Studies on L-cystine hydrobromide single crystals for nonlinear optical applications

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ABSTRACT

L-cystine hydrobromide (LCHBr) is a novel nonlinear optical material which has been synthesized and grown. The low-temperature solution growth technique was employed to grow the single crystal of LCHBr. The structure of the grown crystals was characterized by single-crystal XRD. The different functional groups of the grown LCHBr crystal are studied using FTIR spectroscopy. The transparent nature of the grown crystal was analysed by UV–Vis–NIR study. The mechanical strength of the grown crystal was analysed using microhardness study. The optical second harmonic generation conversion efficiency of the LCHBr crystal was studied using Nd:YAG laser. The laser damage threshold value of this grown crystal has been evaluated.

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1. Introduction

The nonlinear optical (NLO) materials have been reported to have several applications in the fields of optical computing, optical disk data storage, medical diagnostics, etc. [1]. Recently, a variety of semi-organic crystals for NLO applications have been developed [2–5]; among them, the amino acids are found to have a definite edge over other materials due to the following special features: (i) the absence of strongly conjugated bonds and (ii) the zwitterionic nature of the molecules, which favours a wide transparency window in the visible region and physicochemical stability of the materials. In view of this, a series of amino acids used as semi-organic materials, such as L-arginine phosphate [6], L-histidine hydrobromide [7], L-cystine hydrochloride [8], L-valine hydrochloride [9], beta-alanine zinc chloride [10] and L-phenylalanine L-phenylalaninium perchlorate [11] as potential NLO crystals has been reported.

L-cystine belongs to the sulphur-based proteinogenic amino acid family. L-cystine with inorganic acid-based new complexes can be synthesized; identifying this material as new NLO materials has been reported [8,12–14]. The crystal structure of this L-cystine hydrobromide (LCHBr) compound has already been reported [15,16]. To the best of our knowledge, there is no report available on the growth, characterization and NLO properties of this LCHBr compound. The present study includes the synthesis, growth of LCHBr by a solvent evaporation method using deionized water as a solvent. The grown crystals were studied by single-crystal XRD, FTIR and UV–vis–NIR analyses. The mechanical behaviour studies were also carried out on the grown crystals. The NLO behaviour of this crystal on factors such as the second harmonic generation (SHG) conversion efficiency and Laser damage threshold value has been evaluated using Nd:YAG laser.

2. Experimental procedure

2.1. Synthesis and crystal growth

LCHBr was synthesized from L-cystine (Loba Chemie) and hydrobromic acid (AR grade). A homogeneous solution of L-cystine was prepared by constant stirring and heating at room temperature for 1–2 h. The clear equimolar solution of hydrobromic acid was added to the L-cystine solution. The reaction that took place was as follows:

$$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2 + \text{HBr} \rightarrow [\text{C}_6\text{H}_{13}\text{N}_2\text{O}_4\text{S}_2]^+ \cdot \text{[Br]}^-.$$ 

The calculated amounts of L-cystine and hydrobromic acid were systematically dissolved in double-distilled water and simultaneously heated at room temperature. The vigorous stirring was continuous for 4–5 h to get a saturated solution. The prepared saturated solution was purified by filtering through the fine pores using Whatman filter paper. The purity of the synthesized materials of LCHBr was increased using the recrystallization method. The homogeneously prepared saturated solution was filtered and transferred to new...
cleaned crystal growth vessels and closed with perforated sheets so that it evaporates slowly. Using the slow evaporation technique, a well-developed optical quality single crystal of LCHBr was obtained after 30 days of growth, this is shown in Figure 1.

3. Characterization

The ENRAF NONIUS CAD4 diffractometer was used to estimate crystallographic data of the LCHBr crystal and the lattice parameter values of the grown crystal. The coordination of L-cystine with hydrobromic acid was confirmed by FTIR studies using the BRUKER 66 V FTIR spectrometer in the range of 4000–400 cm$^{-1}$. The optical transmission spectra of LCHBr crystals have been recorded in the region of 200–1400 nm using a Shimadzu UV-1061 UV–vis spectrometer. Microhardness measurements of the LCHBr crystal were carried out using a Vickers microhardness tester. The NLO property is confirmed by Kurtz powder SHG efficiency using Nd:YAG laser.

4. Results and discussions

4.1. Single-crystal X-ray diffraction analysis

The lattice parameter value of the grown crystal was analysed by single-crystal XRD and refined with the full-matrix least-squares technique using SHELX program. The lattice parameter values are calculated using the above program which was in accordance with the reported parameters [15,16]. The calculated lattice parameter values are tabulated and compared with the reported values in Table 1. LCHBr belongs to the orthorhombic space group $P_{2_1}2_12_1$, which is recognized as a noncentrosymmetric structure, this is the basic essential requirements for the generation of second harmonic efficiency in the crystal [17].

4.2. FTIR analysis

The infrared spectrum of the grown LCHBr crystal recorded using the KBr pellet method is shown in Figure 2. The presence of various functional groups in the LCHBr crystal is tabulated in Table 1. There was a broad, strong absorption range in 2700–3500 cm$^{-1}$ including and the peak at 3406 cm$^{-1}$ corresponds to the $\text{NH}_3^+$ stretching of the amino acid. These regions superimposed of those $\text{O–H}$ and $\text{NH}_3^+$ vibrations and also the lower wave number side band gives multiple fine structures and weak absorption due to COO$^-$ ions. A strong band arising from CH$_2$ wagging is observed at 1293 cm$^{-1}$. Also, the prominent strong symmetrical $\text{NH}_3^+$ deformation band is around 1582 cm$^{-1}$ [18]. Strong absorption peaks at 1337 and 1040 cm$^{-1}$ are assigned to C–C and C–N stretching vibrations, respectively. The strong carbonyl absorption at 1736 cm$^{-1}$ confirms the COOH and COO$^-$ groups of

![Figure 1. As-grown LCHBr single crystal.](image)
the L-cystine material [19]. The appearance of this band confirms the formation of a bromic salt of L-cystine [20]. This justifies the protonation of the carbonyl group in LCHBr. The absorptions of LCHBr have been compared with the L-cystine material in Table 2. The characteristic peak shifts in the positions confirm the protonation of cystine by hydrobromic acid.

4.3. Optical transmission studies

The UV–visible range gives an idea of the structure of the molecule because the absorption of visible light raises the energy of the ground state to higher energy states and this involves movement of the electron from σ to π orbital. This spectrum plays an important role in the field of optical materials because practically only these group of materials that have a wide transparency window in this region and are used for NLO applications. To find the transmission range of LCHBr, the optical transmission spectrum was recorded for the grown crystal in the region between 200 and 1400 nm. In Figure 3, the absorption is not registered up to the wavelength 248 nm is reached from 1400 nm. At 248 nm, a sharp fall of transmittance which goes to nearly zero is observed, this indicates that the material has a single transition in the near UV region of LCHBr. So this LCHBr crystal is transparent in the wavelength range of 248–1400 nm. More than 70% of transmittance and no absorption in the visible region are advantages and the prerequisite nature for crystals used in NLO applications.

4.4. Powder second harmonic generation measurement

Kurtz and Perry [21] performed the SHG test to find the NLO property of the LCHBr crystal. The fine crushed powdered material was filled in a microcapillary tube and it was illuminated using Q-switched Spectra Physics Quanta Ray Nd:YAG laser. The incident laser beam has 10 Hz repetition rate, 8 ns pulse width and 1064 nm output. From the powdered material bright green light was emitted and confirmed by SHG and it was collected by a Philips Photomultiplier tube

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Table 2. FTIR spectral band assignments of the LCHBr.

| Wave number (cm⁻¹) | L-cystine [20] (present work) | Assignments |
|-------------------|-------------------------------|-------------|
| 457              | 501                           | S–S stretching, C–C deformation |
| 540              | 586                           | C–C deformation |
| 675              | 658                           | C–S stretching |
| 775              | 764                           | C–H₂ rocking vibration |
| 845              | 861                           | NH⁴⁺ rocking |
| 1043             | 1040                          | C–N stretching |
| 1090             | 1081                          | C–C stretching |
| 1126             | 1123                          | C–C stretching |
| 1194             | 1182                          | C–C stretching |
| 1298             | 1293                          | CH₃ wagging |
| 1342             | 1337                          | C–C stretching |
| 1408             | 1388                          | CH₃–CO symmetric deformation |
| 1489             | 1480                          | COO⁻ symmetric stretching |
| 1585             | 1582                          | NH⁴⁺ symmetric deformation |
|                  | 1736                          | COO⁻ stretching |
| 2096             | 2071                          | NH⁴⁺ stretching |
| 2839             | 2898                          | CH₃ stretching |
| 2920             | 2974                          | CH₃–S asymmetric stretching |
| 3429             | 3406                          | NH⁴⁺ asymmetric stretching |

Figure 2. FTIR spectrum of the LCHBr crystal.
After being monochromator (model Triax-550) only 532 nm radiation is collected. The collected optical incident signal was converted into voltage output at CRO (Tektronix). The same experiment was repeated using the reference material KDP. The result obtained for LCHBr shows a powder SHG efficiency of about two times higher than that of standard KDP. This LCHBr crystal SHG efficiency has a higher value than that reported from other L-cystine-based NLO materials, such as L-cystine hydrochloride being 1.2 times [8], L-cystine dihydro bromide being 0.38 times [12], L-cysteine tartrate monohydrate being nearly 0.2 times [13] and L-cystine dihydrochloride being 0.34 times [14].

4.5. Laser damage threshold

In the NLO material, the laser damage threshold property is important. As high optical intensities are involved in this nonlinear material, it must be able to withstand high power laser intensities. Using a Q-switched Nd:YAG laser, the laser damage threshold value of the LCHBr single crystal was evaluated. The laser contains a pulse width of 5 ns with a repetition rate of 10 Hz and a wavelength of 1064 nm. As the crystal has a higher dislocation density it has low resistance to laser damage because of this in the present study defect-free polished surface crystals were used. The laser surface damage threshold of the grown crystals was evaluated using the power density = \( E/A \) (GW/cm²), where \( E \) (mJ) is the energy required to cause damage and \( A \) is the area of the laser circular spot. The laser-induced breakdown of crystals is caused by the avalanche and multi-photon ionizations. The damage threshold analysis has to increase the temperature because the strong absorbing of crystalline materials this induces the strains with fractures [22]. The laser damage threshold energy density of the LCHBr crystal was found to be 3.65 GW/cm². This is a higher energy range compared to L-cystine dihydro bromide crystal (2.15 GW/cm²) [23].

4.6. Microhardness study

The mechanical strength depends upon the structure and composition of the crystalline solids. To understand the mechanical behaviour of the material such as yield strength, cracking temperature, Brittle value and etc., are calculated using hardness, this is the one of the method for simple and effective [24]. This micro-hardness value has evaluated from the Vicker’s indenter method fitted with a diamond pyramid. In this study, polished crystals are used and different magnitudes (10, 50 g) were applied over a fixed interval of time such as 10 s. Vicker’s hardness value has been calculated using \( H_v = \frac{1.8544P}{d^2} \) kg/mm², where \( P \) and \( d \) are the applied load and mean diagonal length of the impression, respectively. Figure 4 is a plot between the applied load and hardness number. From the graph it can be seen that when the applied load increases the hardness value initially increases and then attains near saturation. The hardness number of the compound is found to be 89.5 kg/mm². When the load was increased to 40 g, multiple cracks developed on the surface of the crystal because the internal stress is generated locally due to the indentation. This LCHBr crystal hardness values were found to be high, when compared with other L-cystine-supported NLO materials, such as L-cystine hydrochloride being 56.9 kg/mm² [8], L-cystine dihydro bromide being 44.8 kg/mm² [12], L-cysteine tartrate monohydrate being 84.3 kg/mm² [13] and L-cystine dihydrochloride being nearly 82 kg/mm² [14].

5. Conclusion

Optically transparent, the single crystal of LCHBr has been grown using the solvent evaporation solution technique with dimensions of about 9 × 4 × 3 mm³. The single-crystal X-ray diffraction data reveal that LCHBr belongs to the orthorhombic system. The XRD results are found to be in agreement with the reported values. The spectroscopic evaluation suggests that the
grown crystalline material has several functional groups. The lower cut-off wavelength (248 nm) and the transmittance range (248–1400 nm) have been observed from the UV spectrum confirming that the grown crystal is suitable for SHG applications. The powder SHG measurement shows that the grown LCHBr crystal has high efficiency when compared with KDP. The laser damage threshold value has been calculated and this value has higher than that of other reported parent L-cystine NLO crystal. Owing to the high transparency nature, high SHG, high damage threshold and high mechanical strength, the LCHBr crystal has been suggested to be suitable for optoelectronic applications.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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