International Journal of Scientific Research in Science and Technology
Volume 11 | Issue 7 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X (www.ijsrst.com)

Optical Study of Zinc Chloride Doped L-Arginine Phosphate Monohydrate Single Crystal for Nonlinear Optical Applications

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ABSTRACT

The nonlinear optical single crystal of semi-organic zinc chloride doped L-arginine phosphate monohydrate (LAP:ZnCl) was harvested using the slow evaporation solution technique at 32°C. The harvested single crystal LAP:ZnCl was studied with ultraviolet-visible-infrared spectroscopy in the wavelength range of 200-900 nm. This analysis helped to determine the optical quality and transparency of the crystal.The Band gap of the crystal has been estimated by using Tauc's plot. The second harmonic generation from the crystal has been confirmed by the Kurtz and Perry method.

Keywords : Slow evaporation solution technique, second harmonic generation, nonlinear optics, band gap

I. INTRODUCTION

In recent years, Many researchers have focused on small organic molecules with a large dipole moment and chiral structure, which are often linked through hydrogen bonds.[1]. One of the best semi-organic nonlinear optical (NLO) crystals is L-arginine phosphate monohydrate (LAP). It has high nonlinear coefficient (> 1 pm/V) and high laser damage threshold (>15 J/cm^2).The nonlinear coefficient of this material is three times higher than that of potassium dihydrogen orthophosphate (KDP) [2–8]. Amino acids form a family of molecules which have a common functionality at one end of the molecule, coupled to a range of gradually differentiated functionalities at the other end. Hence the amino acid-based systems are good candidates for the study of the effect of deliberately added impurities. The effect of metal impurities as additives (copper oxide and magnesium oxide) on the crystal growth and characterization of LAP has already been studied. L-arginine phosphate monohydrate (LAP)isfound to exhibit interesting non-linear optical properties [9].One of the methods for raising the efficiency of second harmonic generation (SHG) is introduction of organic molecules, e.g., amino acids, which possess high nonlinear coefficients. As shown by Xue et al. [10], hydrogen bonds play a very important role in optical nonlinearities of inorganic crystals. For instance, L-arginine phosphate (LAP), a typical NLO semi-organic crystal, combines the advantages of both inorganic NLO crystals, e.g., high optical damage threshold, and of organic NLO crystals, such as considerable optical nonlinearity [11].LAP belonging to KDP family crystals consists of alternating layers of the inorganic dihydrogen phosphate anionic groups,water molecules and L-arginine the organic crystal[$(H_2N)CNH(CH_2)_3CH(NH_3)COO]^+$, held together by plentiful hydrogen bonds.The organic L-arginine molecule, the inorganic dihydrogen phosphate anionic group and the water molecules are all attributed to the NLO response of the crystal, but the major contribution is made by intrinsic optical nonlinearity of organic L-arginine molecule and inorganic dihydrogen phosphate group[12].Nonlinear optical materials find extensive optoelectronic applications such as optical frequency conversion, optical communication, optical data storage and optical switches in inertial confinement laser fusion experiments [13-15].Recently, attempts have been increasing to modify the crystal properties by adding metallic [16-17], inorganic [18-19] and organic [20-23] dopants and by mixing different compounds in different proportions [24-25]. In the present work,zinc chloride dopedL-arginine phosphate single synthesis, growth, and characterization, that is ultraviolet visible spectroscopy and SHGhave been reported for nonlinear optical applications.

II. METHODS AND MATERIAL

L-arginineand orthophosphoric acid (both AR grade) were taken in the equi-molar ratioand dissolved in double distilled water. Then add 1 mol% zinc chloride to this solution. The solutionstirred well for about 8 hours using a magnetic stirrer until it becomes homogenous.This solution was filtered by using Whatman filter paper to remove the suspended impurities. The resulting solution was then kept in a constant temperature bath with an accuracy of ±0.01at 32°C for crystallization. After3weeks, a good quality transparent well defined single crystal was collected from the solution, which has dimensions of 9x9x3 mm^3 as shown in Fig. 1.

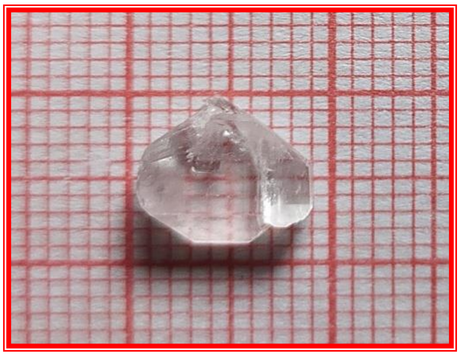

Figure 1: LAP:ZnCl Single Crystal

III.RESULTS AND DISCUSSION

A. Ultraviolet-visiblespectroscopy analysis

The optical transparency of LAP:ZnCl crystals was measured using a UV-visible spectrophotometer (Model-Black-C-SR, Stellarnet Inc. USA) to determine the optical transmission in the range of 200-900 nm.The graph presented in Figure 2 indicates that the LAP:ZnCl crystal has an optical transparency of up to 94% throughout the visible spectrum. This is significantly higher than what is observed in pure LAP crystal. The LAP:ZnCl crystal is characterized by a lower cutoff wavelength of 205 nm, which is a crucial property for certain applications that require high transmittance and a lower cutoff wavelength. These optical parameters are vital for SHG.

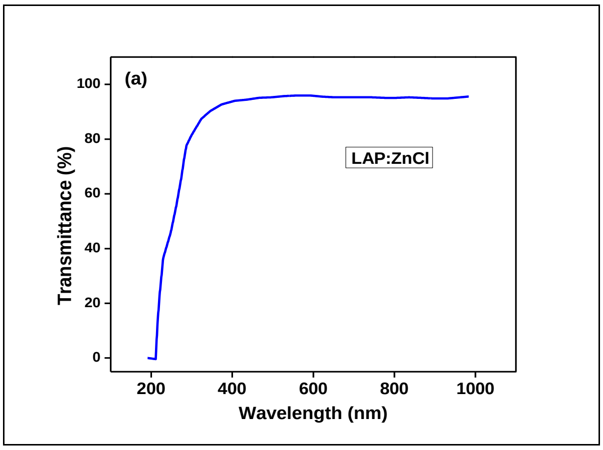

Figure 2:UV-Vis NIR spectrum of LAP:ZnCl single crystal.

The absorption coefficient (α) of a material depends on the energy of the incident photons. To calculate α for different wavelengths, we use the formula $\alpha=(2.3026/t)\log_{10}(100/T)x10^3(m^{-1})$, where T represents the percentage of transmitted light, t represents the thickness of the sampleand the coefficient 2.3026 comes from the conversion factor In(10) or$1/(\log_{10}(e))$. The dependence of the optical absorption coefficient (α) with photon energy helps to study the band structure andthe type of optical transition. According to Tauc's relation, the value of α was used to determine the optical band using the equation $(\alpha h\nu) = A(h\nu - E_g)^m$where, α denotes the absorption coefficient, hυ represents photon energy, E_g is the optical band gap energy, A is a constant, and m denotes the optical transition number[26]. When electromagnetic radiation is passed through a material, it is absorbed at a certain wavelength when the energy equals the optical band gap energy of the material, causing electrons to transition from the valence band to the conduction band. Electron transition between the valence band and conduction band can either be direct or indirect andalso both possess forbidden transition [27].The direct allowed transition hasa transition number of 1/2, the indirect allowed transition has a transition number of 2, the direct forbidden transition has a transition number of 3/2 and the indirect forbidden transition has a transition number of 3. [28]. In this case, we have to determine the value of m and it determines the type of optical transition of LAP:ZnCl crystal. Taking logarithm on both sides and differentiating equationwith respect to hυ we get the following form [29]. $\ln(\alpha h\nu) = \ln(A) + m\ \mathrm{In}(h\nu-E_g)$ $d(\mathrm{In}(\alpha h\upsilon))/d(h\upsilon) = m/(h\upsilon-E_g)$. The value of E_g can be calculated from a graph plotted between (ln (αhυ))/hυ and hυ which are shown in Fig. 2 (b).

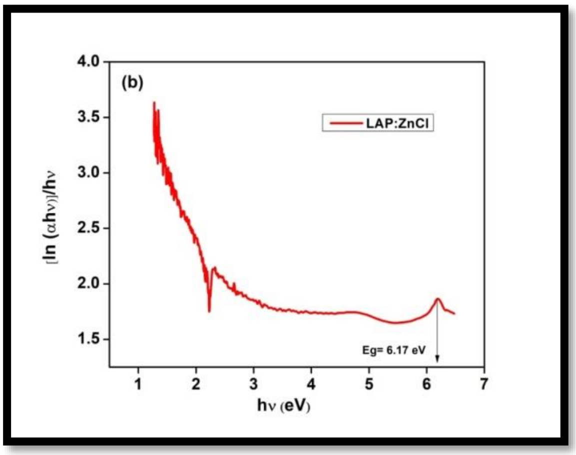

Figure 2(b):plot of [ln (ahv) /hv] versus hv (ev)

The discontinuity in line gives the information about both single [30] and multiple [31] stage optical transitions. These transitions are indicated at a particular maximum energy value where a particular transition might have taken place corresponding to a specific value of m. In the present case, there is a single stage of optical transition with discontinuity at a particular maximum energy value of knee point. Plotting the graph between ln(αhυ) and ln(hυ-Eg), the value of m is obtained. The value of m was found to be 2.69 ≈ 3 ≈ 3 by extrapolating linear fit as shown in Fig. 2 (c).

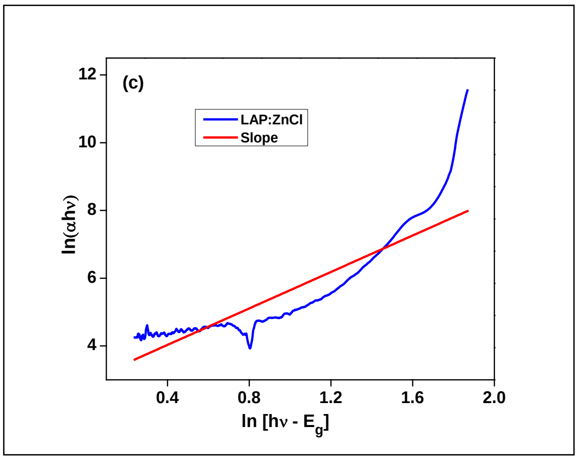

Figure 2(c):Plot of ln(αhv) versus ln(hv-E_g)

This shows and confirms that the optical transition of LAP:ZnCl crystal is allowed for indirect allowed transition gap nature. The Tauc's plot relation has been rearranged as given below for condition of indirect forbidden energy transition which gives a graph is plotted between photon energy hυ and $(αhυ)^2$. By extrapolating the linear portion of the curve to absorption coefficient (α) becomes zero as shown in Fig. 2(c).According to Plank's equation, the optical band gap energy of LAP:ZnCl crystal was calculated theoretically as follows: E = hc/$λ_e$ (eV) where h is the Plank's constant (6.626×10^{-34} J/s), c is the velocity of light in vacuum (3×10^8 m/s), λ is the lower cut-off wavelength (205nm) and e is the charge of electron (1.602×10^{-19}C).

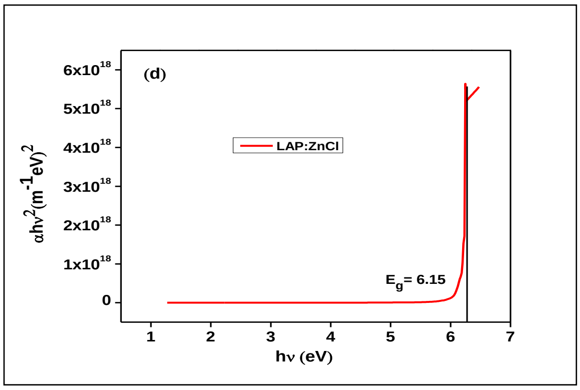

Fig 2(d)optical band gap spectrum

The calculated direct band gap energy of LAP:ZnCl single crystal was 6.04 eVwhich is in good agreement with the value obtained from Fig. 2 (b) and Fig. 2(d)i.e. 6.17 eV and 6.16 eV.

B. Second harmonic generation (SHG) analysis

The second harmonic generation efficiency of LAP:ZnCl single crystal has been determined using the Kurtz-Perry powder technique.[32]Q-switched High Energy Nd:YAG Laser (QUANTA RAY Model LAB-170-10)has been used for present studies operates at wavelength 1064 nm, having the repetition rate of 10 Hz and pulse width of 6 ns delivering the input energy of 0.50 Joule. Thefinely powdered of grown single crystal is used and tightly filled in a microcapillary tube of uniform bore. The prepared samples were illuminated by the Gaussian beam of Nd: YAG laser through sample the wavelength wavelength 532 nm of bright green light confirmed emitted from sample confirmed the second harmonic generation of zinc chloride doped LAP crystal. The corresponding output voltages have been recorded and it is found that LAP:ZnCl is 1.05 times greater than that of pure LAP single crystal. The high SHG efficiency of LAP:ZnCl materials are readily demanded for nonlinear optical applications.

IV. CONCLUSIONS

Semi-organic LAP:ZnCl single crystal of dimension 9×9×3 mm^3 has been successfully grown by slow evaporation solution technique.UV-visible studies revealed that doped LAP:ZnCl crystal is highly transparent within the range of 200-900 nm making it promising material for optical applications.SHGanalysis reveals that LAP:ZnCl is 1.05 times more efficient than pure LAP single crystal.Therefore, LAP:ZnCl crystal is used for NLO applications.

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