Tuijin Jishu/Journal of Propulsion Technology
ISSN: 1001-4055
Vol. 45 No. 2 (2024)

Influence of Doping on the Structural, Optical, Thermal, NLO and Dielectric Properties of L-Histidine Tetrafluoro Borate Crystal

T.Rasappan[1], C.Besky Job[2], Chellaian Justin Dhanaraj[3]

[1] *Research Scholar, Department of Physics, Scott Christian College (Autonomous), affiliated to Manonmanium Sundaranar University, Nagercoil-62900.*

[2] *Associate Professor, Department of Physics, Scott Christian College (Autonomous), affiliated to Manonmanium Sundaranar University, Nagercoil-629001.*

[3]*Assistant Professor, Department of Chemistry University College of Engineering, Konam Nagercoil -629001*

***Abstract*:-** Since amino acids are naturally biocompatible, they can be used in a variety of biological and biomedical settings, such as medication delivery systems, implanted devices, and biosensors. Amino acid-based crystals can be incorporated into microelectronic devices to improve their biocompatibility and lower the possibility of adverse impacts when interacting with biological systems. In our present study, we made an attempt to grow pure and $SrCl_2$, $CdCl_2$ doped L-Histidine Tetra Fluoro Boarate (L-HTFB), and semi organic single crystal via simple solution growth technique. The crystals were subjected to structural, optical, thermal, NLO and electrical analysis. Structural analysis evident that $SrCl_2$adition in L-HTFB crystal lattice induce a phase transition from monoclinic to orthorhombic system, whereas cadmium chloride induce only volume expansion of L-HTFB lattice. TG/DTA thermograms elucidate the enhanced stability with $CdCl_2$ doping whereas $SrCl_2$ lower the thermal stability. Reduction in optical bandgap and high transparency in the entire visible region of the doped sample suggests the use of doped crystals for opto-electronic devices. Also dielectric analysis promises the role of $SrCl_2$ doped L-HTFB single crystals with high transparency in the visible region, for the development of advanced devices for laser systems, electro-optic modulation, energy storage, sensing applications

Key words: Dielectrical properties, Optical properties, Semi organic crystal.

1. Introduction

Nonlinear optics is a field that is significantly fascinated by semiorganic materials [1]. The organic ligand in semiorganic materials forms an ionic interaction with the inorganic host, leading to the creation of novel materials that possess elevated optical nonlinearities [2]. Organic NLO crystals show stronger nonlinear nature with lower mechanical stability, whereas purely inorganic NLO materials have outstanding mechanical and thermal properties but very minor optical nonlinearity due to the lack of broad π - electron delocalization [3]. Therefore, semiorganic crystals that mix the advantageous qualities of organic and inorganic materials and provide effective nonlinear optical properties may be created. Numerous researchers have recently revealed that semi-organic crystals based on amino acids have the capacity to be NLO candidates for a variety of applications, including optical disc data storage, frequency conversion, and optical computing. L-arginine, L-Alanine, L-Histidine, L-Lysine, are few of the amino acid, explored as good choice of producing NLO crystals [4,5,6].

L-Histidine - an alpha amino acid, which has hydrophilic character. The imidazole side chain of L-histidine is distinguished by the presence of two nitrogen atoms within a five-membered ring. Histidine differs from other amino acids in its chemical and biological characteristics due to the imidazole group [7]. Reena Ittachiyan and Sahayaraj reported the growth of L-histidine bromide single crystals. They observed from the X-ray diffraction

data that the LHB crystal is orthorhombic in structure with space group of P_{212121} [8]. Madhavan et al. have reported on the growth and certain characterizations of L-histidine hydrochloride monohydrate [9]. By using the slow evaporation solution growth approach, single crystals of tartaric acid mixed L-histidine hydrochloride monohydrate and L-histidine hydrochloride monohydrate have been formed. For both crystals, a broad transparency window between 300 and 1000 nm is discovered, making it appropriate for the second harmonic production of lasers in the blue range [10].

Furthermore the properties of this amino acid based NLO crystals can be tuned by doping process. Doping of divalent transition metal ions or rare earth metal ions enlightens the NLO behavior and optical transparency is very common among reported research [11]. Reme-dios et al. report on the impact of Ni (II) doping on the structure of L-histidine hydrochloride monohydrate crystals using Raman spectroscopy and X-ray diffraction [12]. Rietveld analysis revealed that, at room temperature, the doped sample had the same structure as the pure one with just a very slight variation in the lattice parameters [12]. Cadmium chloride doped sulphamic acid crystal has superior magnitudes of third order nonlinear susceptibility and refractive index, according to Anandaraj and Jothi [13].

For non-linear optical applications, Thirumuruganantham et al. examined DAST and Cd (Cd 1:0.01 mol%, Cd 3: 0.03 mol%, and Cd 5: 0.05 mol%) doped DAST crystals. It's interesting to note that the Cd-doped DAST crystals' SHG efficiencies increased to 1.29, 1.41, and 1.79 times higher than those of the pure DAST crystal [14].Cadmium chloride doped with lithium sulphate monohydrate (LS) single crystals of excellent and optically transparent quality were produced in aqueous solution using the slow evaporation process at room temperature by Latha Mageshwari et al [15].

Doping L-aspergine single crystal with $CdCl_2$ increased its micro hardness, decreased its dielectric loss, and improved its optical absorption [16]. In light of this, there are, as far as the authors are aware, no publications of this kind on the doping of L-Histidine tetra fluoro borate single crystals with cadmium and strontium chlorides. In order to enhance the characteristics of L-HTFB single crystals for cutting-edge technological applications, we attempted to develop L-HTFB that was both pure and 5 mol% doped with $CdCl_2$ and $SrCl_2$ using the slow evaporation method in the current study. Additionally, structural, optical, mechanical, NLO, and dielectric analyses are performed on the produced crystals. These are the comprehensive reports.

2. Materials and Methods

2.1 Slow Evaporation method for the growth of Pure and $CdCl_2$, $SrCl_2$ doped L-HTFB single crystals

Tetra fluoroboric acid and L-histidine were combined in an equimolar ratio and stirred continuously at 50°C for around five hours. After that, a beaker was used to hold the supersaturated solution as it slowly evaporated. In the saturated solution, 0.5 moles of strontium chloride and 0.5 moles of cadmium chloride were added individually to promote the development of doped crystals. After 30 days, the solvent evaporates and crystals of high optical quality are formed. The photographs of harvested crystals were shown in figure 1.

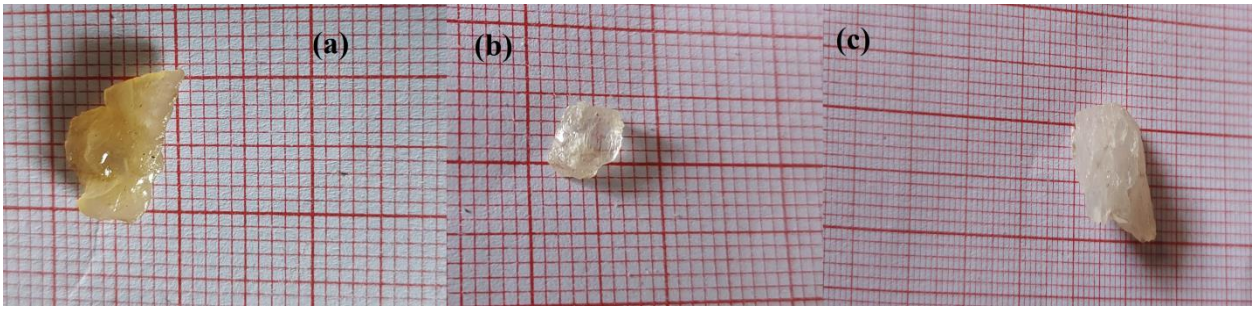

Figure 1: Photograph of as grown crystals of a) pure L-HTFB b) $SrCl_2$ doped L-HTFB and C) $CdCl_2$ doped L-HTFB

2.2 Characterizations Made

A single crystal X-ray diffractometer was used to study the crystal system and determine the lattice parameters with the effect of dopant $CdCl_2$and $SrCl_2$ in L-HTFB crystal. For as-grown and doped crystal, optical tests were carried out using a Perkin Elmer Lamda 35 UV-Visible spectrophotometer. Single crystals of pure and doped L-HTFB have been examined for dielectric characteristics after being sliced into the correct orientation. A small layer of graphite was applied to each sample surface in order to create a good conductive surface layer. The specimen's capacitance and dissipation factor were measured as a function of frequency in the 1 kHz–1 MHz range using an Agilent 4284A LCR metre. Using the powder SHG, the nonlinearity of produced crystals was evaluated. Micro hardness analysis was used to test the crystal's mechanical stability. The impact of dopants on the thermal stability of L-HTFB crystals was investigated utilizing TG/DTA analysis.

3. Results and Discussion

3.1 XRD Analysis

Single crystal XRD unit cell data obtained for $CdCl_2$ and $SrCl_2$ doped crystals are predicted in Table 1**.**From the table it was clear that , $CdCl_2$ doped crystal exhibit the same crystal system as that of pure L-HTFB single crystal as reported by Aggarwal et al [17].But the $SrCl_2$ doping completely alter the atomic arrangement of pure L-HTFB and produce a orthorhombic structure. This may be due to change in bonding interaction of the dopant atom with the host, leading to favor the equal axes angles ($\alpha=\beta=\gamma=90$). However $CdCl_2$ doping expands the volume lattice, by producing expansion along c axis. Orthorhombic crystal systems have distinct symmetry properties because they have three axes that are mutually perpendicular and have varying lengths. Materials' chemical and physical characteristics are influenced by this symmetry. For instance, orthorhombic crystals differ from other crystal types in their optical, electrical, and mechanical characteristics [18]. So we may expect the typical behavior of $SrCl_2$ doped L-HTFB single crystal because of this phase transformation.

Table1: Unit cell parameters obtained through Single crystal XRD for pure and doped L-HTFB

Parameters	Pure L-HTFB	$CdCl_2$ doped L-HTFB	$SrCl_2$ doped L-HTFB
Crystal system	monoclinic system	Monoclinic	Orthorhombic
Unit cell dimensions	a=5.032 Å b= 9.129 Å c= 10.254 Å β=93.39	a = 5.015(7) Å b = 9.102(7) Å c = 10.345(15) Å β = 94.00(14)°	a = 6.8362(20) Å b = 8.934(2) Å c = 15.304(4) Å
Volume	470.21 Å3	471.1(9) Å3	934.7(3) Å3
Z	2	2	4

Moreover to single crystal XRD, the crushed powder of the single crystals were also characterized by PXRD analysis. The PXRD pattern of prepared pure and doped LHTFB were shown in figure 2. The Bragg's peaks of L-HTFB were indexed for the monoclinic system and which were well matched with the reported results by Raj et al [19]. Crystalinity of the $CdCl_2$ doped LHTFB crystal is increased than the pure LHTFB.

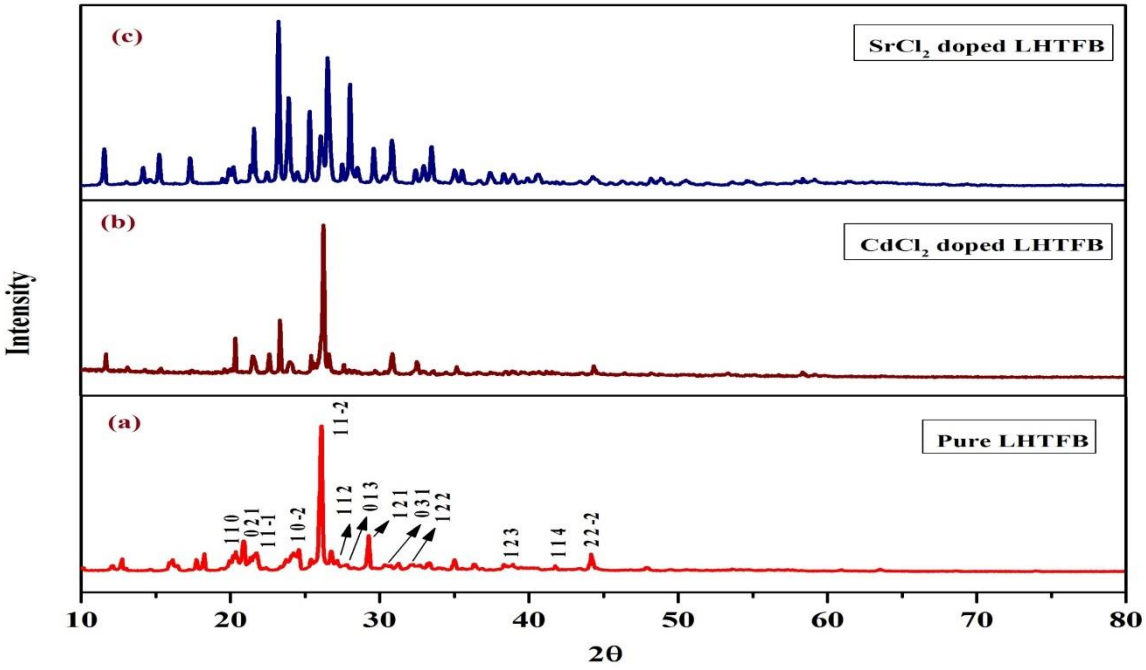

Figure 2: PXRD pattern of grown crystals a) pure L-HTFB b) $CdCl_2$ doped L-HTFB and C) $SrCl_2$ doped L-HTFB

3.2 UV-Vis Spectral analysis of Pure and doped L-HTFB single crystals

Understanding the band structure and the different types of electron transitions is aided by the correlation between the optical absorption coefficient and photon energy [20,21]. In order to find the dopant influence in the band structure of L-HTFB single crystals, UV-Vis spectral absorption of the grown crystals were recorded in the wavelength range of 200 -1100 nm and illustrated in Figure 3. Throughout the whole wavelength range, the pure crystal exhibits perfect transparency. The material exhibits potential as an appropriate substitute for optical materials spanning the visible spectrum, with no absorption occurring between 400 and 900 nm. These attributes make it a promising option for optoelectronic and frequency converter applications.

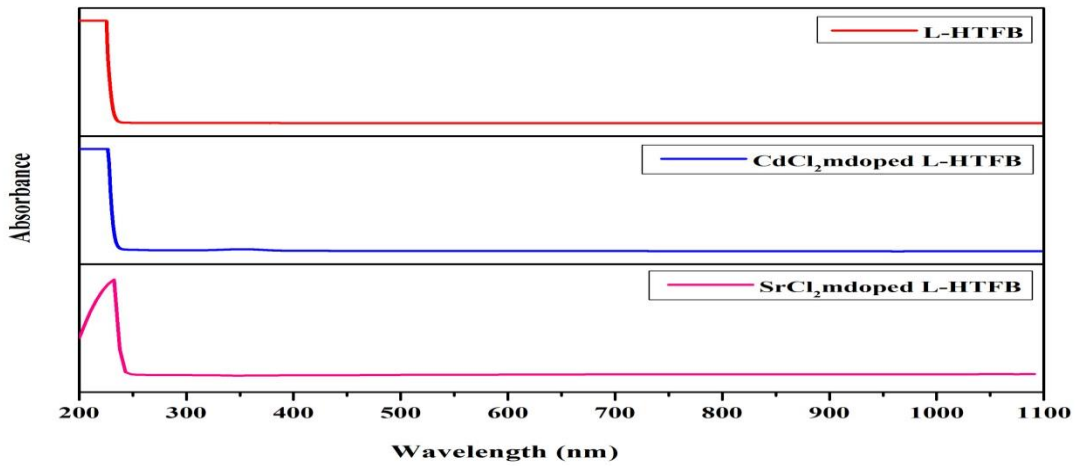

Figure 3: UV-Vis spectral diagram of pure and doped L-HTFB single crystals

Interestingly, akin to the pure crystal, both $CdCl_2$ and $SrCl_2$ doped crystals exhibited remarkable transparency across the entire spectrum. Notably, no significant absorption was observed between 400 and 900 nm, suggesting potential applications in optoelectronic and frequency conversion technologies similar to the undoped crystal. These findings underscore the promise of doped L-HTFB crystals, indicating their viability as versatile optical materials with wide-ranging utility in various technological domains.

As estimate of optical band gap of the grown crystals were done through Taue plot for allowed direct electronic transitions [22]. Taue plot exhibited in Figure 4, evident the lowering of optical bandgap with doping. The optical bandgap of pure L-HTFB crystal is 5.3 eV and which reduced to 5.08 eV for $CdCl_2$ doped L-HTFB crystal and further reduced to 4.74 eV for $SrCl_2$ doped L-HTFB. Doping ($CdCl_2$ and $SrCl_2$) in L-HTFB crystal plays a crucial role in reducing their optical bandgap, leading to significant enhancements in their optoelectronic properties. When dopant ions are introduced into the crystal lattice of L-HTFB, they disrupt its regular structure, creating localized energy states within the bandgap [23]. These dopant-induced states serve as additional pathways for electron transitions, effectively lowering the energy required for excitation and promoting absorption across a broader range of wavelengths. Furthermore, dopants can introduce impurity energy levels that interact with the host material's electronic structure, modifying its band structure and promoting the formation of intermediate energy levels [24].

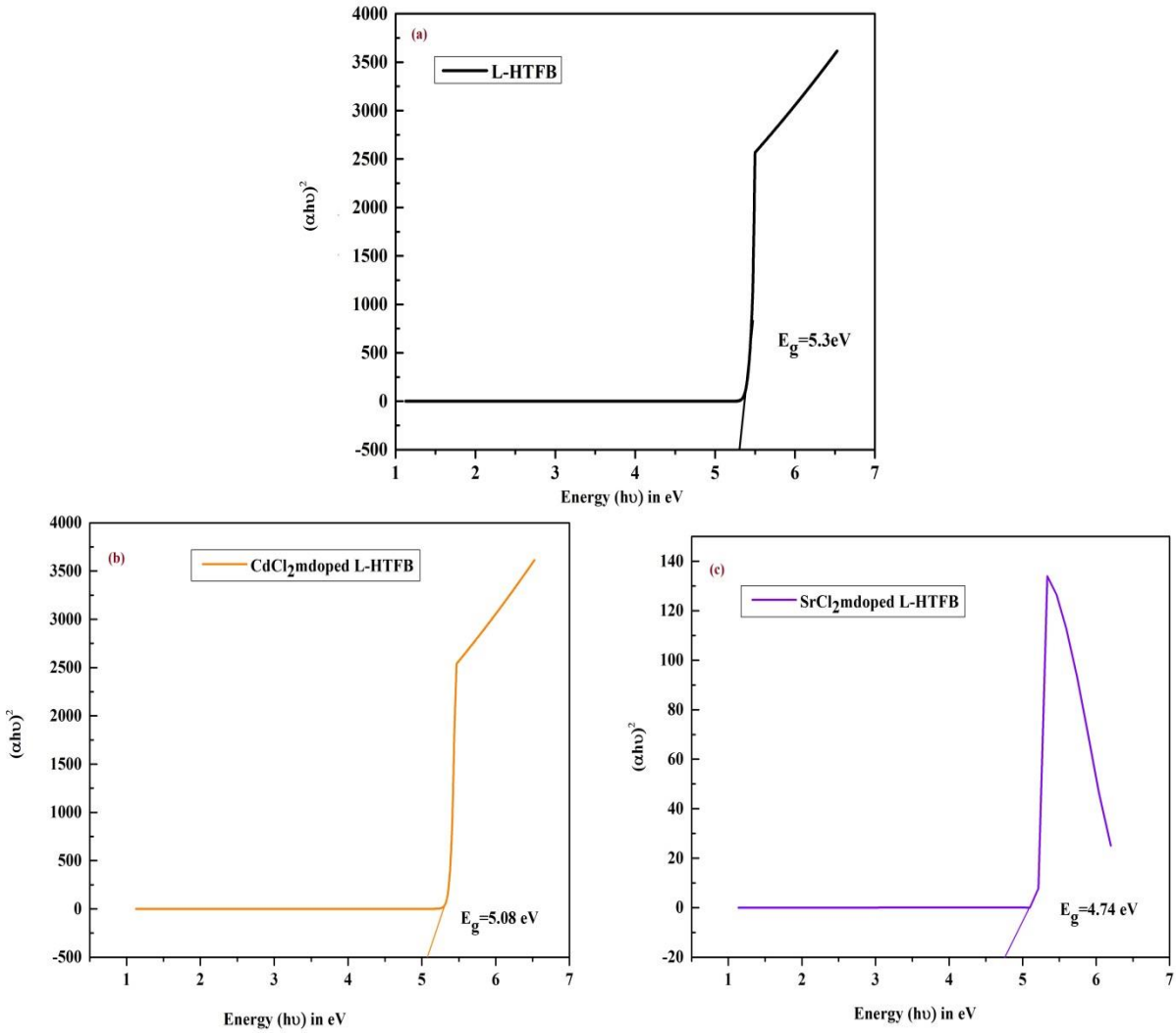

Figure 4: Taue plot for pure and doped L-HTFB single crystals for allowed direct electronic transitions

This optical bandgap reduction effectively lowers the energy required for electrons to transition from the valence band to the conduction band, thereby enhancing their conductivity and enabling them to absorb photons of lower energy, such as in the visible or near-infrared spectrum. This feature is particularly advantageous for applications like photovoltaics, where efficient absorption of solar radiation is crucial for energy conversion, or in photonic devices for telecommunications, where transmission at specific wavelengths is desired. Moreover, a reduced bandgap can also facilitate the development of novel light-emitting diodes (LEDs) or lasers operating at longer wavelengths, expanding the scope of optoelectronic technologies for various industrial and scientific purposes [25]. Therefore, the ability to control and decrease the optical bandgap of doped L-HTFB crystals holds promise for advancing a wide range of optoelectronic applications with improved performance and efficiency.

3.3 Thermal analysis of Pure and doped L-HTFB single crystals

We recorded the TG/DTA thermogram of doped samples in the nitrogen atmosphere in the temperature range of 100-800ºC in order to investigate the impact of dopants on the stability of L-HTFB single crystals. Pure L-HTFB single crystals have been reported to melt at 235°C, go through an endothermic transition due to breakdown at 278°C, and then undergo another endothermic peak at 360°C. These findings were made by S. Dhanuskodi and J. Ramajothi[26]. They also stated that, TGA curve indicates that the compound's volatile ingredients, most likely carbon dioxide and ammonia, cause a weight loss of roughly 20% at 334°C. The DTA curve has no endothermic or exothermic peak beyond 500°C, but the TGA curve gradually loses weight and yields only 38% of the residual weight at 800°C. The recorded thermograms of the doped crystals were shown in Figure 5.

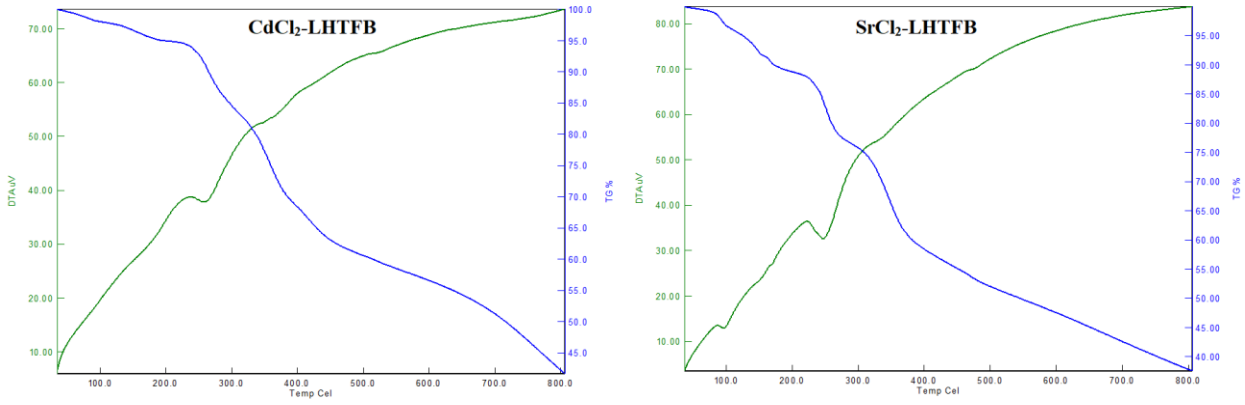

Figure 5: TG/ DTA thermo grams of doped L-HTFB single crystals

As illustrated in figure 5, thermal stability of $CdCl_2$ doped L-HTFB single crystals get increased than pure L-HTFB .Also the melting point of crystal upon doping shifted to higher temperature (258ºC). However, $SrCl_2$ doping induce an endothermic peak in DTA around 120ºC may be due to loss of water of crystallization.

3.4 NLO Test of Pure and doped L-HTFB single crystals

NLO efficiency of the grown crystals were tested via Kurtz-powder technique. In order to obtain the greatest powder SHG, the input laser beam was focused on the as-grown crystal powder. An oscilloscope assembly and photo multiplier tube were used to measure the light that was released after passing through an IR filter. A photomultiplier tube recorded the green light intensity and transformed it into an electrical signal. The output energy of the measured electrical signal evident, the dopant addition highly reduces the SHG efficiency of pure L-HTFB single crystals. However $CdCl_2$ doped samples exhibit 1.7 times efficiency than KDP whereas $SrCl_2$ doped samples have only 1.5 times efficiency than KDP.

3.5 Dielectric analysis

Dielectric measurement is used to examine the electrical characteristics of the grown crystal and analyse its appropriateness for real-world device applications. NLO-property crystals have recently demonstrated improved dielectric conduct [27]. A material's dielectric constant, which provides a contour about the makeup of its atoms, ions, and bonds, is one of the most often utilized key parameters [28-31]. The electro-optical property of the crystal may be determined by measuring its dielectric property. The distribution of electric fields in solids may be explored by the measurement of dielectric property. With an accuracy of ± 2%, the dielectric loss factor and capacitance measurements of both pure L-HTFB single crystal and doped L-HTFB crystal were performed as a function of various frequencies from 100 Hz to 1 MHz.

Figure 6 shows the result of the dielectric constant of pure and doped L-HTFB single crystal with temperature and various frequencies. This makes it abundantly evident that the dielectric constant falls with increasing frequency and rises with temperature at low frequencies. At lower frequencies, the dielectric constant disperses quickly because to interfacial polarization. Due to the dipole's rotational displacements at higher frequencies, which cause orientational polarization, the dielectric constant dispersion becomes less noticeable and almost entirely frequency independent.

Doping $CdCl_2$ and $SrCl_2$ in L-HTFB crystal shows the enhanced dielectric constant than the pure L-HTFB crystal. Notably $SrCl_2$ doped L-HTFB crystal slightly raises the value of ε_r upto 90°C, after which the dielectric constant increases suddenly at all frequencies. This sudden increase in the dielectric constant of $SrCl_2$ crystal after reaching a certain temperature can often be attributed to a phenomenon known as a phase transition. At lower temperatures, the $SrCl_2$ doped L-HTFB crystal may exist in a phase where molecular alignment or interactions restrict the movement of charge carriers in response to an electric field, resulting in a relatively low dielectric constant. However, as the temperature rises past a critical point, the crystal undergoes a phase transition, leading to changes in molecular arrangement or dynamics. This transition can enhance the material's susceptibility to polarization, allowing it to respond more effectively to an applied electric field. Consequently, the dielectric constant of the organic crystal experiences a sudden increase as the temperature surpasses this threshold, reflecting the altered electrical properties associated with the new phase.

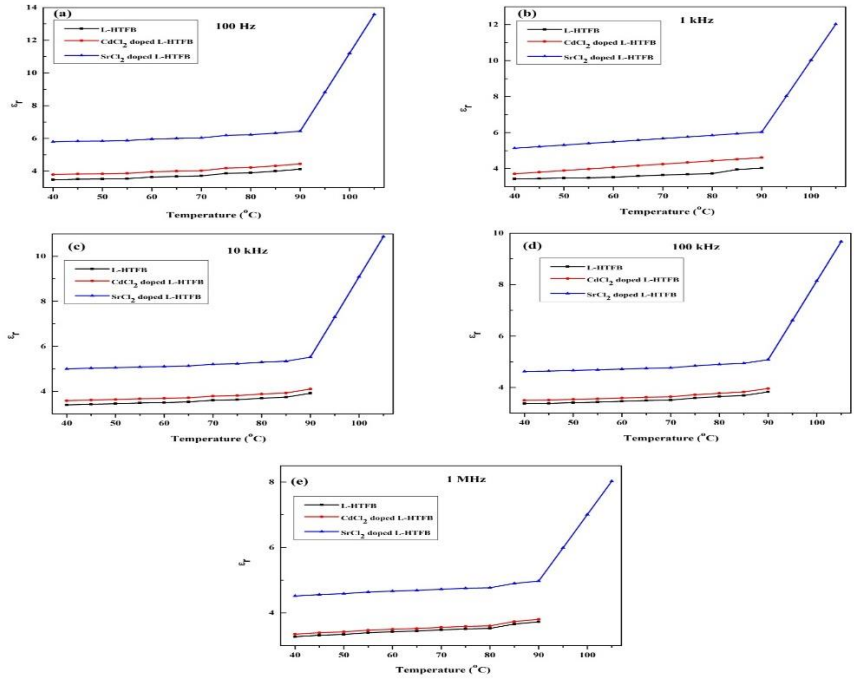

Figure 6. Dielectric constant of pure and doped L-HTFB single crystals

Figure 7 illustrate the variation of dielectric loss as a function of temperature and frequency. From the figure it was noted that the prepared L-HTFB and doped L-HTFB crystals dielectric loss shows the same behavior of dielectric constant.

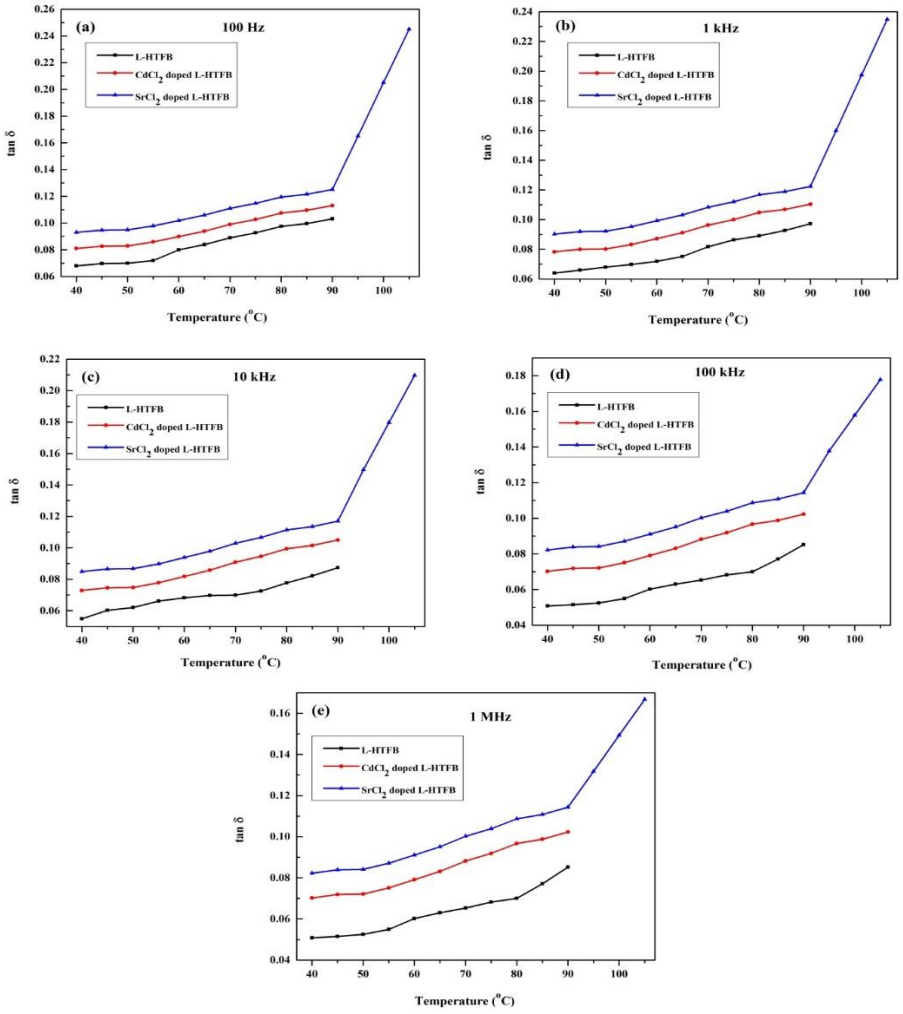

Figure 7. Dielectric loss of pure and doped L-HTFB single crystals

Figure 8 shows the AC conductivity of the grown pure and doped crystal. The AC conductivity increases with increase in temperature and frequency of all the grown crystals. The increase in conductivity may be confidently may be attributed to the optimistic mechanism and this appears by applying the electrical field [32]. Moreover to this $CdCl_2$ and $SrCl_2$ doped crystal shows the enhanced AC conductivity than the bare L-HTFB crystal. In addition to this $SrCl_2$ doped crystal shows the sudden increase in AC conductivity after 90°C. This sudden increase in AC conductivity observed in $SrCl_2$ doped crystal after reaching a particular temperature can often be attributed to a transition from a localized to a delocalized charge carrier regime. At lower temperatures, the mobility of charge carriers may be restricted due to factors such as disorder or trapping sites within the crystal lattice. However, as the temperature surpasses a critical point, thermal energy becomes sufficient to overcome these barriers, promoting the generation of free charge carriers and facilitating their movement through the crystal lattice. This transition from a localized to a delocalized charge carrier regime significantly enhances the $SrCl_2$ doped crystal's electrical conductivity, leading to the observed sudden increase in AC conductivity. Additionally, changes in molecular dynamics or structural rearrangements associated with the temperature-induced phase transition can also influence the crystal's conductivity by altering charge transport mechanisms or reducing scattering events, further contributing to the observed behavior.

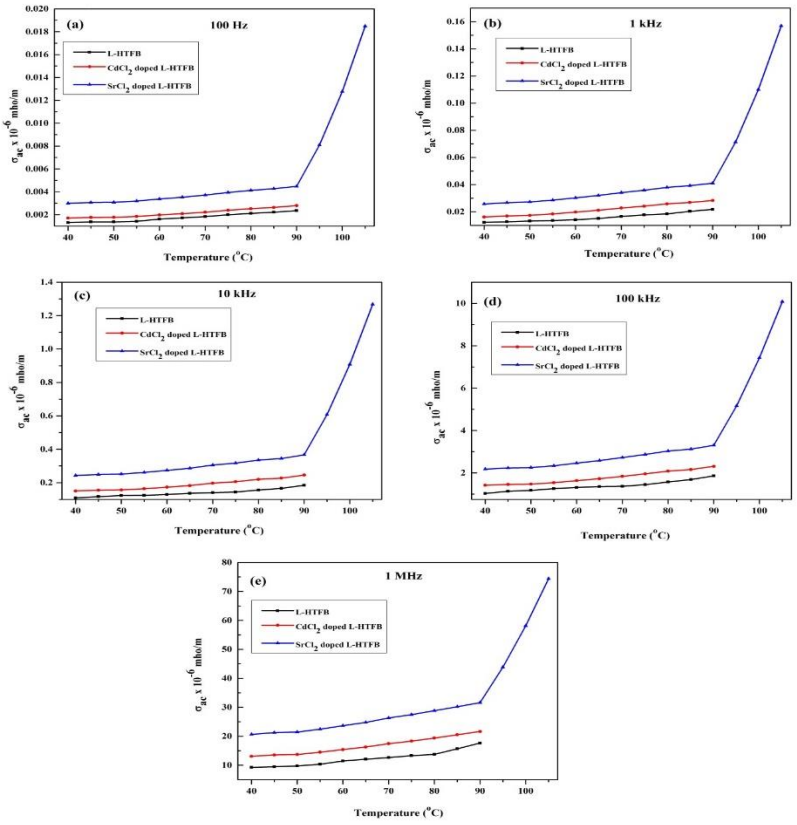

Figure 8. AC conductivity of pure and doped L-HTFB single crystals

Conclusion

Single crystals of L-HTFB doped with $CdCl_2$ and $SrCl_2$ were successfully produced using the slow evaporation method. While $SrCl_2$ doping causes the phase transition from moncoclinic to orthorhombic, $CdCl_2$ doping causes the volume to expand in the L-HTFB lattice. According to TG/DTA Analysis, this phase shift supports the crystals' thermal stability up to 130 degrees Celsius. Additionally, the addition of inorganic dopants reduces the optical bandgap and increases the dielectric constant, making these crystals useful for employing in optoelectronic devices such optical fibres, photodetectors, and light-emitting diodes (LEDs). They can be used as substrates or insulating layers to help in the effective creation, transmission, and detection of light signals.

Reference

[1] A. Joseph Arul Pragasam, M. Divya, A.V. PaniVignesh, G. Vinitha, P. Malliga, Analysis on linear and nonlinear optical properties of an efficient semi-organic crystal: Thiourea borate, Optics & Laser Technology, Volume 107, 2018, Pages 428-434, ISSN 0030-3992, https://doi.org/10.1016/j.optlastec.2018.06.003.

[2] J. Uma, V. Rajendran, Growth and properties of semi-organic nonlinear optical crystal: L-Glutamic acid hydrochloride, Progress in Natural Science: Materials International, Volume 26, Issue 1, 2016, Pages 24-31, ISSN 1002-0071, https://doi.org/10.1016/j.pnsc.2016.01.013.

[3] Ramajothi, J., Dhanuskodi, S., &Nagarajan, K. (2004). Crystal growth, thermal, optical and microhardness studies of tris (thiourea) zinc sulphate - a semiorganic NLO material. Crystal Research and Technology, 39(5), 414–420. doi:10.1002/crat.200310204

[4] M. Mahadevan, M. Magesh, K. Ramachandran, P. Anandan, M. Arivanandhan, Y. Hayakawa, Synthesis, growth, crystal structure and characterization of a new organic NLO crystal: l-Lysine 4-nitrophenolate

monohydrate (LLPNP), SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy, Volume 130, 2014, Pages 416-422, ISSN 1386-1425, https://doi.org/10.1016/j.saa.2014.04.033.

[5] Kumar, B. Suresh, and K. RajendraBabu. "Effect of L-arginine, L-histidine and glycine on the growth of KDP single crystals and their characterization." (2008).

[6] Aravindan A, Srinivasan P, Vijayan N, Gopalakrishnan R, Ramasamy P. A comparative study on the growth and characterization of nonlinear optical amino acid crystals: L-alanine (LA) and L-alanine alaninium nitrate (LAAN). SpectrochimActa A MolBiomolSpectrosc. 2008 Nov 15;71(2):297-304. doi: 10.1016/j.saa.2007.12.023.

[7] Vazquez-Salazar A, Becerra A, Lazcano A. Evolutionary convergence in the biosyntheses of the imidazole moieties of histidine and purines. PLoS One. 2018 Apr 26;13(4):e0196349. doi: 10.1371/journal.pone.0196349.

[8] Ittyachan, R., &Sagayaraj, P. (2003). Growth and characterization of a new promising NLO L-histidine bromide crystal. Journal of Crystal Growth, 249(3-4), 557–560. doi:10.1016/s0022-0248(02)02116-4.

[9] Madhavan, J., Aruna, S., Thomas, P. C., Vimalan, M., Rajasekar, S. A., &Sagayaraj, P. (2007). Growth and characterization of L-histidine hydrochloride monohydrate single crystals. Crystal Research and Technology: Journal of Experimental and Industrial Crystallography, 42(1), 59-64.

[10] Anandan, P., &Jayavel, R. (2011). Crystal growth and characterization of semiorganic single crystals of L-histidine family for NLO applications. Journal of crystal growth, 322(1), 69-73.

[11] P.R. Rougier, J.Y. S. Douillard, E. Culine, P. Suc, Y. Brunet, Becouarn (1997) Phase II study of irinotecan in the treatment of advanced colorectal cancer in chemotherapy-naive patients and patients pretreated with fluorouracil-based chemotherapy Journal of Clinical Oncology 15(1) 251-260.

[12] Remédios, C. M. R., Paraguassu, W., Lima Jr, J. A., Freire, P. T. C., Mendes-Filho, J., Melo, F. E. A., … Miranda, M. A. R. (2008). Effect of Ni(II) doping on the structure of L-histidine hydrochloride monohydrate crystals. Journal of Physics: Condensed Matter, 20(27), 275209. doi:10.1088/0953-8984/20/27/275209.

[13] Anandaraj, L., &Jothi, L. (2022). Investigation on synthesis, growth, optical, mechanical, dielectric and third order non linear optical properties of cadmium chloride monohydrate doped sulphamic acid crystals for nonlinear optical device fabrications. Journal of Molecular Structure, 1250, 131672.

[14] Sivakumar, T., Anna Lakshmi, M., Anbarasan, R., Eniya, P., Vignesh, S., &KalyanaSundar, J. (2022). Exploring the influence of CdCl2 on the nonlinear properties of 4–N, N–dimethylamino–4–N–methyl–stilbazoliumtosylate (DAST) crystal for optoelectronic applications. Materials Technology, 37(8), 618-630.

[15] Mageshwari, P. L., Priya, R., Krishnan, S., Joseph, V., & Das, S. J. (2012). Optical and dielectric studies of cadmium chloride doped single crystals of lithium sulphate. Advanced Materials Research, 584, 65-69.

[16] Selvapandiyan, M. (2019). Growth and studies of cadmium chloride doped L-asparagine single crystal. Int. J. Appl. Eng. Res., 14(1), 137-139.

[17] Aggarwal, M. D., Choi, J., Wang, W. S., Bhat, K., Lal, R. B., Shields, A. D., ... & Frazier, D. O. (1999). Solution growth of a novel nonlinear optical material: L-histidinetetrafluoroborate. Journal of crystal growth, 204(1-2), 179-182.

[18] Md. MijanurRahaman, Mirza H.K. Rubel, Md. Abdur Rashid, M. AshrafulAlam, KhandakerMonowerHossain, Md. Imran Hossain, AnjumanAraKhatun, Md. MukterHossain, A.K.M. Azharul Islam, Seiji Kojima, NobuhiroKumada, Mechanical, electronic, optical, and thermodynamic properties of orthorhonmbic LiCuBiO4 crystal: a first–priciples study, Journal of Materials Research and Technology, Volume 8, Issue 5, 2019, Pages 3783-3794, ISSN 2238-7854, https://doi.org/10.1016/j.jmrt.2019.06.039.

[19] Raj, S. G., Kumar, G. R., Mohan, R., Pandi, S., &Jayavel, R. (2005). Structural, optical and dielectric studies on solution-grown semi-organic L-histidinetetrafluoroborate single crystal. Materials chemistry and physics, 90(1), 144-147.

[20] Greenaway, D. L., &Harbeke, G. (2015). Optical Properties and Band Structure of Semiconductors: International Series of Monographs in The Science of The Solid State (Vol. 1). Elsevier.

[21] Shujahadeen B. Aziz, Rawezh B. Marif, M.A. Brza, Amir N. Hassan, Hiwa A. Ahmad, Younis A. Faidhalla, M.F.Z. Kadir, Structural, thermal, morphological and optical properties of PEO filled with biosynthesized Ag nanoparticles: New insights to band gap study, Results in Physics, Volume 13, 2019, 102220, ISSN 2211-3797, https://doi.org/10.1016/j.rinp.2019.102220.

[22] Vediyappan, S., Vijayan, M., Muthu, S. P., Perumal, R., &SathyadhassAmbalapushpam, M. B. D. (2018). Crystal growth and characterization of an efficient semi-organic nonlinear optical (NLO) donor-π-acceptor single crystal: 2-amino-5-nitropyridinium nitrate (2A5NPN) grown by slow evaporation solution technique (SEST). Journal of Materials Science: Materials in Electronics, 29, 2091-2109.

[23]Apostolova, I.N.; Apostolov, A.T.; Wesselinowa, J.M. Band Gap and Polarization Tuning of Ion-Doped $XNbO_3$ (X = Li, K, Na, Ag) for Photovoltaic and Energy Storage Applications. Molecules 2024, 29, 1011.https://doi.org/10.3390/molecules29051011

[24] Warren, R., Privitera, A., Kaienburg, P. et al. Controlling energy levels and Fermi level en route to fully tailored energetics in organic semiconductors. Nat Commun 10, 5538 (2019).https://doi.org/10.1038/s41467-019-13563-x

[25] SaravananYuvaraja, Vishal Khandelwal, Xiao Tang, Xiaohang Li, Wide bandgap semiconductor-based integrated circuits, Chip, Volume 2, Issue 4, 2023, 100072, ISSN 2709-4723, https://doi.org/10.1016/j.chip.2023.100072.

[26] Dhanuskodi, S., &Ramajothi, J. (2004). Crystal growth, thermal and optical studies of L-histidinetetrafluoroborate: A semiorganic NLO material. Crystal Research and Technology: Journal of Experimental and Industrial Crystallography, 39(7), 592-597.

[27] G. Deepa, T. H. Freeda, and C. Mahadevan, DC Electrical Conductivity Measurements of KDP Single Crystals Added with NaCl and NaBr, Ind. J. Phys. 76A, 369 (2002).

[28] Rajagopal, B., ·Sarma, A. V., and Ramana, M. V., 2011, "Growth and Characterisation of Nickel Doped Magnesium Hydrogen Maleate Hexahydrate Single Crystals," Arch. Phys. Res. 2(3), pp. 180□185.

[29] D. Shyamala, R. Rathikha and K. Gomathi, Dielectric Investigation on Single Crystals of Morpholium Cadmium Aceto-perchlorate,Int.J.Pure and Applied Physics ISSN 0973-1776 Volume 12, Number 1 (2016), pp. 35-46.

[30] Indira.S, Ramesh.K, Viruthagiri.G, dielectric and ac conductivity studies of some inorganic crystalline compounds, Int.J.Current Research Vol. 7, Issue, 05, pp.16448-16451, May, 2015

[31] Suresh sagadevanet al. Investigations on Electrical Properties of Glycine Magnesium Chloride Single Crystal, 2014. Int.J.chemTechRes. 6(5),pp2645-2649.

[32] M. Meena, C.K. Mahadevan, Growth and dielectric properties of L-arginine acetate and L-arginine oxalate single crystals, 2008.