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TECHNOLOGICAL IMPORTANCE OF L-HISTIDINE FAMILY OF NLO SINGLE CRYSTALS

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Abstract. Non-linear optical (NLO) materials possess an importance in laser technology, optical communication and optical storage technology. This review paper deals with the L-histidine family of a single crystal, a promising crystal for non-linear (NLO) applications. The growth of bulk single crystals of these materials has been a subject of permanent disquiet to be useful for device applications. Non-linear optical studies reveal that the dopant increased the efficiency of the L-histidine family of single crystal, and several reports are discussed. Recent papers reveal that the L-histidine family of NLO single crystal possesses excellent optical, thermal, mechanical properties that make it a strong candidate for photonic devices.

1. Introduction

The Non-linear Optics (NLO) is the study of the interaction of an intense electromagnetic field with materials to create modified fields, which are different from the input field in phase, frequency or amplitude [1]. Some materials change when light passes through them, depending upon the orientation, temperature, light wavelength etc., (red light, lower wavelength) releasing one photon of collected higher energy (blue and green light, higher wavelength). NLO materials typically have a definite crystal structure, which is anisotropic with respect to electromagnetic radiation. The significance of non-linear optics is to understand the non-linear behavior in induced polarization and to study and to control its impact on the propagation of light in matter [2]. The generation of coherent light through is a technological problem that has involved much consideration in the last few years [3]. Second Harmonic Generation (SHG) is a non-linear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency [4]. Materials showing high optical non-linearity have potential applications in signal transmission, data storage, optical switching, laser printing, displays, inflorescence, photolithography, remote sensing, chemical and biological species detection, high resolution spectroscopy, medical diagnosis and underwater monitoring & communication [5]. To be useful in this technology, the materials should possess large second order optical non-linearities, short transparency cutoff wavelength and good thermal stability. Organic materials possess good optical non-linearity compared with inorganic crystals, but they are thermally unstable and exhibit a low laser damage threshold [6]. Semi organic crystals have a large damage threshold, wide transparency range, less deliquescence, an excellent nonlinear optical coefficient, low angular sensitivity and exceptional mechanical properties [7, 8]. The present review focuses on and discusses the important properties of L-histidine family of NLO single crystals.

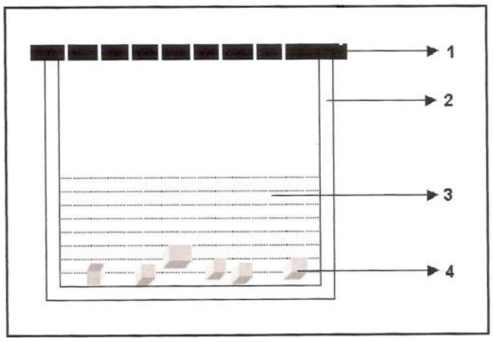
2. Materials and methods

Among various methods of growing single crystals, solution growth at low temperature occupies a prominent place, owing to its versatility and simplicity. Low temperature solution growth can be subdivided into three methods:

i) Slow cooling method
ii) Slow evaporation method and
iii) Temperature gradient method

Among these methods, the slow evaporation method is widely used to produce crystals. This is a simple and convenient method for growing crystals of large size. The processes of the slow evaporation method are briefly discussed.

Slow evaporation technique. As far as the apparatus is concerned, slow cooling and slow evaporation methods are similar to each other. In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation. If the solvent is non-toxic like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve a temperature stabilization of about 0.05 °C and the rate of evaporation of a few mm^3/h. The evaporation technique has an advantage; viz., the crystals grow at a fixed temperature. But, inadequacies of the temperature control system still have a major effect on the growth rate. This method can effectively be used for materials having a very low temperature coefficient of solubility. The evaporation of solvent from the surface of the solution produces high local super saturation and formation of unwanted nuclei. Small crystals are also formed on the walls of the vessel, near the surface of the liquid from the material left after evaporation. These tiny crystals fall into the solution and hinder the growth of the single crystal. This is a simple and convenient method for growing single crystals of a large size. Seed crystals are prepared by self-nucleation under slow evaporation from a saturated solution (Fig. 1). Seeds of good visual quality, free from any inclusion and imperfections are chosen for growth. Since the strain free refaceting of the seed crystal results in low dislocation content, a few layers of the seed crystal are dissolved before initiating the growth.



1. Perforated closed lid;
2. Crystallization vessel;
3. Supersaturated solution;
4. Seed crystal

Fig. 1. Apparatus for the preparation of seed crystals.

3. L-histidine family of NLO single crystals

Nonlinear optics is a new frontier of science and technology playing a major role in the emerging area of photonics. Photonics involves the application of photons for information and image processing and is branded to be the technology of the 21st century, wherein nonlinear optical (NLO) processes have applications in vital functions such as frequency conversion and optical switching. These require materials that exhibit second-order NLO effects and hence, there is a great need for good quality single crystals for device fabrication. The inorganic materials were the first to be exploited for such applications. Further investigations on organic

NLO materials have subsequently produced very good materials with highly desirable characteristics.

Materials with large second-order nonlinearities, short transparency cut-off wavelengths and stable physicochemical performances are needed in order to realize many of the applications. Because of the effectiveness in generating new frequencies from existing lasers, viz; harmonic generation and sum and difference frequency generation, there has been an extensive effort in recent years to identify effective materials for such processes. Along with high nonlinearity, these materials must be transparent not only for the laser frequency but also for the newly generated frequency. These materials should (i) be resistant to optical damage, (ii) have sufficient mechanical hardness, (iii) exhibit good thermal and chemical stability, (iv) be capable of being grown in useful sizes, and (v) have the appropriate phase – matching properties.

Frequency conversion is one of the important and popular techniques to extend the useful wavelength range of lasers. Despite all the efforts, only a handful of nonlinear crystals are commonly available for frequency conversion. Complexes of amino acids with inorganic salts are promising materials for optical Second Harmonic Generation (SHG). The present review is aimed towards the development of L-histidine family of NLO single crystals. All these materials are potential candidates for NLO application, due to their high non-linearity, and extended thermal and mechanical stabilities.

3.1. L-histidine hydrofluoride dihydrate (LHHF). Single crystals of L-histidine hydrofluoride dihydrate (LHHF) were grown using the slow evaporation technique by Madhavan et al. [9]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to the orthorhombic crystal system with the space group $P2_1$, and the lattice parameters are a= 8.439 Å, b = 8.562 Å, c = 13.897 Å, V =993.412 $Å^3$. The UV analysis reveals that the cut off wavelength is around 220 nm. The thermal analysis shows that the crystal is thermally stable up to 108 °C. The mechanical property of the grown crystal has been studied by the microhardness test and it is noticed that there is a decrease in the microhardness number with an increase in the load. The SHG efficiency is found to be 6 times that of the KDP crystal.

3.2. L-histidine tetrafluoroborate (LHTFB). Single crystals of L-histidine tetrafluoroborate were obtained from a recrystallized material using the slow evaporation technique by Marcy et al. [10]. The XRD studies of the single grown crystal of LHTFB reveal that it is a monoclinic crystal with the space group $P2_1$. The calculated lattice parameters are a=5.022 Å, b=9.090 Å, c=10.216 Å, β=93.484°. The thermal analysis shows that the LHTFB has a decomposition temperature of 205 °C. The Vicker's microhardness test of LHTFB shows that the microhardness number increases with an increase in the load, which confirms the reverse indentation size effect. The SHG efficiency is 5 times greater than of the KDP.

3.3. Thiourea added L-histidine (TULH). Single crystals of Thiourea added L-histidine have been grown, using the slow evaporation technique by Nalini Jayanthi et al. [11]. The TULH crystal belongs to the orthorhombic crystal system with space group $P2_12_12_1$. The lattice parameters were found to be a=5.14 Å, b=7.33 Å, c=18.61 Å, α =β= γ =90°, and cell volume of 701 $Å^3$. The lower cutoff wavelength was around 310 nm. The TG-DTA studies reveal that the crystal is thermally stable up to ~285.67 °C. The Vicker's microhardness values were measured and the mechanical study reveals the reverse indentation size effect. The NLO efficiency is 4.1 times of the KDP.

3.4. L-histidine acetate (LHA). L-Histidine acetate single crystal was grown using the slow evaporation technique by Prabagaran et al. [12]. The grown crystal was characterized by single X-ray diffraction (XRD) studies to confirm the crystal structure. The lattice parameters of the grown crystals are a= 8.530 Å, b=9.150 Å, c=9.063 Å, α =61.73°, β=86.64°, γ=86.28° and the crystal has a monoclinic structure with the space group P_1. The thermal stability of the materials was established by the TG/DTA and it is observed that the material is stable up to 274.6 °C. The microhardness studies reveal that the hardness of the grown crystal increases with an increase in the load. The SHG efficiency is 3.8 times that of the KDP.

3.5. L-histidine hydrochloride monohydrate (LHHC). Single crystal of L-histidine hydrochloride monohydrate was grown using the slow evaporation technique by Suresh et al. [13]. The grown crystals have an orthorhombic structure with the $P2_12_12_1$ space group. The lattice parameter values of the grown crystals are a = 6.82 Å, b = 8.91 Å, c = 15.286 Å. The thermal studies show that the crystal is stable up to 172 °C. The microhardness test shows the decrease in the hardness number with an increase in the load. The output power intensity of LHHC has been found to be 3.0 times that of the output power intensity of the KDP.

3.6. L-histidinium dipicrate dihydrate (LHDD). The single crystals of L-histidinium dipicrate dihydrate were grown using the slow evaporation method by Sethuram et al. [14]. The grown crystals were characterized by the single crystal XRD. The crystal is monoclinic with the space group $P2_1$ and the lattice parameters are a = 6.606 Å, b= 25.700 Å, c =7.962 Å, α =90°, β= 107.5°, γ =90°, V =1289 Å^3. The UV cut-off is found to be at 354 nm. The thermal stability was found to be 210°C using the TGA and DTA analyses. The Vicker's microhardness test of LHDD shows that the microhardness number increases with an increase in the load, which confirms the reverse indentation size effect. The SHG efficiency of L-histidinium dipicrate dihydrate is 2.5 times greater than that of the standard potassium dihydrogen phosphate (KDP) sample.

3.7. L-histidinium 2-nitrobenzoate (LHNB). Nonlinear optical active single crystals of L-histidinium 2-nitrobenzoate were grown using the slow evaporation method by Moovendaran et al. [15]. Single crystal X-ray diffraction analyses have been made to confirm the monoclinic structure with the non-centrosymmetric space group $P2_1$ and the lattice parameters are a = 5.147 Å, b = 7.228 Å, c = 18.887 Å, β = 92.72°, V= 701.8 Å^3. The thermo gravimetric analysis shows that the thermal stability was found to be 189 °C. The microhardness test reveals that the microhardness number increases with an increase in the load. The SHG efficiency of L- histidinium 2-nitrobenzoate is 2 times greater than that of the KDP sample.

3.8. L-histidine hydrobromide (LHHB). Single crystals of semi-organic L-histidine hydrobromide have been grown by the slow evaporation technique by Anandan et al. [16]. The grown crystals possess an orthorhombic crystal structure with the space group $P2_12_12_1$ and the lattice parameter values are a= 7.046 Å, b=9.061 Å and c= 15.271 Å. The crystals possess a UV cutoff below 300 nm as seen from the UV analysis. The grown materials are thermally stable up to 162.5 °C. The microhardness study shows the increasing of the microhardness number with an increase in the load. The SHG efficiency of LHHB has been found to be 1.6 times that of KDP.

3.9. L–histidine sodium thiosulphate (LHST). A semi organic non-linear optical single crystal of L–Histidine sodium thiosulphate was grown using the slow evaporation technique by Radha Ramanan et al. [17]. The lattice parameters of the grown crystals are a=5.341 Å, b=7.301 Å, c = 18.739 Å and the crystal structure is monoclinic. The optical absorption studies have confirmed that the grown crystal possesses less absorption in the entire visible region and the UV cut-off is found to be at 230 nm. The microhardness value increases with increases of applied load. The TG-DTA studies reveal that the crystal is thermally stable up to ~200 °C. The output power of L-HST is found to be greater than that of the KDP.

3.10. L-histidinium maleate (LHM). L-Histidinium maleate, an organic nonlinear optical material has been grown using the slow solvent evaporation method by Alosious et al. [18]. The grown crystal was subjected to single crystal X-ray diffraction study and the calculated lattice parameters of the grown crystals are a = 11.465 Å, b = 8.053 Å, c =

14.970 Å, V = 1353.7 Å^3, α= γ = 90º and β = 101.65°. The grown crystal is completely transparent in the UV and visible spectral regions, with the lower cut off wavelength around 280 nm. The thermal analysis reveals that the sample is thermally stable up to 117.5 °C. The microhardness studies reveal that the hardness of the grown crystal increases with an increase in the load. The SHG efficiency of L-histidinium maleate is equal to that of the standard potassium dihydrogen phosphate (KDP) sample.

3.11. L-histidinium trifluoroacetate (LHTA). Single crystals of L-histidinium Trifluoroacetate were grown using the slow evaporation technique by Suresh et al. [19, 20]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to the triclinic crystal system with the space group P1 and lattice parameters are a = 5.17 Å, b = 8.84 Å, c = 12.48 Å, α =96.19°, β = 100.02° and γ =102.01°. The optical transmission studies show that the crystal is transparent in the entire visible region with a cut off wavelength of 230 nm. The grown materials are thermally stable up to 216 °C. The mechanical property of the grown crystal has been studied by the microhardness test and it is noticed that there is an increase of the microhardness number and of the material is soft. The SHG efficiency is 1.2 times greater than that of KDP.

3.12. L histidine nitrate (LHN). Single crystals of L-Histidine Nitrate were grown from an aqueous solution using the slow evaporation technique by Suresh et al. [21]. The single crystal X-ray diffraction analysis reveals that the crystal belongs to the orthorhombic system with the space group $P2_12_12_1$ having lattice parameters of a = 5.23 Å, b = 7.13 Å and c = 25.02 Å, α= β = γ = 90°. The UV absorption edge for the grown crystal was observed to be around 230 nm. The TGA/DTA studies showed that this crystal is stable up to 234 °C. The microhardness test reveals that the microhardness number decreases with an increase in the load. The SHG efficiency is 1.5 times greater than that of KDP.

4. Results and discussion

The growth of crystals from aqueous solution, one of the methods of crystal growth, which is extremely popular in the production of many technologically important crystals, was adopted to grow the NLO crystals. Various physical properties of the crystals are studied from the application point of view. This paper summarizes the work carried out on the L-histidine family of NLO single crystals. Materials having moderate to high solubility can be grown by the low temperature solution growth technique that is well suited for growing NLO crystals. The lattice parameters and the important properties of the grown crystals are listed in Table 1.

Table 1. Important properties of L-histidine family of single crystals

S. no	Name of compound	Single crystal analysis	Thermal analysis	Microhardness	SHG
1	L-Histidine Hydrofluoride dihydrate	a= 8.439 Å, b = 8.562 Å, c = 13.897 Å, V =993.412 Å^3, Orthorhombic, $P2_12_12_1$	108 °C	Microhardness of the crystal decreases with increasing load	Six times greater than of KDP
2	L -Histidine Tetra-fluoroborate	a=5.022 Å, b=9.09 Å, c=1.0216 Å β=93.484°, Monoclinic, $P2_1$	205 °C	Microhardness of the crystal increases with increasing load	5 times greater than of KDP
3	Thiourea added L-Histidine	a=5.14 Å, b=7.33 Å, c=18.61 Å, α =β= γ =90°, V=701 Å^3, Orthorhombic, $P2_12_12_1$	285.67 °C	Hardness number increases with increase in load	4.1 greater than KDP

Table 1 *(continued)*

4	L-Histidine Acetate	a=8.53 Å, b=9.15 Å c=9.06 Å, β=86.64°, α=61.73°, γ =86.28°, V=611.8 $Å^3$, Triclinic, P1	274.6 °C	Hardness number increases with increase in load	3.8 greater than KDP
5	L-Histidine Hydrochloride Monohydrate	a= 6.82 Å, b= 8.91 Å, c= 15.286 Å, Orthorhombic, $P2_12_12_1$	172 °C	Decrease in hardness number with increase in load	3 times greater than KDP
6	L-Histidinium Dipicrate Dihydrate	a= 6.606 Å, b= 25.700 Å, c=7.962 Å, α =90°, β = 107.5°, γ =90°, V =1289.0 $Å^3$, Monoclinic, $P2_1$	210 °C	Hardness number increases with increase in load	2.5 times greater than KDP.
7	L-Histidinium 2-nitrobenzoate	a= 5.147 Å, b= 7.228 Å, c= 18.887 Å; β = 92.72°, V= 701.8 $Å^3$, Monoclinic, $P2_1$	189 °C	Hardness number increases with increase in load	2 times greater than that of KDP
8	L-Histidine Hydrobromide	a=7.046 Å, b=9.061 Å, c=15.271 Å, Orthorhombic, $P2_12_12_1$	162.5 °C	Increase of hardness number with increase in load	1.6 times greater than KDP
9	L-Histidine Sodium Thiosulphate	a=5.341 Å, b=7.301 Å, c=18.739Å, β=90.3°, V=370 $Å^3$, Monoclinic	200 °C	Increases with increases of applied load	Greater than KDP
10	L-Histidinium Maleate	a=11.4656 Å, b=8.0530 Å, c=14.9705 Å, β=101.65°, α=γ=90°, V=1353.75 $Å^3$, Monoclinic, $P2_1$	117.5 °C	Hardness number increases with increase in load	Equal to KDP
11	L-Histidinium Tri-flouroacetate	a=5.17 Å, b=8.84Å, c=12.48 Å, β=100.2°, α= 96.19°, γ =102.01°, Triclinic, P1	216 °C	Hardness number increases with increase in load	1.2 times greater than that of KDP
12	L- Histidine Nitrate	a = 5.23Å, b = 7.13Å, c = 25.02Å, α= β = γ = 90°, Orthorhombic system, space group $P2_12_12_1$	234 °C	Hardness number decreases with increase in load	1.5 times greater than that of KDP

The organic and semi-organic crystals have increased thermal stability. The thermal stability of the grown crystals is found to be more. Among the grown crystals, the SHG efficiencies are LHHF> LHTFB> TULH> LHA> LHHC> LHDD> LHNB> LHHB> LHN> LHTA> LHST> LHM. The L-histidine family of NLO crystals is found to be semi-organic and to possess the NLO efficiency and thermal stability.

5. Conclusion

The Non-linear optical material, L-histidine family of single crystal growth has been dealt with in this review. The crystals were mostly grown from aqueous solution by slow evaporation technique. This review will provide encouraging inputs to continue the research with various dopants in the growth of L-histidine family of single crystals that will be a highly useful NLO material.

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