPLICATION

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ABSTRACT- In recent years study of non-linear optical (NLO) materials is gaining rapid momentum due to their needs in several device applications. Ammonium Dihydrogen Phosphate (ADP) is a well-known NLO material, whose nonlinearity is enhanced by doping with amino acids. Therefore, in the present work we have grown good quality single crystal of L-Tartaric acid (0.2%) doped Ammonium Dihydrogen Phosphate (ADP) using slow evaporation technique. The lattice parameters of the grown crystal have been determined by Powder X-ray diffraction studies. A Fourier transform infrared (FT-IR) study confirms the functional groups of the LTADP crystals. The UV-visible study confirms the wide optical transmittance window for the doped crystals imperative for optoelectronics applications. The second harmonic generation test for LTADP confirmed the nonlinear nature of the crystal. The Kurtz Perry test confirmed the SHG efficiency of LTADP crystal is 1.7 times higher than KDP crystal material, The electrical properties of the grown crystal have been analysed by dielectric constant and dielectric loss with frequency.

KEYWORDS – PXRD, FTIR, UV vis, NLO, Dielectric studies.

I. INTRODUCTION

Ammonium dihydrogen orthophosphate (ADP) $(NH_4)\ H_2PO4$ is an interesting material and it belongs to isomorphous series of phosphates and arsenates that presents a strong piezoelectric activity. ADP is antiferroelectric below 148.5 K and belongs to P21 21 21 space symmetry group, while above this temperature it becomes paraelectric having I 4/2 d symmetry [1-3]. ADP belongs to scalenohedral class of tetragonal crystal systems. ADP has unit cell parameters of a = b = 7.510 Å and c = 7.564 Å [4,5]. It is known that, very little amount of additives can strongly suppress the metal ion impurities and promote the crystal quality. Oxalic acid and amino acids as additives in ADP crystals give appreciable change in optical, thermal, dielectric and mechanical behaviors [6,7]. One of the earliest applications of ADP was that it was used in design of hydrophone for acoustically active mines, due to its zero-aging characteristic ADP remains stable during many year of storage [8]. ADP crystal exhibits properties like second harmonic generation, sum and difference frequency conversion etc., for improvement of NLO performance and other properties various amino acids are used as a dopant. Second order nonlinear optical materials were used to convert the IR radiation into useful UV-vis wavelength of the blue-violet light emission for the several applications such as high-density data storage, laser printing, displays, high resolution spectroscopy and inflorescence, photolithography, remote sensing, chemical and biological species detection, [9]. L-Tartaric acid doped with ADP will be of special interest as a fundamental building block to develop complex crystal with improved NLO properties. The grown crystals were characterized by Powder X-Ray Diffraction, FT-IR analysis, UV-vis spectroscopy, NLO Studies and Dielectric studies.

2. EXPERIMENTAL DETAILS

Analytical reagent grade (AR) samples of $(NH_4)\ H_2PO4$ and L-tartaric acid along with deionized water were used for the growth of single crystals by slow evaporation solution growth technique (SEST). The solutions were allowed to stirrer at constant speed to achieve the homogeneity throughout the volume. The Prepared solutions were then filtered and covered with thick paper with fine pores in order to minimize the rate of evaporation. The purity of the salts was achieved by repetitive recrystallization, good quality and optically transparent crystals were harvested within 25-30 days. The photograph of L-Tartaric acid doped Ammonium Dihydrogen Phosphate (ADP) LTADP crystal is shown in Fig .1

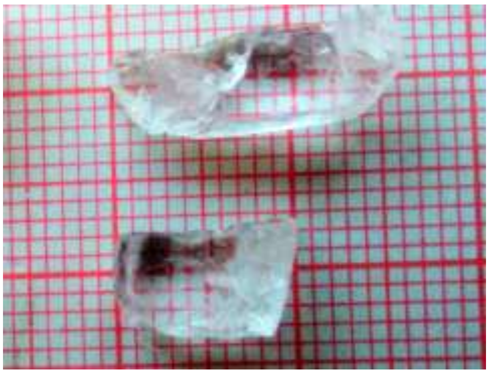

Fig.1.Photograph of as grown single crystal of LTADP

3. Result and Discussion.

3.1. Powder X-ray Diffraction analysis.

The grown single crystals were subjected to Powder XRD analysis was carried out using XPERT–PRO Diffractometer with CuKα (λ = 1.5406Å) radiation. The scanning rate was maintained at over a 2ϴ range of 10-80 (degree). The prominent peaks observed in the diffraction pattern confirm the single crystalline nature of the L-Tartaric acid doped ADP crystals. The cell parameters obtained for the doped LTADP single crystal are a=b= 7.486Å, c=7.540Å, and α=β=γ=90°, so it belongs to tetragonal system. Powder x-ray diffraction pattern for LTADP crystal is graph shown in Fig. 2.

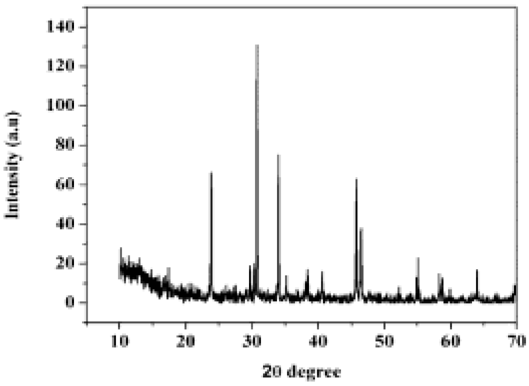

Fig. 2. Powder X-Ray diffraction pattern of LTADP Crystal

3.2. FT-IR analysis.

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify mainly, the functional groups present in organic materials. FTIR analysis provides information about the chemical bonds and molecular structure of a material. In order to qualitatively analyse the presence of functional groups in the grown crystals, the FT-IR spectrum were recorded in the range 500–4000 cm^{-1} using a KBr pellet on Perkin Elmer FTIR spectrometer and the recorded spectra were shown as Fig. In the high frequency region of IR spectra, the sharp peaks observed at 559 cm^{-1} are assigned to PO_4 stretching vibration in the crystal. The vibrational band at 3218 cm^{-1} was assigned to vibration of N-H band. The band at 1716 cm^{-1} was assigned to bending vibrational mode of O-H group. The vibrational mode of P-O-H group was observed at 1091 cm^{-1}. The shifting band of NH_4 was observed at 1397cm^{-1}.

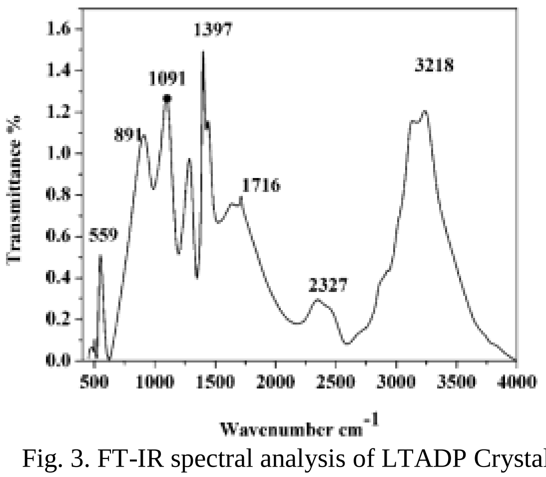

Fig. 3. FT-IR spectral analysis of LTADP Crystal

3.3. Linear optical studies.

The optical transmission spectrum of strontium chloride doped ADP single crystal was recorded by UV-visible spectrometer in the wavelength range 100nm- 900nm as shown in above fig.4(a). For optical fabrication, the crystal must be highly transparent in the considered region of wavelength [10,11]. It is observed that for an entire visible region transmittance is greater than 88% and the as grown crystal is transparent in the UV-Vis-NIR regions of the spectrum. This is a constructive nature of a NLO material [12]. The lower cut-off wavelength is found to be 236nm indicating the wide optical transmission window favourable for second harmonic generation [13]. The optical band gap of the crystal is calculated using the formula Eg =1240/λ (nm) and is found to be 5.2eV suggesting its suitability for optoelectronics applications.

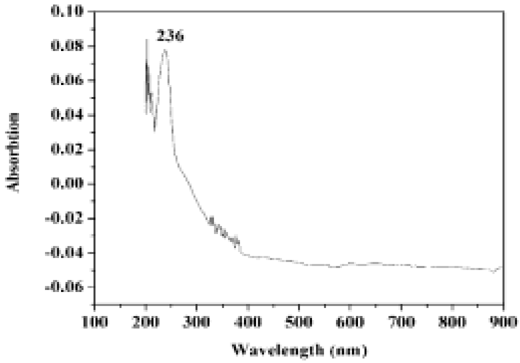

Fig. 4 (a). UV-vis absorption of LTADP Crystal

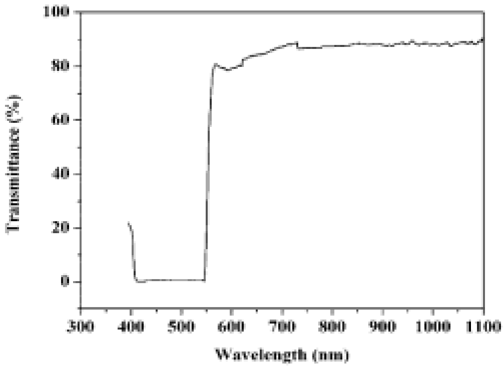

Fig.4 (b). UV-Vis-Transmittance spectrum of LTADP crystal

3.4. SHG analysis.

The SHG conversion of LTADP was determined by modified version of the powder techniques by Kurtz and Perr [14]. In order to confirm the NLO property of the grown crystals, they were characterized with Nd:YAG laser with wavelength of about 1064 nm with pulse width of 8 ns ad repetition rate 10 Hz with beam energy 2.149mJ/pulse was allowed to pass through the powdered sample. The second harmonic green signal was generated (λ=532nm) by the material confirmed that the material reveals the NLO property. The results show that SHG efficiency of the grown crystals was 1.7 times that of the standard Potassium dihydrogen orthophosphate (KDP) crystal.

3.5. Dielectric studies.

Dielectric studies were carried out to investigate the electrical parameters such as dielectric constant (ε_r) and dielectric loss (tan d). The presence of a dielectric between the plates of a condenser enhances the capacitance. The dielectric parameters depend on the applied frequency and temperature of the samples. The variations of dielectric parameters of the samples with frequencies are presented in the fig. 5(a) and 5 (b). From the graphs, it is observed that dielectric parameters like dielectric constants and loss factors decrease with increase in frequency and the high values of εr at low frequencies may be due to presence of space charge polarization and its low value at high frequencies may be due to the loss of significance of the four type of polarizations viz. space charge, orientational, ionic and electronic polarization. In accordance with Miller’s rule, the low value of dielectric constant at higher frequencies may be due to the fact that the dipoles cannot follow up the fast variation of the applied field and is a suitable parameter for the enhancement of SHG coefficient and extending the samples application towards photonic, electro-optic and NLO devices [15].

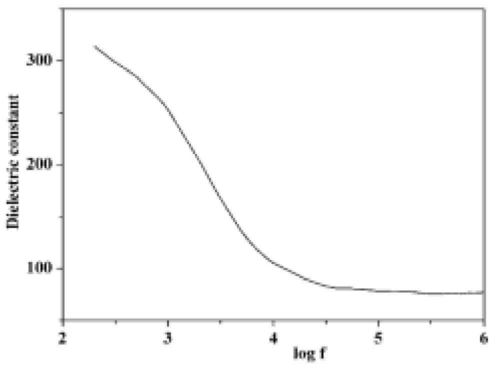

Fig 5. (a). Dielectric constant Vs Log f of LTADP crystal

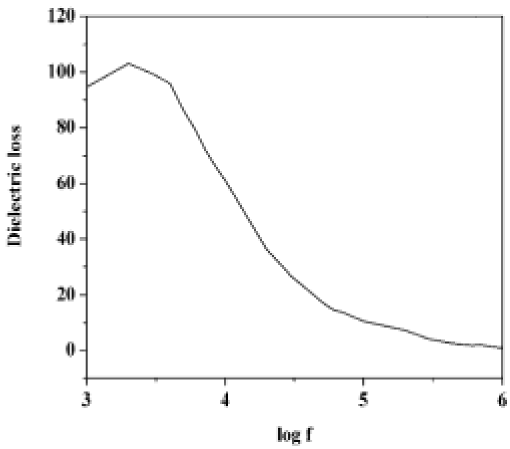

Fig. 5. (b). Dielectric loss Vs Log f of LLADP crystal

CONCLUSION.

L-Tartaric acid doped ADP crystals were grown from aqueous solution using doubled distilled water as a solvent by slow evaporation solution growth technique (SEST). Powder XRD studies shows that the grown crystals are crystalline in nature and tetragonal in structure. The FT-IR spectrum confirms the presence of functional groups. Transparency range of LTADP was found to be from 200 nm to 1000 nm that confirms wider optical transmission range to extend its applications in the entire visible and UV region NLO property of the crystal is confirmed by Kurtz Powder method and SHG efficiency is found to be 1.7 times of KDP. The low dielectric constant and dielectric loss of LTADP at higher frequencies show that the material is a more suitable for nonlinear optical application.

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REFERENCES.

[1] M.E. Lines, A.M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Clarendon Press, Oxford, 1977.
[2] N.G. Parsonage, L.A.K. Staveley, Disorder in Crystals, Clarendon Press, 1978.
[3] L.Tenzer, B.C. Frazer, R. Pepinsky, Acta Cryst. 11 (1958) 505.
[4] N. P. Rajesh, et al, Mater. chem. Phy 76 (2002) 181-186]
[5] R.W.G. Wyckoff, crystal structure, 2nd edition, Interscience, New York, 1960,P.160
[6] P.V. Dhanaraj, G. Bhagavannarayana and N.P.Rajesh, Materials Chemistry and Physics, 112 (2008) 490-495.
[7] P.Rajesh, J.Cryst.Growth 311(2009)1611.
[8] Massa F, Sonar Transducer: A History, ST Special Report, Massa Products Corporation
[9] G. Zhang, M. Lin, D. Xu, D. Yuan, J. Mater. Sci. Lett. 19 (2000) 1255-1257.
[10] Krishnakumar, V, and Nagalakshmi, R, Crystal growth and vibration spectroscopic studies of semi organic nonolinear optical-bisthiourea zinc chloride, spectrochim Acta Part, 61, 499-507(2005)
[11] Krishnakumar V, and John Xavier R, FT Raman and FT-IR spectral studies of 3- Mereapto-1, 2, 4- triazole, spectrochim Acta Part A 60, 709-714(2004).
[12] S.K. Kurtz, T.T. Perry, *Journal of Applied Physics*, Vol. 39, pp. 3798, **1968**.
[13] R. Santhakumari , K. Ramamurthi, Structural, thermal and optical characterization of an organic NLO Material-Benzaldehyde thiosemicarbazone monohydrate single crystals, *Spectrochimica Acta part A, 78*, 2011, 653-659.
[14] S K Kurtz ; T TPerry *J. Appl. Phys*. **1968**, 39,3798–3813.
[15] U Von Hundelshausen, *Phys. Lett. A*, **1971**, 34 (7),405–406.