Synthesis, Growth and Characterization of Lanthanum doped L - Alanine Tartrate Nonlinear Optical Materials

L. Jothi [1], V. Kumudha [2]
[1] Department of Physics, Namakkal Kavignar Ramalingam Government Arts College for Women, Namakkal, India.
[2] Research Scholar, Research and development Centre, Periyar University, Salem, India.
[2] Block Resource Centre, Paramathy, Namakkal, Tamilnadu, India.

ABSTRACT: Lanthanum doped L - alanine tartrate (LAT) was synthesized by solution method and solubility study was carried out. Single crystals of LAT were grown by slow evaporation method. The cell parameters were determined by single crystal X-ray diffraction study. Transparency range of the crystal was determined using UV-VIS-NIR spectrophotometer. The functional groups of LAT crystals were analyzed by FT-IR spectroscopy. The hardness of the material was measured by a Vickers micro hardness tester. The dielectric response of the crystal was investigated in the frequency region of 50 Hz – 500 KHz. The nonlinear optical property was tested by Kurtz-Perry powder technique for second harmonic generations.

Keywords: Solution growth, Characterization, X-ray diffraction, Micro hardness, Second Harmonic Generation.

1. INTRODUCTION

In recent years organic nonlinear optical (NLO) crystals have attracted much attention for their large nonlinear coefficient, high laser damage threshold. However, most of organic NLO materials have poor mechanical and thermal properties, resulting in the damage of crystal during processing. To avoid this drawback, a new type of NLO material has been grown from organic-inorganic complexes. These semi organic materials have high optical nonlinearity of a purely organic compound combined with the mechanical and thermal properties of inorganic materials.

Amino acids have attracted a wide interest of the researchers, since all the compounds in the class consist of an optically active property. Thus, amino acids have special physical properties which make them an ideal candidate for their NLO applications. Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, non fiber optic communications, which depend on materials such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, nonlinear optics, piezoelectric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries [1-5].

In optoelectronic technologies and communications, fiber optics plays a vital role. In optic fiber communication for proper transmission and reception of laser light communication link is very essential. Researchers are trying to fabricate materials with high transmitting range. Initially investigations were focused on purely inorganic materials. But later on attention has been drawn towards organic materials due to their low cost, fast and nonlinearity response over a wide range of frequencies and high optical damage threshold [6-9]. Recently it is found that transition metals, inorganic compounds and coordinated complex have emerged as extremely promising building block for optoelectronic materials.

Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to repair single crystal than polycrystalline material and extra effort is justified because of the outstanding advantages of single crystals [10-12]. The reason for growing single crystals is, many physical properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline material.

The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research. Nonlinear optical crystals are very important for laser frequency conversion. Growth of crystal ranges from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. Single crystals may be produced by the transport of crystal constituents in the solid, liquid or vapour phase [13-15]. The factors during crystals growth which affect the size of the crystals are solubility of compound in the solvent chosen for recrystallization, the number of nucleation sites, mechanical agitation to the systems, and time.

The principle of this method is based on the concepts of solubility and super saturation. At a given temperature, a limited amount of a substance dissolves in a particular solvent. The amount defines the solubility at that temperature. The solubility is a function of the temperature of the solvent. In most cases, the solubility increases with temperature. If a saturated solution is prepared at a certain temperature and then cooled to a lower temperature, it contains more salt than the permitted by the solubility at the lower temperature [16-18]. The same thing happens if some of the solvent is allowed to evaporate. The solution is now in the supersaturated state is metastable and with the slightly induction, the extra salt precipitates.

If a seed crystal is introduced into the solution, the substance precipitating from the solutions will grow around the seed crystal forming a larger single system. In the absence of a seed even dust particles provide a nucleus for crystal growth. A slow growth rate, prevention of multiple nucleations and good control temperature are conditions conductive to the growth of a crystal. The actual temperature of growth, pH of the solutions and the presence of deliberately added impurities are additional parameters that determine the rate of growth and also morphology of the crystal [19-23].

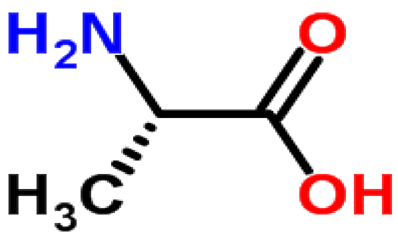
Recently, L-Alanine crystals have increased attention for photo induced nonlinear optical effects and dispersion of the linear and nonlinear optical susceptibilities. Photo induced nonlinear optical effects of L-Alanine single crystals show that the increasing time of illuminations leads to slight changes in the absorption backgrounds without changes in the spectral features. In the present work, a systematic study has been carried out on the growth of pure and Lanthanum doped L-Alanine Tartrate (LAT) crystals. An attempt has been made to improve the physiochemical properties of LAT by adding Lanthanum dopant. Single crystal X-ray diffraction study has been carried out to confirm the grown pure and doped crystals. FT-IR, UV-VIS-NIR, micro hardness, dielectric analysis and NLO property were studied for grown pure and doped crystals.

2. EXPERIMENTAL PROCEDURE

2.1. Raw Materials

Alanine: Alanine is an aliphatic amino acid, because the side-chain connected to the α-carbon atom is a methyl group (-CH_3), making it the simplest α-amino acid. The methyl side-chain of alanine is non-reactive and is therefore hardly ever directly involved in protein function. Alanine is a small non-essential amino acid in humans; Alanine is one of the most widely used for protein construction and is involved in the metabolism of tryptophan and vitamin pyridoxine. Alanine is an important source of energy for muscles and central nervous system, strengthens the immune system, helps in the metabolism of sugars and organic acids, and displays a cholesterol-reducing effect in animals.

Molecular Structure:



Molecular Formula : $C_3H_7NO_2$

Molecular Weight : 89.094 g/mol

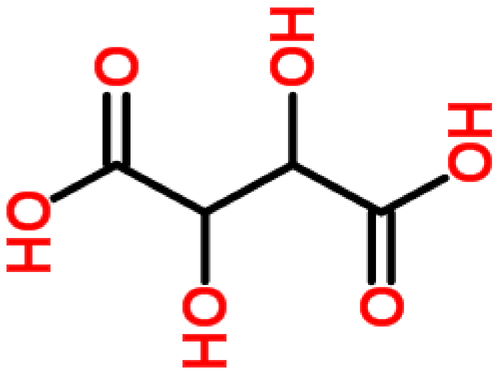
Melting point : 314.5 °C

Solubility in water : 166.5 g/1 L (25 °C)

Density : 1,432 g/cm^3

Tartaric Acid: Tartaric acid is a white crystalline diprotic organic acid. The compound occurs naturally in many plants, particularly in grapes, bananas, and tamarinds. It is also one of the main acids found in wine. Tartaric acid can be added to food when a sour taste is desired. It is used as an antioxidant. It also has many industrial uses such as in photographic printing and development, polishing metals, wool dyeing. The chemical is a dihydroxy derivative of succinic acid. Tartaric acid is found in cream of tartar and baking powder. The chemical compound is used in silvering mirrors, tanning leather, and in Rochelle salt. In medical analysis, tartaric acid is used to make solutions for the determination of glucose.

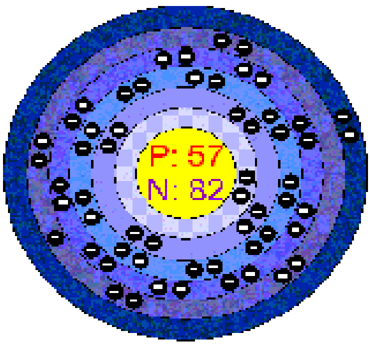
Molecular Structure:



Molecular Formula	:	**$C_4H_6O_6$**
Molecular Weight	:	**150.086 g/mol**
Melting point	:	**206°C**
Solubility in water	:	**1.33 kg/L**
Density	:	**1.79 g/mL**

Lanthanum: Lanthanum (La)**,** chemical element, a rare-earth metal of Group 3 of the periodic table, that is the prototype of the lanthanide series of elements. Lanthanum is a soft, malleable, ductile, silver-white metal. It is chemically active and it is one of the most reactive of the rare-earth metals: it oxidizes rapidly in air and it reacts with water to form the hydroxide. Lanthanum becomes superconducting at atmospheric pressure below 6.0 K (−267. 2°C), in the face - centred cubic β-phase or 5.1 K (−268.1 °C) in the double close-packed hexagonal α-phase. Lanthanum salts are often very insoluble. Lanthanum is one of the rare chemicals, that can be found in houses in equipment such as colour televisions, fluorescent lamps, energy-saving lamps and glasses. All rare chemicals have comparable properties. La_2O_2 is used to make special optical glasses like infrared adsorbing glass, camera and telescope lenses. If added in small amounts it improves the malleability and resistance of steel. Lanthanum is used as the core material in carbon arc electrodes. Lanthanum salts are included in the zeolite catalysts used in petroleum refining because they stabilize the zeolite at high temperatures.

Electronic configuration:



Atomic number	:	**57**
Atomic mss	:	**138.905 g/mol**
Melting point	:	**826 °C**
Density	:	**6.18 g/ cm^3 at 20°C**
Specific gravity	:	**6.146 at 24 °C**

2.2. Material synthesis and Crystal growth

The commercially available analytical grade L-Alanine and Tartaric acid have been used to synthesize the pure LAT crystal. All the preparation and growth process are carried out in aqueous solution. Pure LAT are prepared by taking the raw material in 1:1 molar ratio and then dissolved in the de-ionised water. Saturated solution was prepared, filtered and allowed to evaporate at room temperature under optimized conditions as shown in Figure 1. Seed crystals were obtained in a period of one month. Good quality crystals were obtained by successive recrystallization method. The same procedure was applied to grow the metal doped crystals by adding 2mol% of Lanthanum to the LAT solution. The aqueous solution was maintained in the undisturbed condition. The solution was periodically inspected and good quality crystals were obtained in a period of three weeks. The incorporation of dopant into the pure solution has improved the growth rate and the quality of the crystals. The grown crystal was further studied by various characterization techniques. The photographs of grown pure and Lanthanum doped crystals are shown in Figure 2.

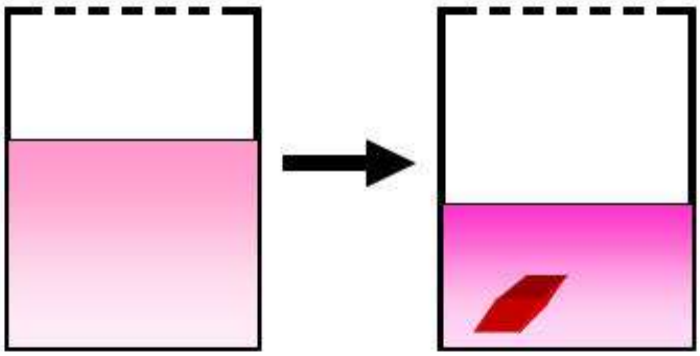
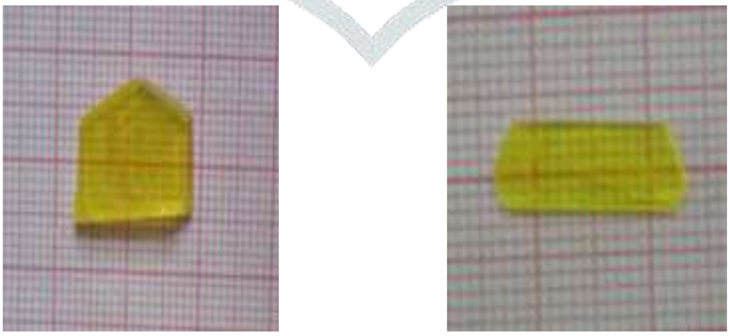


Figure 1: Slow Evaporation Method.



(a) Pure LAT (b) La^{2+} doped LAT

Figure 2: Photographs of grown pure and Lanthanum doped crystals.

3. RESULTS AND DISCUSSION

3.1. Single Crystal X-Ray Diffraction

Single crystal X- ray diffraction studies of pure and Lanthanum doped LAT crystals were carried out using ENRAF NONIUS CAD4 diffractometer. The observed results indicate that both the pure and doped LAT crystals belong to monoclinic crystal system with the space group $P2_1$. The lattice parameter values of pure and doped crystals are shown in Table 1. There is a slight variation in the lattice parameters of doped LAT compared with pure LAT. These variations are due to the incorporation of Lanthanum in the LAT crystal lattice.

Table 1: Lattice parameter values for the pure and doped LAT crystals.

Lattice Parameters	Pure LAT	La^{2+} doped LAT
a (Å)	5.795 (˚ A)	5.859 (˚ A)
b (Å)	6.390 (˚ A)	6.398 (˚ A)
c (Å)	12.494 (˚ A)	12.454 (˚ A)
V ($Å^3$)	450.602 ($Å^3$)	450.613 ($Å^3$)
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$

3.2. Fourier Transform Infrared Spectral Analysis

The fine powdered samples of pure and doped LAT crystals are taken for this experiment. The FT-IR spectrum is recorded for the pure and doped LAT single crystals at room temperature in the range of 400 – 4000 cm^{-1} by employing BRUKKER IFS 66V FT-IR spectrometer, using KBr pellet method. The FT-IR spectra of pure and doped crystals are shown in Figure 3 and Figure 4. The OH stretching vibrations were observed for both of the pure and metal doped LAT crystals at 3085cm^{-1}. Both of the pure and doped metal doped compounds show strong absorption at 2601 cm^{-1} indicating the presence of amine group. The absorption at 2111cm^{-1} is due to NH3+ asymmetric deformation and NH3+ hindered rotation. It shows that addition of metal dopant do not show any significant from the pure crystal spectrum.

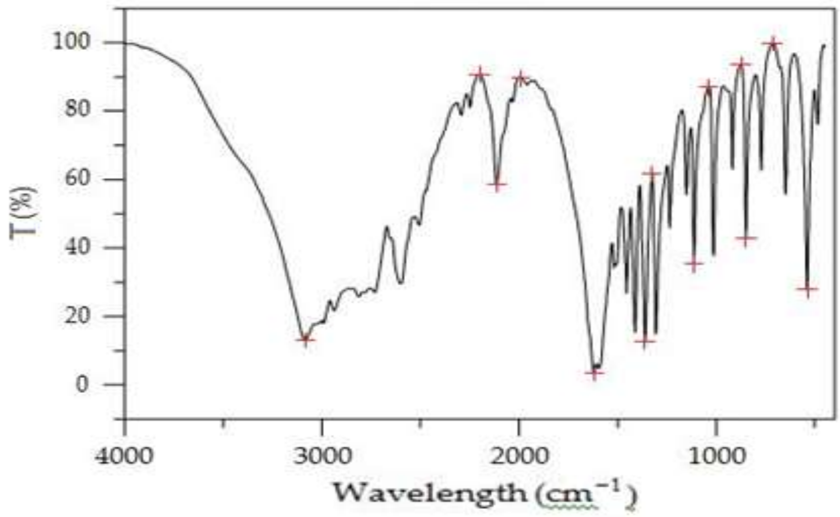


Figure 3: The FT-IR spectrum of pure LAT crystals

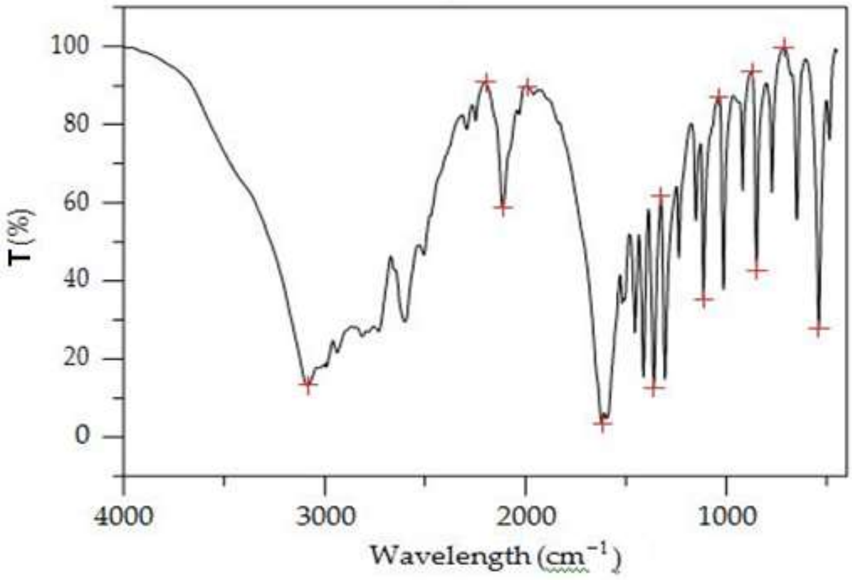


Figure 4: The FT-IR spectrum of doped LAT crystals

3.3. UV - VIS - NIR Analysis

The UV absorption study of the pure and doped LAT crystals was carried out by UV-VIS-NIR spectrophotometer. Figure 5 and Figure 6 show the maximum absorption of pure and doped LAT crystals starts from 203 nm. After this wavelength, absorption abruptly decreases to nearly 2% for pure and 1.5% for doped LAT crystals. The lower cut-off wavelength of pure and doped crystals occurs at 246 nm and 235 nm, respectively. Thus it is clear that both of materials possess very good optical transparency up to 1500 nm. The doped crystal has better transparency window compared to the pure one. This property makes the material suitable for the many potential and nonlinear applications.

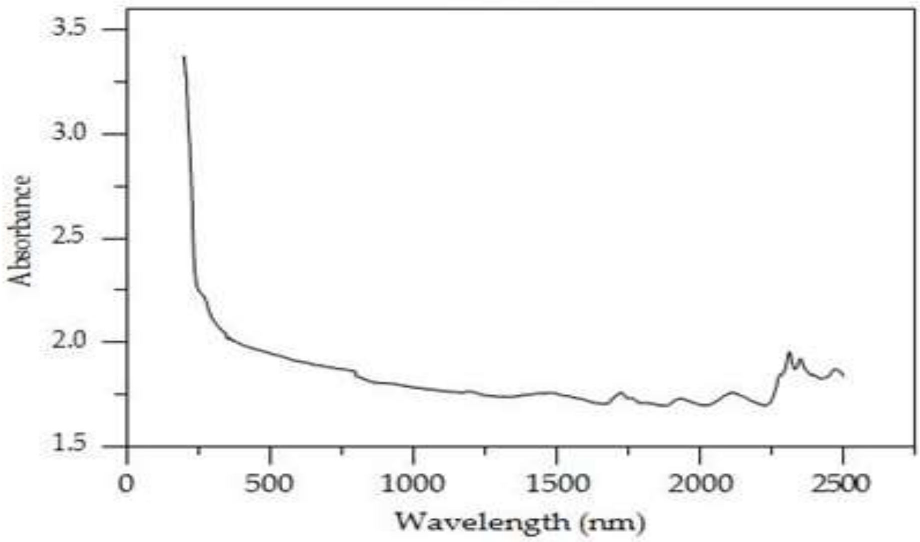


Figure 5: UV-VIS-NIR spectrum of pure LAT crystals.

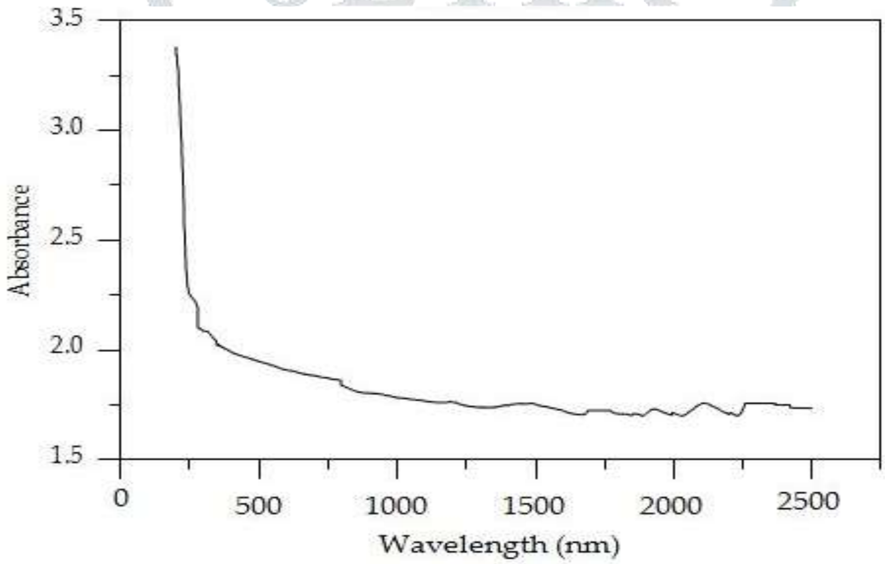


Figure 6: UV-VIS-NIR spectrum of doped LAT crystals.

3.4. Microhardness Studies

Microhardness studies of pure and doped LAT crystals have been carried out using HMV SHIMADZU microhardness tester, fitted with diamond Vickers pyramidal indenter. The microhardness measurements are carried out on the well developed face (1 0 0). The static indentations were made at with a constant indentation time of 15 seconds for all indentations. Maximum indenter load applied for LAT crystal was 50 g, and above this load micro cracks were observed. The plot of variation of Vickers hardness number with applied load for the plane (1 0 0) of pure and doped LAT crystals are shown in Figure 7 and Figure 8. For pure LAT crystal the hardness value increases as load increase up to 45 g. Beyond 45 g, cracks were found to develop. Thus the pure material is mechanically stable up to the load of 45 g. In metal doped LAT crystal the cracks were found when the load value is 50 g. This indicates that the metal dopant in the compound increases the mechanical hardness of the material. By plotting log P verses log d, the value of the working hardness coefficient n value for pure and doped LAT crystals was found to be 1.38 and 1.27. According to Onitsch, n lies between 1 and 1.6 for hard materials and n is greater than 1.6 for soft materials. Hence, it is concluded that the pure and doped LAT crystals belong to hard material category.

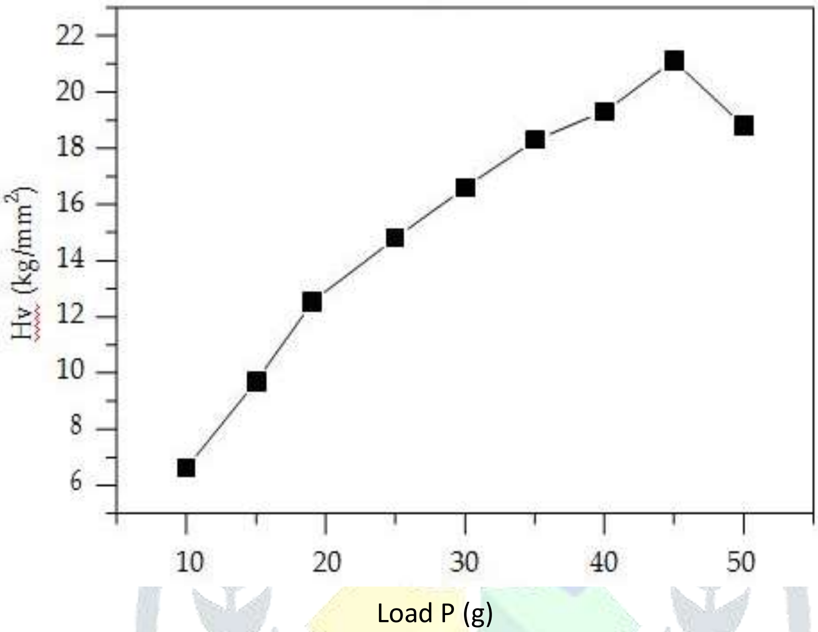


Figure 7: Variation of Vickers hardness number with applied load of pure LAT crystals.

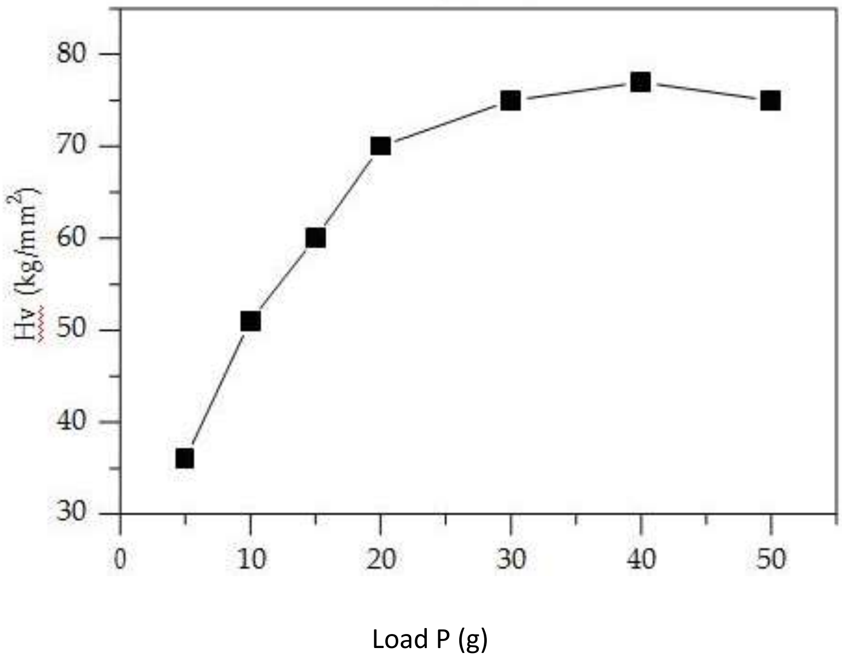


Figure 8: Variation of Vickers hardness number with applied load of doped LAT crystals.

3.5. Dielectric Analysis

The dielectric study of pure and doped LAT single crystals was carried out using the HIOKI 3532-50 LCR HITESTER instrument. The capacitance values for both pure and doped crystals are found for frequencies varying from 50Hz to 5MHz at room temperature. Figure 9 and Figure 10 show the variations of dielectric constant with log frequency for pure and doped LAT crystals. It is observed from the plot that the dielectric constant decreases with increasing frequency and attains a constant value in the high frequency region. At room temperature, the dielectric constant decreases with applied frequency. From the graph it is clearly evident that the La^{2+} doped LAT crystal shows more efficiency than the pure one. Thus the dielectric nature of pure LAT is altered by the presence of La^{2+} metal. In La^{2+} doped LAT crystal the low dielectric constant with high frequency suggests that the crystal possesses enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications.

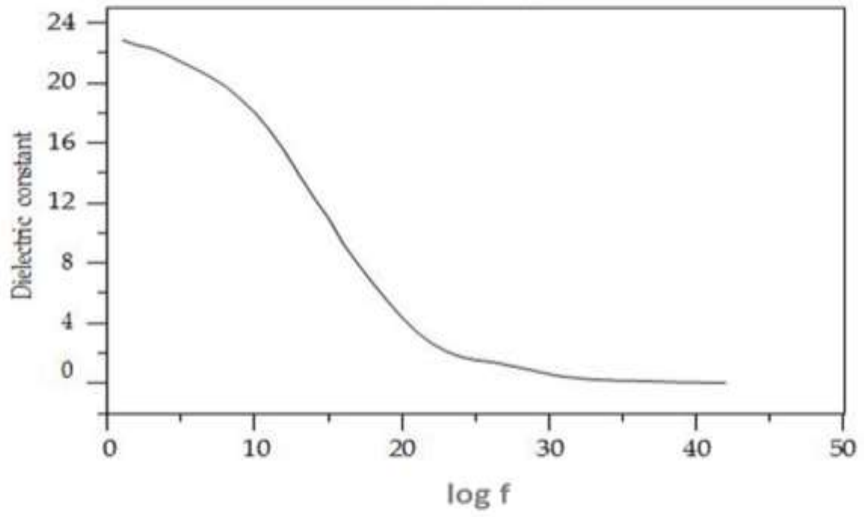


Figure 9: Dielectric constant with frequency for pure LAT crystals.

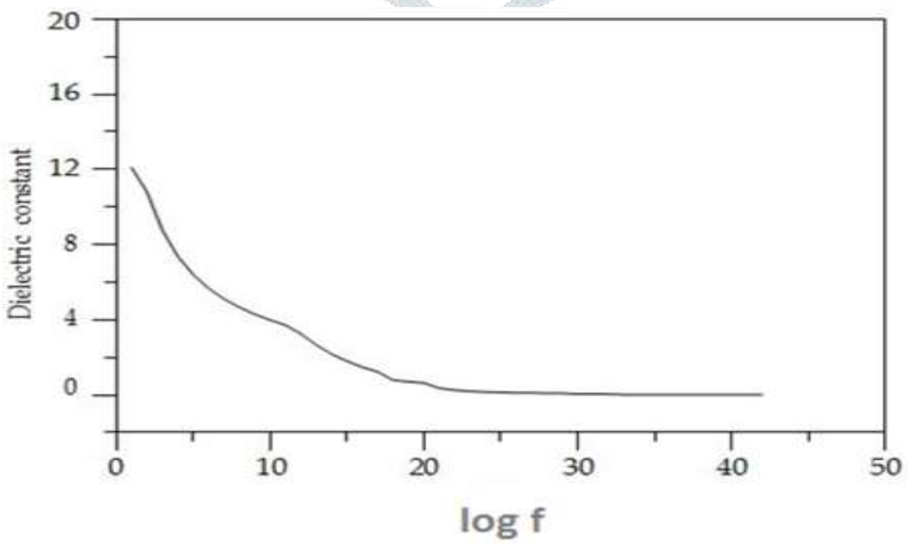


Figure 10: Dielectric constant with frequency for doped LAT crystals.

3.6. Nonlinear Optical Studies

Nonlinear optical (NLO) property of pure and doped LAT crystals was carried out from Kurtz powder second harmonic generation (SHG) test using the Nd: YAG Q-switched laser beam. The sample of same size was illuminated using Q-switched, mode locked Nd:YAG laser with input pulse of 6.2 mJ. The second harmonic signals of 324mV and 384mV, respectively, were obtained for pure and doped LAT crystals with reference to KDP. Thus, the SHG efficiency of pure and doped LAT crystals is nearly 1.18 and 1.40 times greater than KDP. The doped LAT crystal is found to have efficiency higher than that of pure LAT. The increase in the SHG efficiency of the doped crystals is due to the presence of metal dopant in the crystal lattice. It is concluded that the doped LAT crystal can be used for desired NLO applications.

4. CONCLUSIONS

The novel LAT material was synthesized and the single crystals of pure and Lanthanum doped LAT were grown successfully by slow evaporation technique. The lattice parameters and crystal structure were obtained by the single crystal X-ray diffraction studies. FTIR studies confirmed the presence of various functional groups in the crystal and the vibrational structure of the compound has been elucidated. UV-VIS-NIR studies revealed that the pure and doped crystals possess wide transparency in the entire visible region. Hardness of both pure and doped LAT crystals indicated that these crystals are hard materials. The dielectric studies revealed that the dielectric constant decreases with log frequency. NLO studies showed that the Lanthanum dopant has increased the efficiency of pure LAT. Thus it is concluded that the presence of dopant has improved the NLO properties of the grown crystals.

REFERENCES

[1] Ramasamy. P, Santhana Raghavan. P, Crystal Growth Processes and Methods, KRU Publication, Kumbakonam, 2000.

[2] Vijayan. N, Ramesh Babu. R, Gunasekaren. M, Gopalakrishnan. R and Ramasamy.P, Growth, optical, thermal and mechanical studies of methyl 4-hydroxybenzoate single crystals**,** Journal of Crystal Growth, 256,174, 2003**.**

[3] Rajan Babu.D, Jayaraman. D, Mohan Kumar. R, Jayavel. R, Growth and Characteri-zation of Nonlinear Optical L – Alanine Tetrafluoroborate Single Crystals, Journal of Crystal Growth, 245, 121-125, 2003.

[4] Ittyachan. R, Sagayaraj. P, Growth and characterization of a new nonlinear optical l-histidine diphosphate single crystal, Journal of Crystal Growth, 249, 553-556, 2003.

[5] Boyd. R.W, Nonlinear Optics, Academic Press, San Diego, Calif, USA, 1992.

[6] Pal. T, Kar. T, Single crystal growth and characterization of the nonlinear optical crystal L-arginine hydrofluoride, Journal of Crystal Growth, 234, 267-271, 2002.

[7] Narayan Bhat. M, Dharmaprakash. S. M, Growth of nonlinear optical γ-glycine crystals, Journal of Crystal Growth, 236, 376-380, 2002.

[8] Jothi. L, Ramesh Babu. R, Ramamurthi. K, Synthesis, Growth and Characterization of Organic Nonlinear Optical Single Crystals of 4 - Bromo - 4'- Methyl Benzylidene Aniline, Journal of Minerals and Materials Characterization and Engineering, 2, 308-318, 2014.

[9] Jothi. L, Vasuki. G, Ramesh Babu. R, Ramamurthi. K, Synthesis, crystal growth and characterization of organic NLO material: 4 - Bromo - 4' - hydroxybenzylidene aniline, Optik, 125, 2017-2021, 2014.

[10] Wojciechowski. A, Ozga. K, Reshak. A. H, Miedzinski. R, Kityk. I. V, Berdowski. J, Tylczyn. Z, Photoinduced effects in l-alanine crystals, Materials Letters, 64, 1957-1959, 2010.

[11] Ali Hussain Reshak, Auluck. S, Dalibor Stys, I. V. Kityk, H. Kamarudin. J, Berdowski Tylczynski. Z, Dispersion of linear and non-linear optical susceptibilities for amino acid 2-aminopropanoic CH_3 CH (NH_2) COOH single crystals: experimental and theoretical investigations, Journal of Materials Chemistry, 21, 17219, 2011.

[12] Mukerji. S, Kar. T, Vicker's microhardness studies of L-arginine hydro bromide monohydrate crystals (LAHBr), Crystal Research and Technology, 34, 1323-1328, 1999.

[13] Balarew. C, Duhlew. R, Application of the hard and soft acids and bases concept to explain ligand coordination in double salt structures, Journal of Solid State Chemistry, 55, 1- 6, 1984.

[14] Praveen Kumar. P, Manivannan.V, Tamilselvan. S, Senthil. S, Victor Antony Raj, Sagayaraj. P, Madhavan. J, Growth and characterization of a pure and doped nonlinear optical L-histidine acetate Single Crystals, Optics Communications, 281, 2989-2995, 2008.

[15] Aakeroy. C. B, Hitchcock. P. B, Moyle. B. D, Seddon. K. R, A novel class of salts for second harmonic generation, Journal of the Chemical Society, Chemical Communications, 23, 1856-1859, 1989.

[16] Kitazawa. M, Higuchi. R, Takahashi. M, Ultraviolet generation 266 nm in a novel organic nonlinear optical crystal, Applied Physics Letters, 64, 2477-2479, 1994.

[17] Misoguti. L, Verela. A. T, Nunes. F. D, Bagnato. V. S, Melo. F. E. A, Mendes Filho. H, Zilio. S. C, Optical properties of L-alanine organic crystals, Optical Materials, 6, 147-152, 1996.

[18] Monaco. S. B, Davis. L. E, Velsko. S. P, Wang. F. T, Eimerl. D, Zalkin. A. J, Synthesis and characaterization of chemical analogs of L-arginine phosphate, Journal of Crystal Growth, 85, 252-255, 1987.

[19] Aruna. S, Bhagavannarayana. G, Sagayaraj. P, Investigation on the physico-chemical properties of nonlinear optical (NLO) single crystal: L-histidinium dinitrate, Journal of Crystal Growth, 304, 184 -190, 2007.

[20] Ramesh Kumar. G, Gokul Raj. S, Mohan. R, Jayavel. R, Growth and characterization of new nonlinear optical L-threonium acetate single crystals, Journal of Crystal Growth, 283, 193-197, 2005.

[21] Natarajan. S, Martin Britto. S. A, Ramachandran. E, Growth, Thermal, Spectroscopic and Optical Studies of L-Alaninium Maleate, a New Organic Nonlinear Optical Material, Crystal Growth and Design, 6, 137-140, 2006.

[22] Martin Britto Dhas. S. A, Bhagavannarayana. G, Natarajan. S, Growth and characterization of a new potential NLO material from the amino acid family- l-prolinium picrate, Journal of Crystal Growth, 310, 3535-3539, 2008.

[23] Uma Devi. T, Lawrence. N, Ramesh Babu. R, Ramamurthi. K, Growth and characterization of L-prolinium picrate single crystal: A promising NLO crystal, Journal of Crystal Growth, 116-123, 2008.