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Growth and optical properties of L-alanine hydrobromide: A nonlinear optical single crystal

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ABSTRACT

Good quality single crystals of L-alanine hydrobromide (LAlHBr) were grown by slow solvent evaporation technique. Single crystal X-ray diffraction studies were carried out to confirm the grown LAlHBr crystals. UV–Vis–NIR studies have been carried out and the absorption of these grown crystals were analyzed. It was found that these crystals possess minimum absorption in the entire visible region. The functional groups of LAlHBr crystals were analyzed by Fourier transform Infrared (FT–IR) studies. Photoconductivity studies were carried out and it reveals that LAlHBr shows negative photoconductivity. Nonlinear optical studies of crystals were carried out and the second harmonic generation efficiency of the powdered sample was measured using Nd:YAG Q-switched laser. SHG efficiency of LAlHBr crystal is found to be greater than KDP.

INTRODUCTION

Nonlinear optical (NLO) organic materials have received much importance for optical second harmonic generation (SHG) owing to their practical applications in the domain of optoelectronics and photonics. Nonlinear optical (NLO) crystals are used in frequency conversion for lasers. The frequency conversion processes include frequency doubling or Second Harmonic Generation (SHG), sum frequency generation (SFG), differential frequency generation (DFG) and optical parametric generation (OPG). Frequency Doubling or Second Harmonic Generation (SHG) is a special case of sum frequency generation if the two input wavelengths are the same. Amino acids are the potential candidates for optical Second Harmonic Generation (SHG) because they contain chiral carbon atom and crystallize in noncentro symmetric space groups.

In the field of nonlinear optical crystal growth, amino acids are playing a vital role [1]. Aminoacid family crystals are of great interest due to their attracting nonlinear optical properties [2]. L-Alanine is one of the 20 proteinogenic amino acids and has been currently recognized as one of the most abundant aminoacids in natural proteins [3]. In the present investigation, a systematic study has been carried out on the growth of L-Alanine hydrogen bromide crystals. Single X-ray diffraction studies were carried out to confirm the grown crystals. UV-Vis-NIR studies have been carried out for the grown crystal to study the optical properties of the grown crystals. Photo conductivity studies were also carried out for the grown crystals. The SHG efficiency of the L-Alanine hydrogen bromide crystals were also studied using Nd:YAG Q-switched laser.

MATERIALS AND METHODS

Growth of LA*l*HBr single crystals

L-Alanine hydrogen bromide (LA*l*HBr) single crystals were prepared by dissolving L-Alanine (AR grade) and hydro bromic acid in double deionized water. L-Alanine and hydro bromic acids are taken as 1:1 equimolar ratio and dissolved in double deionized water. The supersaturated solution is prepared. The resulting aqueous solution was filtered and allowed to evaporate under optimized conditions to grow crystals by slow evaporation method at room temperature (30°C).

Seed crystals were formed after one week of preparing the solution, the seeds then carefully collected and purified. The recrystallization process carried out in such a way that to grow bulk crystals. Single crystals were grown at room temperature, by slow evaporation technique in a period of 50 days. The crystals are found to be transparent and free from defects. Fig.1 shows the photograph of grown L-Alanine hydrogen bromide crystal.

Figure 1 Photograph of the as grown LA*l*HBr crystal

RESULTS AND DISCUSSION

3.1 Single Crystal X-Ray Diffraction (XRD)

Single X-ray diffraction studies were carried out for the LA*l*HBr single crystal in order to confirm the grown crystal, and to study the structural properties. The grown crystal was subjected to single crystal XRD studies using automated Enraf Nonius diffractometer to confirm the crystallinity and also to estimate the lattice parameters.

LA*l*HBr crystallizes in orthorhombic structure with $P2_12_12_1$ space group. The lattice parameter values of the LA*l*Br crystal are shown in Table 1.

Table 1 Lattice parameter values of LA*l*HBr

Lattice parameters	LA*l*HBr
a (Å) b (Å) c (Å)	5.772 6.058 12.365
Crystal System	Orthorhombic
Space group	$P2_12_12_1$
Volume (Å^3)	428.62

3.2 UV-Vis-NIR SPECTROSCOPY

Optical absorption data for LA/HBr were taken on these polished crystal samples of about 4 to 6 mm thickness using a Varian carry 5E model dual beam spectrophotometer between 200 nm – 2000 nm.

Figure 2 shows the UV-Vis-NIR spectrum of LA*l*HBr. The spectrum indicates that LA*l*HBr crystal is having minimum absorption in the entire visible region. The LA*l*HBr crystal has better cut off wave length starting at 210 nm, indicating the suitability of LA*l*HBr for NLO applications. The required properties for NLO activity are minimum absorption and low cut-off wavelength. These crystals possess a good transparency for the wavelengths of sources which are essential for photonic devices.

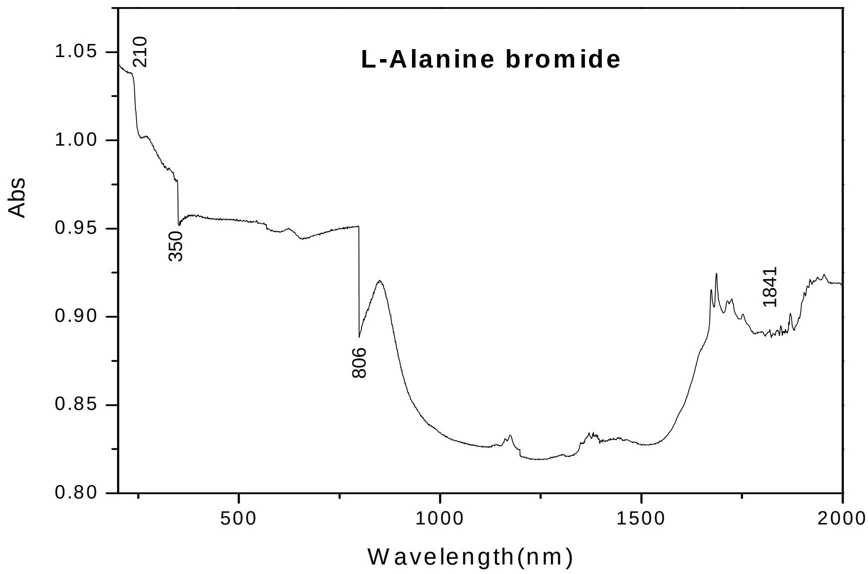

Figure 2 Optical absorption spectrum of LA*l*HBr crystal

3.3 FT-IR ANALYSIS

FTIR spectrum was recorded for L-Alanine Hydrogen Bromide single crystal using a Bruker model IFS 66V spectrometer in the frequency range 400-4000 cm^{-1}. The FTIR spectrum of the crystal is shown in the Figure 3. The peak at 3083 cm^{-1} corresponds to asymmetric NH_3^+

stretching and that at 2937cm^{-1} corresponds to – CH stretching. The frequency observed at 2601cm^{-1} corresponds to NH stretching. The absorptions 2292-2031cm^{-1} corresponds to stretching of CH_3 vibrations. The peak appeared at 1618cm^{-1} corresponds to NH_2 –scissoring. A peak at 1454cm^{-1} corresponds to CH_3 deformation. The presence of carboxyl group can be assigned from the bands at1361 cm^{-1} corresponds to COO^- stretching vibrations.

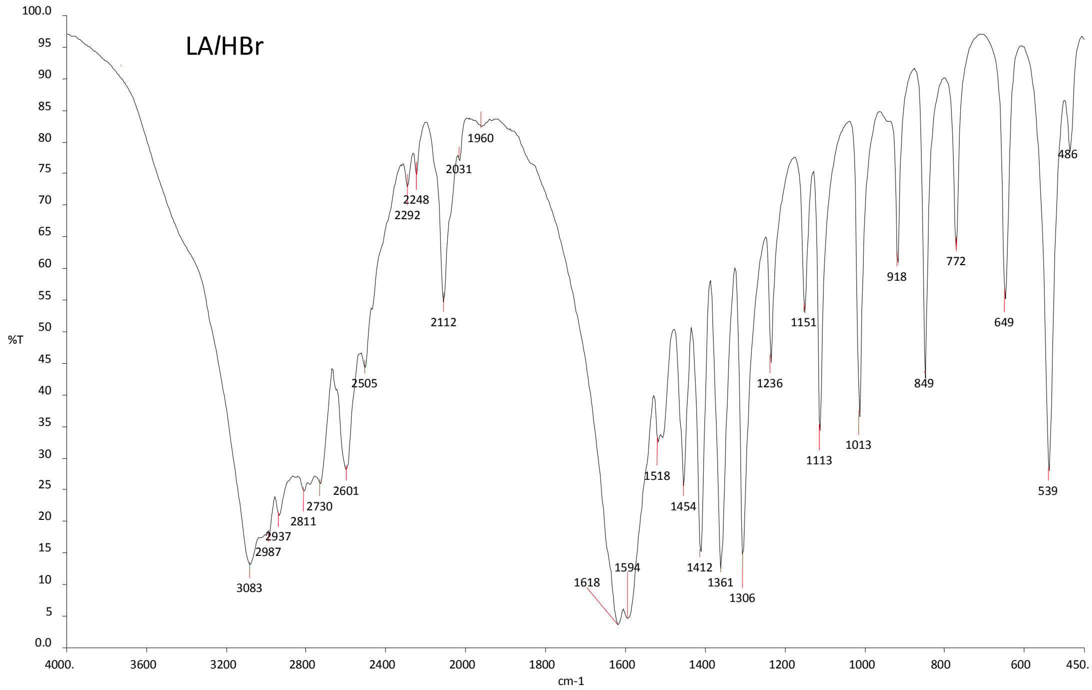

Figure 3 FTIR spectrum of the LA*l*HBr crystal

3.4 Photoconductivity Studies

Using keithley 485 picoammeter, photoconductivity studies were carried out at room temperature for the LA*l*HBr crystals. By connecting the samples to a DC power supply and a picoammeter, dark conductivity of the samples were studied. The light from the halogen lamp (100 W) containing iodine vapour is focused on the respective samples and the photo currents of the respective samples were measured [4]. The DC inputs were increased in steps and the photo currents were measured for the LA*l*HBr samples.

Figure 4 shows the plot of photocurrent and dark current as a function of the applied field for LA*l*HBr. It is observed from the plot that dark current (I_d) and photo current (I_p) of the sample increase linearly with the applied field and the dark current is always higher than the photo current, hence it is concluded that LA*l*HBr shows negative photoconductivity.

3.5 Nonlinear Optical (NLO) Study

Kurtz SHG test was performed on LA*l*HBr crystal to confirm the second harmonic signal generation efficiency [5]. Microcrystalline materials of KDP were used for comparison with L-Alanine Hydrogen bromide single crystal for second harmonic generation experiments. For a laser input pulse of 3.2 mJ, the second harmonic signal 532 nm of 91.66 mW and 109.95 mW respectively were obtained for KDP and L-Alanine Hydrogen bromide samples. The SHG efficiency of LA*l*HBr crystal is 1.2 times greater than KDP.

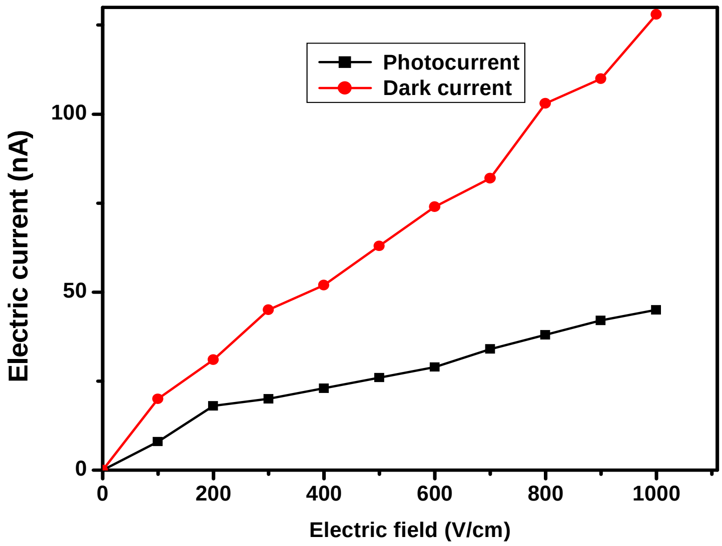

Figure 4 Photo conductivity of LA*l*HBr crystal

CONCLUSION

Good quality LA/HBr crystal was grown by slow evaporation method at room temperature**.** Single crystal X-ray diffraction studies were carried out for the grown crystal. The optical absorption spectral studies confirm that the crystals have minimum absorption in the entire visible and Infra Red region, with lower UV cut off around 210 nm, which is an essential characteristic of NLO crystals. Photoconductivity studies were also carried out for the grown LA*l*HBr crystal. It is found that the crystal posses negative photo conductivity. NLO studies showed that the SHG efficiency of LA/HBr crystal is 1.2 greater than KDP. Thus, it is concluded that the LA/HBr crystals can be effectively used as promising NLO material.

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