Growth And Characterization Of L-Isoleucine Doped Ammonium Dihydrogenphosphate (ADP) Single Crystal A Nonlinear Optical Application

[1]A.Venkatesan, [2]S. Arulmani, [3]S. Senthil, [4]M. E. Rajasaravanan
[1]Research scholar, [2]Research Scholar, [3]Assistance professor, [4]Assistant Professor
[1]Department of Physics, Aringnar Anna Government Arts College, Villuppuram – 605 602. India.
[2,3]Department of Physics, Govt. Arts College for Men (Autonomous), Nandanam, Chennai - 600 035. India.
[4]Department of Physics, Government Arts College, Salem – 636 007. India.

***Abstract*- Owing to its exceptional application in nonlinear optical device, ammonium dihydrogen phosphate (ADP) is considered as potential candidate in modern era of hi-tech applications. Therefore, in the present work we have grown good quality single crystal of L-Isoleucine (0.2%) doped ADP using slow evaporation technique.The lattice parameters of the grown crystal have been determined by single crystal X-ray diffraction studies. Vibrational spectrum is recorded to determine symmetries of molecular vibrations. Optical absorbance spectrum recorded revealed that this crystal has good transparency in the visible region. The second harmonic generation test of LIADP confirmed the nonlinear nature of the crystal. The Kurtz Perry test confirmed the SHG efficiency of LIADP crystal is 0.8 times higher than KDP crystal material. The electrical properties of the grown crystal have been analyzed by dielectric constant and dielectric loss with frequency. Intensity can be observed from the photoluminescence study.**

Key words-*S*ingle crystal XRD, FTIR, UV vis, NLO, Dielectric studies, PL.

I.INTODUCTION

Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) is an inorganic, piezoelectric, antiferro-electric and nonlinear optical material. It is well known for its diverse uses as electro-optic modulator, harmonic generators and parametric generators **[1]**.In the last decade, the numerous applications of the nonlinear optical (NLO) crystals have been discussed in the field of science and technology **[2-7]**.But recent interest is focused on the development of the properties of the new semi organic (NLO) materials. Semi organic materials possess the advantage of both organic and inorganic materials in terms of high thermal and mechanical stability as well as broad optical frequency range, higher SHG (second harmonic generation) and high damage threshold **[8-10]**.Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid (-COOH) group and proton acceptor amino (-NH2) group in them **[11]**. Amino acids, when added as impurities, have improved material properties **[12]**. Amino acid, L-Isoleucine has formed several complexes, which are promising materials for second harmonic generation. In the light of research work being done on ADP crystals, to improve the properties, it was thought interesting and worthwhile to investigate the effect of L-Isoleucine on ADP. In this work, the spectral and nonlinear optical behavior of single crystals of L-Isoleucine added ADP against pure ADP has been studied and reported.

II.Experimental Procedure.

L- Isoleucine of 0.2% has been doped with pure Ammonium dihydrogen phosphate (ADP). The calculated amount of salts was dissolved in double dissolved water. The solution was stirred well for more than four hours and filtered using Whatmann filter paper. The pH value of the reaction mixture was monitored. It was porously sealed and placed in a dust free atmosphere for slow evaporation at room temperature. Optically transparent crystals were harvested within 30 days. The photograph of as grown doped LIADP crystal is shown in **Fig1.**

Figure1. As grown single crystal of LIADP

III. Result and Discussion.

Single crystal X-ray Analysis.

Single Crystal X-ray diffraction analysis of grown L-Isoleucine doped ADP single crystal was carried out using Enraf Nonius CaD4 X-ray diffractometer with Mokα radiation of wavelength of 0.71073 Å. The obtained lattice parameter values and volume of grown crystal are a=6.543 Å, b=6.526 Å, c=6.503Å, $\alpha \neq \beta \neq \gamma = 90°$ and V=211.2' Å (3). Further, the analysis reveal that the title compound belongs to triclinic crystal system.

FT-IR Analysis.

FT-IR spectra of LIADP crystal were recorded in range of 500-4000cm^{-1} by KBr PELLET technique. The functional groups of LIADP crystals have been identified and it was shown in **Fig 2.** The characteristic peaks of functional groups of LIADP are observed at 3223,2442, 1711, 1395, 1328, 1113, 913cm^{-1}. The broad band in the high-energy regions is due to the O-H vibration of water, P-O-H group and N-H vibration of ammonia. The peaks at 1113 and 913 cm^{-1} represent P-O-H vibrations. The PO_4 vibration gives their peaks at 548 cm^{-1} **[13].**The bending vibration of water gives it peak at 1711 cm^{-1} in IR. The peak at 1395 cm^{-1} is due to bending vibrations of ammonium. The PO_4 vibration of the parent is shifted from 548 cm^{-1}, which was confirm by the presence of L-Isoleucine on the lattice of ADP crystals.

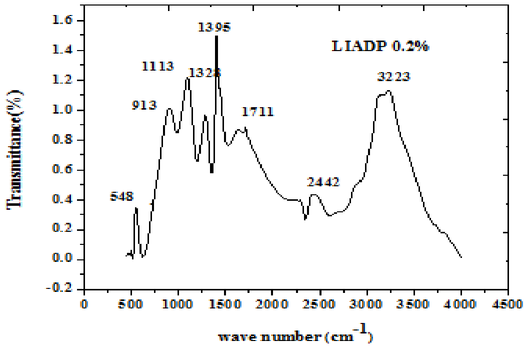

Figure 2. FT-IR spectral analysis of LIADP Crystal

SHG analysis.

Kurtz and Perry techniques **[14]** were employed to measure the SHG efficiency of the grown crystals in reference with the pure KDP. In the measurement, Q-switched Nd:YAG laser of wavelength 1064nm of peak power 2.35 mJ, pulse duration 8 ns and repetition rate 10Hz was used. Output intensity of SHG gives relative values of NLO efficiency of the material. The output energies from the grown sample and reference KDP are found to be 18.8mW and 19.6 mW respectively. It is found that the SHG efficiency is 0.8 times that of standard KDP.

Linear optical studies.

The UV-Vis absorption spectrum of LIADP crystals were recorded using Perkin Elmer UV-Vis spectrometer (Model: Lambda 35) in the wavelength range of 200-1200 nm. Optically polished single crystals of thickness 3mm were used for this study. The optical absorption spectrum of the grown crystal and the cut-off wavelength is found to be 250 nmis shown in **fig 3.** The optical band gap energy value is found to be 3.37 eV from **Fig 4.** The high transparency and low absorption tendency as observed in LIADP crystal may serve advantage for UV-tunable lasers and NLO device active in blue and green spectrum. The LIADP crystal with improved linear optical performance is suggested as potential material to be utilized in NLO device applications.

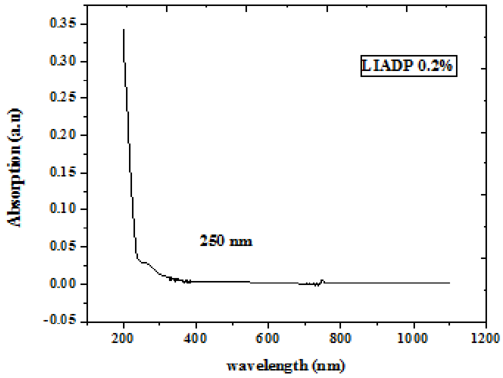

Figure 3. UV-vis absorption of LIADP Crystal

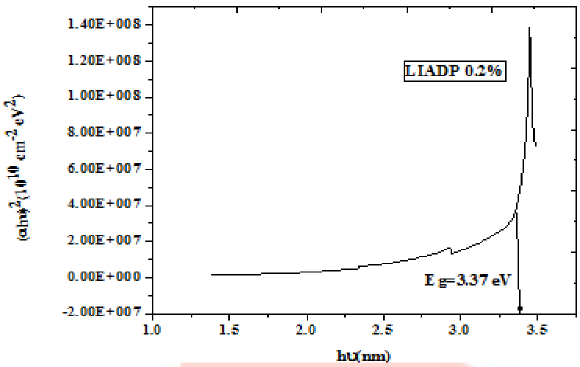

Figure 4. Optical bandgap of LIADP Crystal

Dielectric studies.

The dielectric analysis is an important characteristic that can be used to fetch knowledge based on the electrical properties of a material as a function of frequency. Based on this analysis, the capability of storing electric charges by the material and capability of transferring the electric charge can be assessed.Dielectric properties are correlated with electro optic property of the crystals particularly when they are non-conducting materials **[15].** Normally, when a material has large dielectric constant it requires more voltage in order to polarize the dipoles and this may cause the changes in their refractive index. The current study on L-Isoleucine doped ADP crystals shows that they possess low value of dielectric constant as well as loss. So, it excludes the need of poling of the crystals for maintaining the refractive index. The plots of calculated values of dielectric constant and dielectric loss for LIADP single crystals shown in **fig 5 and fig 6.** It is clear from figure that the dielectric constant has a stable value in entire frequency range except at low frequency. High value of dielectric constant in the low frequency region may be due to the contribution from all four polarizations namely, electronic, ionic, orientation and space charge polarization and its low value at higher frequency may due to the loss of significance of these polarizations gradually. From **fig7**, it can be clearly seen, that the value of σ_{ac} is very low upto5.5 MHz and increases with increase of frequency and can be explained on the basis of frequency power law.

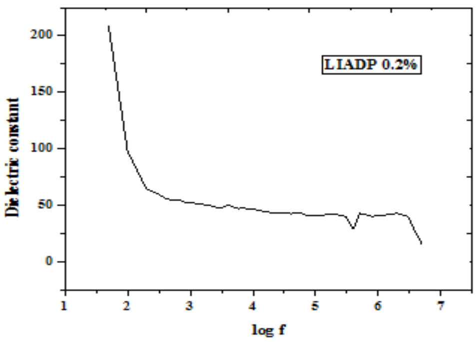

Figure 5. Dielectric constant Vs Log f of LIADP crystal

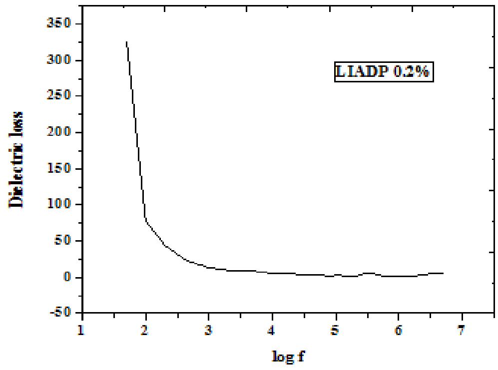

Figure 6. Dielectric loss Vs Log f of LIADP crystal

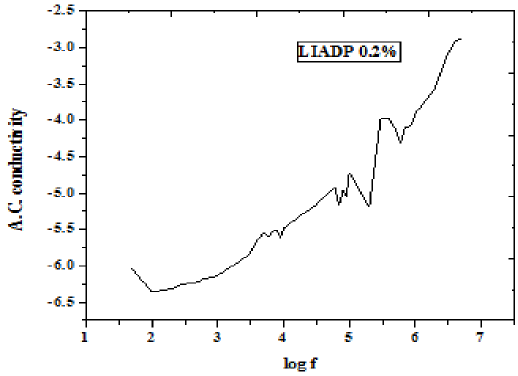

Figure 7. A.C. Conductivity Vs Log f of LIADP crystal

Photoluminescence (PL) study.

Photoluminescence in the solid material occurs by the phenomenon of the electronic sates of solids excited by light of particular energy and the excitation energy and the excitation energy released with wavelength of light, equal or longer than that of the that of the exciting light. This difference in wavelength is caused by a transformation of the exciting light, to a greater or lesser extent, to non-radiation vibration energy of atoms or ions **[16].** Photoluminescence intensity is highly dependent on the crystalline and structural perfection of the crystal. Photoluminescence of LIADP single crystal is carried out using shimadzu spectro fluorophotometer RF-5031 PC series with the slit width of 3nm at room temperature. The powder sample of the grown single crystal was excited nearly at 270 nm and the emission spectrum was recorded between 300nm to 400 nm and 600 nm to750 nm observed spectrum is shown in **Fig.8.** An intense broad emission band appeared in the range 338 and 667 nm. LIADP single crystal exhibit higher intensity emission peaks it is due to the high crystalline perfection. The strong PL emission of the material may find optional applications in optoelectronic devices.

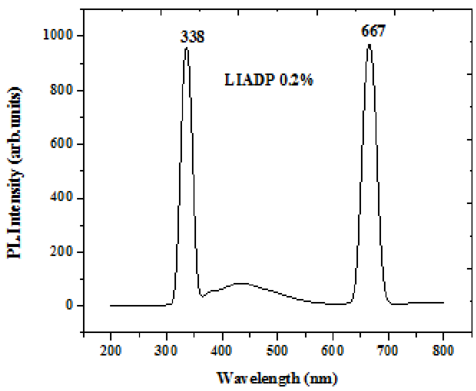

Figure 8. PL Intensity Vs wavelength of LIADP crystal

CONCLUSION.

A novel organic single crystal of LIADP was grown from aqueous solution by the slow evaporation method. The triclinic crystal structure was confirmed by single-crystal X-ray analysis. The FTIR trace reveals the presence of functional groups. The UV cut-off wavelength of LIADP crystal is found to be 250 nm and the optical band gap is 3.37eV. The SHG efficiency of LIADP crystal is 0.8 times that of the KDP. The low dielectric constant and dielectric loss of LIADP at higher frequencies show that the material is more suitable candidate for nonlinear optical application.The strong PL emission of the material may find optional applications in optoelectronic devices.

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