Optical properties of Potassium Iodide doped L-Arginine single crystal synthesised by slow evaporation method

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Abstract- In this work, we have studied the optical properties of L-arginine potassium iodide (LAPI) that has been synthesized by slow evaporation solution growth method using water as solvent. The phase purity of as grown crystal was verified by single crystal and powder X-ray diffraction methods. This paper is focused on the optical properties of as grown LAPI crystal. For that we have studied the optical transparency and dielectric nature of the grown crystals by UV–vis–NIR spectrum. Second harmonic generation (SHG) efficiency of the LAPI crystal was investiagted by Kurtz-Perry technique using Q-switched Nd: YAG laser. We have also studied the dielectric constant and dielectric loss of LAPN crystal as a function of frequency and the obtained results are discussed.

Keywords**:** Solution growth, L-arginine complex, dielectrics, SHG, band gap

I. INTRODUCTION

Second order non-linear optical (NLO) materials are investigated much due to their variety of potential application including optical communication and remote sensing [1,2]. In particular, crystals of optically active amino acids are studied intensively because of their efficient optical second harmonic generation (SHG) and are promising candidates in laser and optical communication technology [3,4]. Moreover, amino acids based organic materials are considered as alternative for NLO application as they consist proton donor carboxyl acid (COO) group and the proton acceptor amino (NH2) group [5]. In this, sense many researchers investigated various semi-organic single crystals to find a new material for potential application. L-Arginine is one of such alternative material which can be synthesised by simple and cost effective method. Besides L-Arginine is one of the smallest chiral naturally occurring amino acid [6].

Such semi-organic materials can be synthesised by various methods. However, the growth mechanism of these materials is usually understood with respect to the kinetic parameters such as the growth rate of crystal, step velocity, and the stability of crystal surfaces. Slow evaporation is one of such versatile method by which one can fabricate single crystals with low cost and time effective [7, 8]. In this paper, we have synthesised L-arginine potassium iodide (LAPI) single crystal by slow evaporation method. Their optical properties have been studied by UV-vis NIR studies and their second harmonic generation nature is analysed.

II. EXPERIMENTAL METHODS

L-arginine potassium iodide was synthesised by dissolving L-arginine and potassium iodide in 1:1 molar ratio in distilled water. The solution was heated at 50°C for about 6 hours to evaporate the excessive water. Then the solution is allowed to evaporates slowly. As time goes, the saturated solution was changed into supersaturated solution and crystal nuclei are formed in the solution. On further evaporation the final product has been formed. The as grown crystal was verified by X-ray diffraction analysis.

We have studied the UV-Vis-NIR transmittance spectrum of LAPI crystal in the region 190-1100 nm using PERKIN ELMER LAMBDA 365 UV-visible spectrometer. ^{1}H NMR spectral analysis of the LAPI crystal was carried out with BRUKER AV 300 ^{1}HNMR spectrometer. The PL spectrum of LAPI crystal was also recorded using a Perkin-Elmer LS45 fluorescence spectrometer that has a 450 W high pressure Xenon lamp as the excitation source. Using a LCR meter the dielectric loss and

dielectric constant of the LAPI crystal were estimated. Powder SHG measurement was carried out using Kurtz and Perry experimental setup using Q-switched Nd: YAG laser (QUANTA RAY MODEL LAB-170-10).

III.RESULT AND DISCUSSION

3.1 UV-Vis-NIR spectral studies

The UV-Vis-NIR transmittance spectrum of LAPI crystal was recorded in the region 190-1100 nm using PERKIN ELMER LAMBDA 365 UV-visible spectrometer and it is shown in the Figure 1. The UV lower cut-off wavelength is observed to be at 235 nm for the sample. The sharp fall at 235 nm for the sample corresponds to fundamental absorption edge which is essential in connection with the theory of band theory of solids. The measured transmittance (T) is used to calculate the absorption coefficient (α) using the relation

$$\alpha = [2.303 \log_{10} (1/T)] / d$$

where T is the transmittance and d is the thickness of the crystal. The plot of absorption coefficient versus the wavelength for the sample is shown in the Figure 2. From this plot, it is noticed that the absorption coefficient values are low in visible region and very high at the cut-off wavelength. Near the absorption edge, the value of absorption coefficient increases rapidly with wavelength. Optical absorption coefficient (α) from the Tauc's equation[9] and it is given as.

$$\alpha h\nu = A \sqrt{(h\nu - E_g)}$$

where E_g is the optical band gap energy of the crystal, h is the Planck's constant, ν is the frequency of the light and A is a constant. The Tauc's plot for LAPI crystal was plotted between $(\alpha h\nu)^2$ with the optical energy ($h\nu$) and it is shown in Figure 3.The band gap energy is found to be 5.27 eV for the sample. In a crystalline material, either direct or indirect optical transitions are possible depending on the band structure of the material. There will be a single linear region in direct transition and two linear portions in indirect transition. For a direct transition, the plot of $(\alpha h\nu)^2$ and ($h\nu$) is taken into account and for the indirect trasition, the plot of $(\alpha h\nu)^{1/2}$ and ($h\nu$) is considered. The single linear portion in the Figure 3 indicates that the sample belongs to the category of the direct band gap materials.
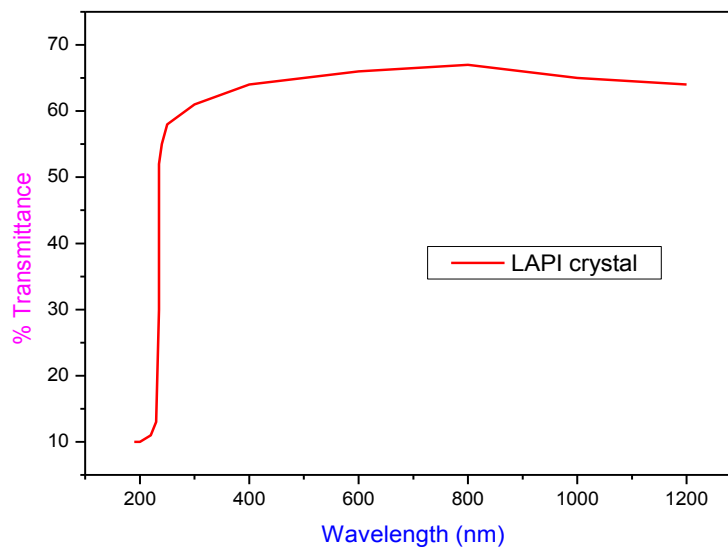

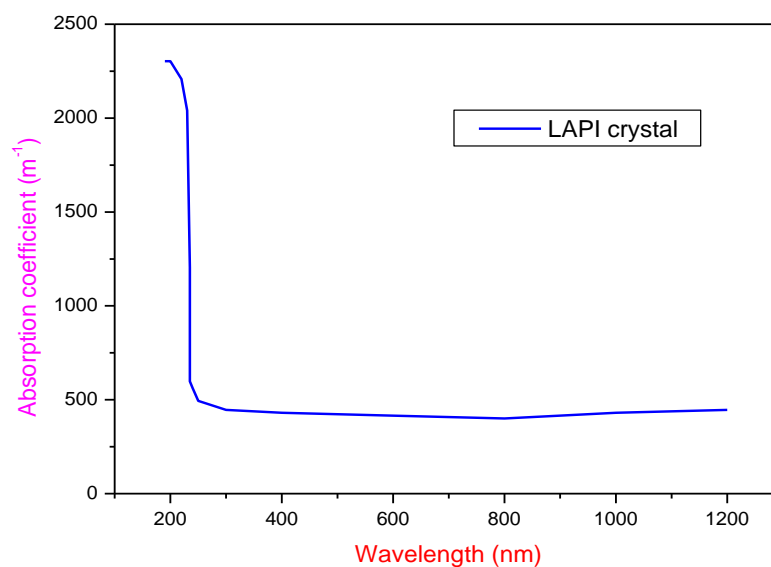Fig.1 Plot of transmittance versus wavelength for LAPI crystal

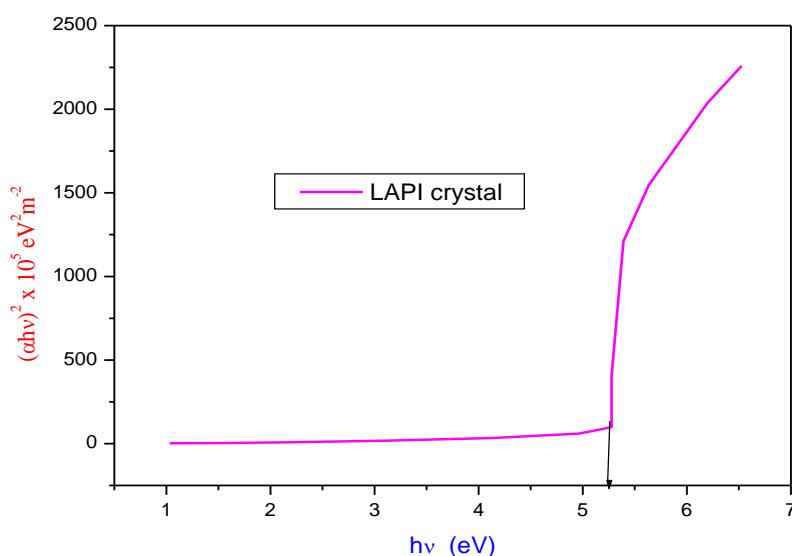Fig.2: Plot of absorption coefficient versus wavelength for LAPI crystal

Fig. 3: Tauc's plot for LAPI crystal

3.2 ^{1}H NMR studies

^{1}H NMR spectral analysis of the LAPI crystal was carried out with BRUKER AV 300 ^{1}HNMR spectrometer and it is shown in the Figure 4. From the spectrum, the multiple peaks between δ=1.698 ppm and δ =1.669 ppm are attributed to C-H proton present in LAPI crystal. The presence of CH_3 proton group in L-arginine and potassium iodide is confirmed due to multiple peaks in the range between δ = 1.716 ppm and δ =1.837 ppm. The multiple triplex signals in the range between δ= 3.109 ppm and δ =3.139 ppm is due to hyperfine splitting of neighboring CH_3 protons. The multiple triplex signals observed between δ = 3.767 ppm and δ = 3.748 for the high triplex value signals in the range between δ = 4.69 ppm and δ = 4.126 ppm in LAPI crystal are attributed to the presence of -CH proton next to the carboxylic acid. The high δ value of this triplet is due to the electron presence of withdrawing -COOH group, adjacent to the -CH carbon atom which, leads to the delocalization of polarization nature to account for the electrons [10].
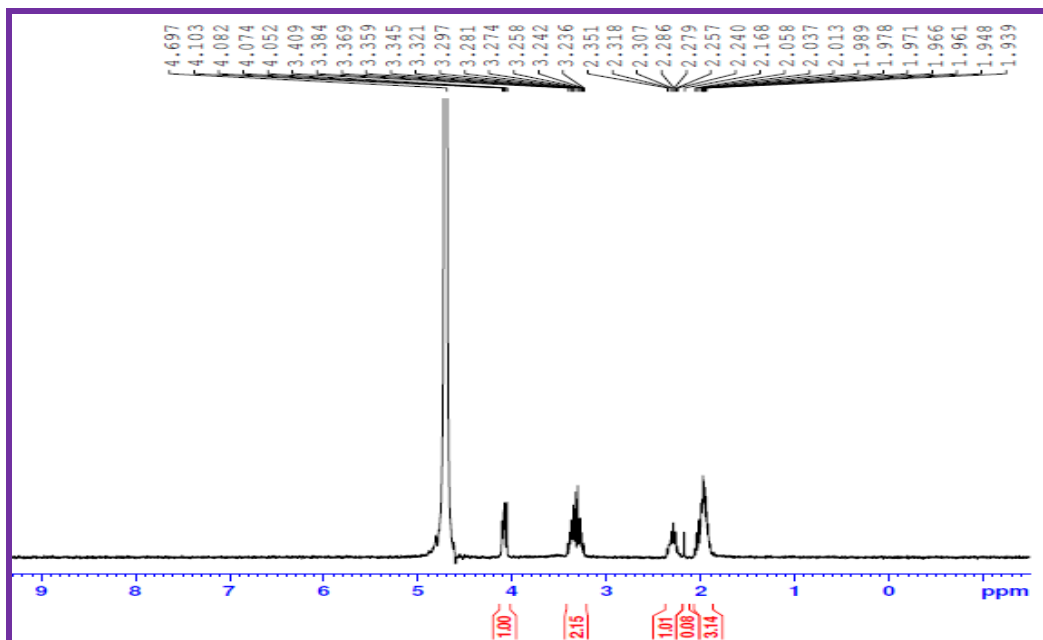
Fig.4: ^{1}H NMR spectrum of LAPI crystal

3.3 Photoluminescence studies

Using the photoluminescence (PL) studies, the emission of light from the sample can be analysed and the photoluminescence is the phenomenon in which electronic states of solids are excited by light of particular energy and the excitation energy is released as light. Usually, the sample is excited with UV light and the emitted light is observed to be in UV-visible range. The PL spectrum of LAPI crystal was recorded using a Perkin-Elmer LS45 fluorescence spectrometer having a 450 W high pressure Xenon lamp as the excitation source. Here the excitation of wavelength of 240 nm was used. The recorded PL emission spectrum of LAPI crystal is presented in the Figure 5. The emission spectrum of LAPI crystal consists of one prominent emission peak at 478 nm. When the sample absorbs UV light at wavelength of 240 nm, the electrons are excited from valence band to higher excitation bands and when they return to lower energy states, visible radiations are emitted. Here, the visible emission peak noticed is at 478 nm. It is observed that there are no other significant emission peaks in UV region and this sample emits violet-bluish light with high intensity.
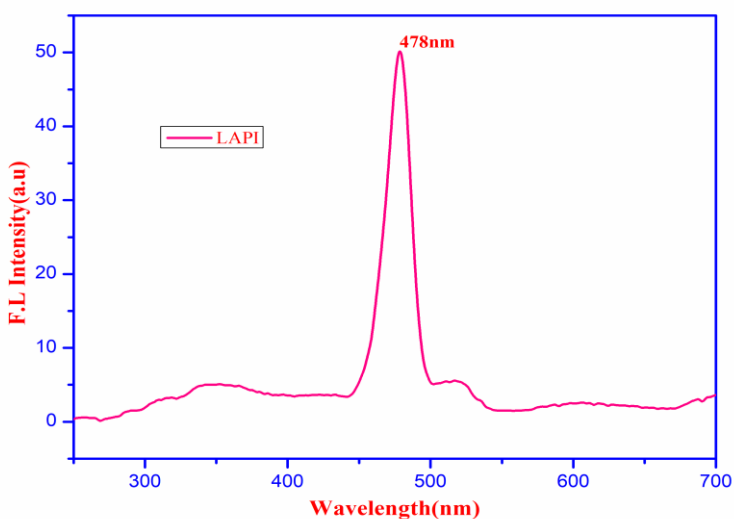

Fig.5: Photoluminescence spectrum of LAPI crystal

3.4 Dielectric studies

The dielectric loss and dielectric constant of the LAPI crystal were estimated using the LCR meter. The variations of dielectric properties like dielectric constant (ε_r) and dielectric loss factor (tan $\square$) as the function of frequency at different temperatures are shown in Figures 6 and 7. It is observed that the both dielectric constant and loss factor decrease as the frequency increases. The high value of dielectric properties in the low frequency region is due to space charge polarization and other types of polarization. The obtained results suggest that dielectric loss and dielectric constant are strongly dependent on the frequency of the applied AC electric field. The low value of dielectric loss of LAPI crystal indicates that the sample has the enhanced dielectric quality with less number of defects and imperfections [11,12]. According to Miller's rule, the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient. The dielectric properties of the sample are found to be increasing with increase of temperature and this is due to expansion of the sample on heating, increase of dipole moment and polarization when the temperature of the sample is increased.
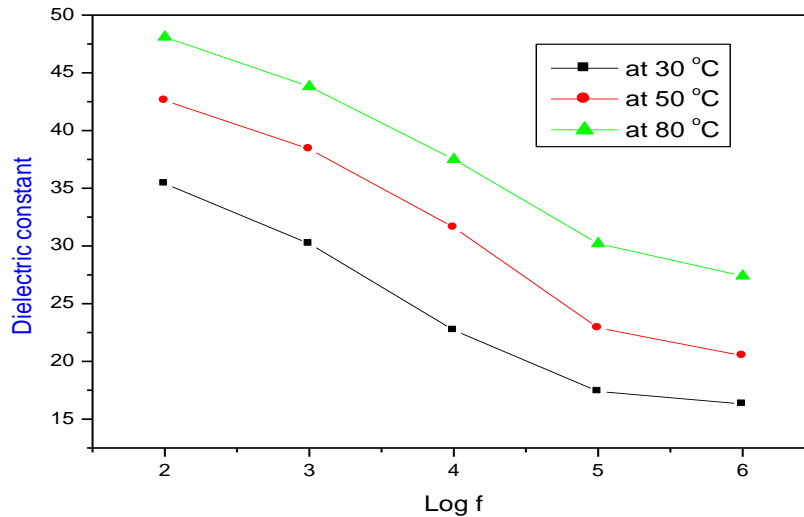

Fig.6: Plot of dielectric constant versus log frequency for LAPI crystal

3.5 Second Harmonic Generation efficiency

Powder SHG measurement was carried out using Kurtz and Perry experimental setup [13]. The Q-switched Nd: YAG laser (QUANTA RAY MODEL LAB-170-10) was used in this experiment. The laser operates at 1064 nm and 8 ns pulse with the repetition rate of 10 Hz and emission of green radiation of wavelength 532 nm from the crystalline sample of LAPI confirms the presence of second harmonic generation. The converted SHG output was displayed on a digital storage oscilloscope [14]. From the obtained data, the SHG efficiency of LAPI sample is 1.48 times that of KDP. Since this value is more, LAPI crystal could be used in all the NLO applications.
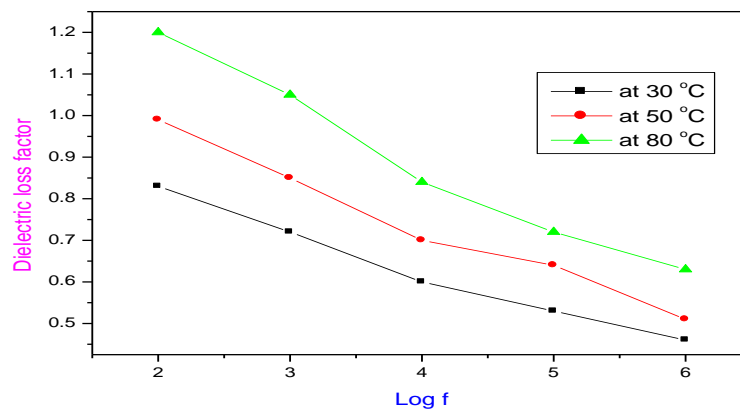

Fig.7: Plot of dielectric loss versus log frequency for LAPI crystal

IV. CONCLUSION

Semiorganic crystals of L-arginine potassium iodide (LAPI) were grown by a slow evaporation method. Optical studies indicated that the grown crystal has the transparency of about 60% in the visible region. From Tauċs plot, the optical band gap of LAPI crystal was found to be 5.27 eV. The PL spectrum reveals that LAPI crystal emits violet-bluish light. The presence of H in the grown crystal was confirmed by NMR Spectral studies. The SHG efficiency of LAPI crystal is found to be 1.48 times that of KDP. The dielectric properties of LAPI crystal were analysed at different frequencies and temperatures.

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