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Growth and Characterization of L-Alanine Oxalate Monohydrate Single Crystal

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ABSTRACT

A new semi-organic crystal of L-Alanine oxalate monohydrate has been grown from saturated solution by slow evaporation technique at room temperature. The grown crystal was confirmed by X-ray diffraction. The vibrational frequencies of various functional groups in the crystals have been derived from FTIR analysis. A wide transparency window useful for optoelectronic applications is indicated by the UV studies. The thermal behavior of the crystals has been investigated by TG/DTA analyses. The mechanical strength of the grown crystals was estimated by using Vicker's microhardness studies. Second Harmonic Generation (SHG) efficiency of the powdered material of L-Alanine oxalate monohydrate (LAOM) tested by using Kurtz method.

1. Introduction

Nonlinear optical (NLO) crystals play a major role in modern technology involving lasers, sensors, interferometers, memory chips detectors, electrical devices and optical components. Of late, lots of efforts are being taken to form and study new nonlinear optical materials with interesting properties such as large nonlinearity, high resistance to laser damage, low UV cut off, moderate birefringence and good mechanical strength [1, 2]. NLO crystals with high conversion efficiencies for second harmonic generation and transparent in the visible and ultraviolet ranges are required for various devices in the field of optoelectronics and photonics [3 – 5].

Until the last decade, materials explored for NLO applications were mostly inorganic. But because of their low damage threshold and high cost, material scientists focused their attention on organic materials. Organic compounds possess a high degree of optical nonlinearity and structural diversity compared to their counterparts [6]. But they are thermally unstable. They also have some incoherent drawbacks such as poor physicochemical stability and low mechanical strength. Even though organic crystals possess large NLO efficiency, they have low laser damage threshold with a limitation in NLO efficiency. Therefore interests have been centered on semi-organic crystals which have the combined properties of both inorganic and organic crystals like high damage threshold, wide transparency range, less deliquescence and nonlinear coefficients which make them suitable for device fabrication [7].

Amino acids are interesting materials for NLO applications exist as zwitter ions as they contain a proton donor carboxyl acid (– COO) group and the proton acceptor amino (– NH_2) group in them. This dipolar nature gives some specific features [8] of amino acids such as molecular chirality which secures acentric crystallographic structures, absence of strongly conjugated bonds leading to wide transparency ranges in the visible and UV spectral regions and zwitter ionic nature of the molecule which favours crystal hardness [9]. Amino acid family crystals have been the subject of extensive investigations for their NLO properties in the last two decades [10, 11]. Among the amino acids, L-Alanine is the simplest molecule with SHG efficiency of about one-third of that of the well known KDP [12, 13].

In this paper, we are presenting a preliminary report on the growth and characterization of new semi-organic nonlinear optical material L-Alanine oxalate monohydrate (LAOM).

2. Experimental Procedure

2.1. Synthesis

The compound L-Alanine oxalate monohydrate (LAOM) was synthesized by taking the chemicals such as AR grade of L-alanine and oxalic acid in the equimolar ratio. The calculated amount of L–Alanine was dissolved in deionized water and then oxalic acid was added to the solution slowly by stirring. The mother solution was thoroughly stirred using a magnetic stirrer to yield a homogeneous mixture of solution. Then the prepared solution was filtered using fine porosity of filter paper. The filtered solution was transferred to crystal growth vessels and allowed to dry at room temperature. The salts were obtained by slow evaporation technique.The purity of the synthesized salt was further improved by successive recrystallization process.

2.2. Growth Procedure

Solution method with slow evaporation technique was adopted to grow the single crystals of the synthesized salt of LAOM at room temperature. The recrystallized salt was taken as the raw material for growth. The deionized water was taken in a beaker and the synthesized material of LAOM was added gradually in order to get the saturation. The saturated solution was further purified by filtering the filter paper provided with fine pores of size 1 μm porosity.

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The filtered solution was tightly closed with perforated sheets so that the rate of evaporation could be minimized. The beaker was kept in a vibration free environment. Transparent crystals of size 11 mm x 4 mm x 1 mm were grown after a typical growth period of 4 weeks. The grown crystals are shown in Fig. 1.

Fig 1. As grown crystals of LAOM crystals.

3. Characterization techniques

The grown single crystals of L-Alanine oxalate monohydrate (LAOM) was confirmed by powder XRD analysis using BRUKER D8 ADVANCE diffractometer. Functional groups present in the sample were analyzed using FTIR spectrum. The optical transmission spectrum was recorded using VARIAN Cary 5000 UV–Vis–NIR spectrophotometer in the range of 200–800 nm. The thermal behaviour of the grown crystals was tested by STA 1500 thermal analyzer. The micro hardness measurements of LAOM crystal were carried out using a Leitz Wetzlar Vicker's microhardness tester fitted with a diamond pyramidal indenter. The NLO property of the grown crystals were confirmed by Nd:YAG laser.

4. Results and Discussion

4.1. Powder X-ray diffraction analysis

The grown crystals have been studied by powder X-ray diffraction studies using BRUKER D8 ADVANCE diffractometer. From the powder X-ray diffraction data, the lattice parameters and the cell volume have been calculated using the celn software. From the X-ray diffraction data, it is observed that the grown crystals belong to orthorhombic crystal system. Fig. 2 represents the powder X-ray diffraction pattern of the grown crystals. The crystallographic data are given in Table 1. The crystal parameters and cell volume are found to be in well agreement with that of reported values [14 – 16].

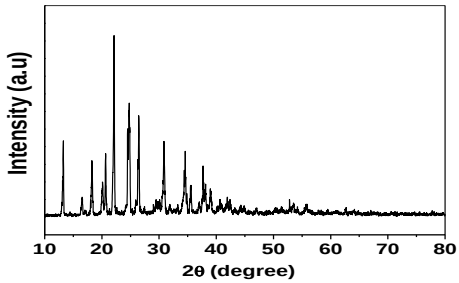
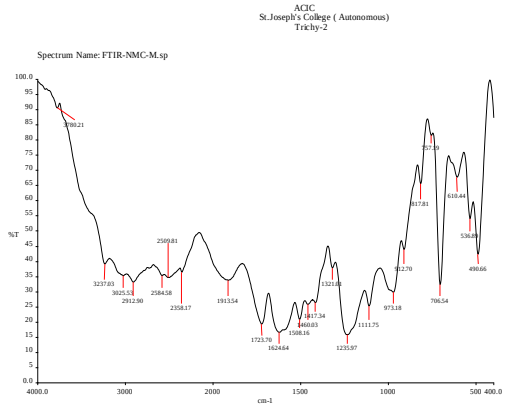


Fig 2. Powder X-ray diffraction pattern of LAOM crystals.

4.2. Fourier transform infrared spectral analysis

Functional groups present in the sample are analyzed using FTIR spectra. Different molecular groups present in LAOM are identified with the vibrational frequencies of amino acids and their complexes. The FTIR spectrum of LAOM crystal was recorded in the region 400 – 4000 cm^{-1} using FTIR SHIMADZU 8400S.

The sample was prepared by pressing LAOM with KBr pellet form. The observed spectrum is shown in Fig. 3.



The absorption peak at 3025.53 cm^{-1} is the indication of the presence of NH_3^+ symmetric stretching mode in the crystal. The peak at 2912.90 cm^{-1} is attributed to the CH_2 symmetric stretching mode vibration. The peak at 2584.58 cm^{-1} is due to CH stretching mode vibration. The absorption peaks observed at 1624.64 and 1508.16 cm^{-1} in the spectrum of LAOM corresponds to the NH_3^+ asymmetric stretching mode vibration. The peak at 1460.03 cm^{-1} is due to the deformation of CH. The observation of IR bands at 1417.34, 1321.01, 1235.97 and 1111.75 cm^{-1} is indicative of the presence of COO^- symmetric stretching mode in the crystal. IR band corresponding to the observation at 912.70 and 817.81 cm^{-1} are assigned to C–C–N stretching mode vibration. The O–C–O stretching mode at 757.19 cm^{-1} has been identified and assigned. The COO^- scissoring mode appears at 610.44 cm^{-1}. The peak at 536.89 cm^{-1} represents the COO^- rocking. The peak at 490.66 cm^{-1} indicates the region of NH_3^+ torsion. The results are summarized in Table. 2.

Table. 2.Assignments of IR band frequencies (cm^{-1}) of L–Alanine and LAOM.

L–Alanine [17]	LAOM	Assignments
3058	3025.53	NH3+ Symmetric stretching
2960	2912.90	CH_2 Asymmetric stretching
2603	2584.58	CH Stretching
1620	1624.64	NH3+ Symmetric stretching
1519	1508.16	NH3+ Symmetric stretching
1455	1460.03	CH Deformation
1412	1417.34	COO–Symmetric stretching
1306	1321.01	COO–Symmetric stretching
1236	1235.97	COO–Symmetric stretching
1113	1111.75	COO– Symmetric stretching
918	912.70	C–C–NStretching
849	817.81	C–C–NStretching
772	757.19	O–C–O Stretching
649	610.44	COO– Scissoring
539	536.539	COO– Rocking
486	490.66	NH_3^+ Torsion

4.3. UV – Visible spectral analysis (L-Cystine)

For optical applications, the material considered must be transparent in the entire visible region. Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window.

To find the transmission range of LAOM crystal, the optical transmission spectrum for the wavelengths between 200 nm and 1200 nm was recorded.

Table. 1.Crystallographic parameters of LAOM crystals.

Crystal	*a* (Å)	*b* (Å)	*c* (Å)	α	β	γ	Volume (Å^3)	System	Space group
L–Alanine	6.032	12.343	5.784	90^0	90^0	90^0	430.09	Orthorhombic	$P2_12_12_1$
LAOM	6.182	12.421	5.853	90^0	90^0	90^0	432.65	Orthorhombic	$P2_12_12_1$

The recorded optical transmission spectrum of LAOM crystal is shown in Fig. 4. The transmittance is found to be maximum in the entire visible and infrared regions. From the spectrum, the crystal shows a good transmittance in the entire visible region. The lower cutoff around 265 nm attest the usefulness of this material for opto-electronic applications and the second harmonic generation of the Nd: YAG laser and for the generation of the higher harmonics of the laser diodes.

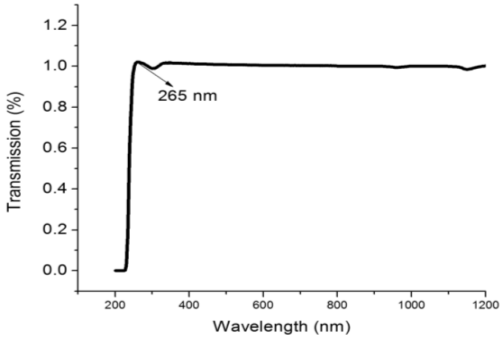


Fig 4. Optical spectrum of LAOM crystal.

4.4. Thermal analysis

To investigate the thermal properties of the sample, LAOM crystals were subjected to TGA/DTA studies. Thermo Gravimetric Analysis (TGA) provides quantitative measurement of any weight change associated with a transition of the sample. It can directly record the loss in weight with the time or temperature due to dehydration and decomposition. Differential Thermal Analysis (DTA) is a thermo analytical technique to record the difference in temperature between substance and a reference when they are subjected to identical heating at controlled rate.

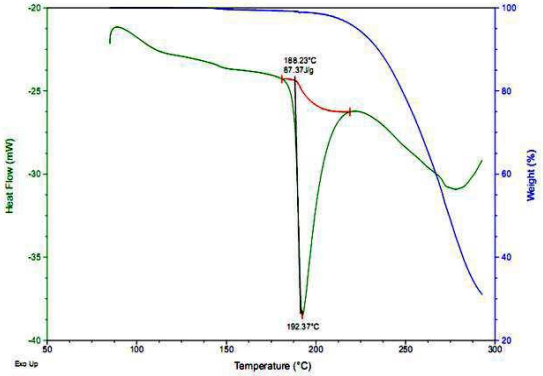


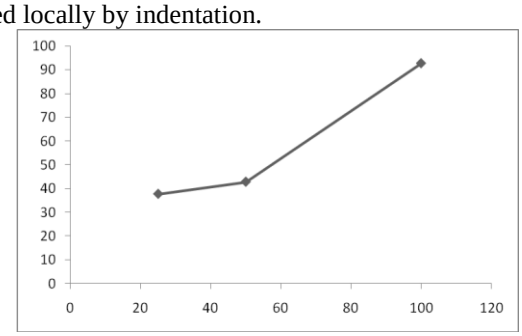
Fig 5.TG/DTA analyses of LAOM crystals.

The TGA/DTA analyzes of the LAOM crystal were carried out between 50^o C and 300^o C in air atmosphere at a heating rate of 10^o C/min. Fig. 5 shows the TGA and DTA spectra of LAOM crystal. From the figure, it is obvious that the crystals exhibit only single stage of decomposition and hence decomposes directly without producing any weight loss dependent intermediate species. Below 213^{o}C, there is no detectable weight loss and hence crystals reject solvent molecules during crystallization. The decomposition starts at 213^{o}C and hence thermodynamically stable up to 290^{o}C. The DTA analysis was also carried out in the same atmospheric condition. The endothermic peak at around 188^{o}C is assigned to melting point of the title compound. It is followed by decomposition and volatilization of the compound above 230^{o}C. Hence, it may be useful for making the NLO devices below its melting point.

4.5. Mechanical properties

Hardness is one of the important mechanical properties of the materials. It carries the information about the strength, molecular bindings, yield strength and elastic constants of the material.. A well-polished LAOM crystal was placed on the platform of Vickers Microhardness tester and the loads of different magnitudes were applied over a fixed interval of time.

The indentation time was kept (8 s) for all the loads. The hardness number was calculated using the relation Hv = (1.8544P)/(d^2) kg/mm^2, where P is the applied load in kg and d is the diagonal length of the indentation impression in the micrometer. A graph has been plotted between hardness number (Hv) and applied load (P) and is shown in Fig. 6. The hardness number increases linearly with the increase of load and above 100 gm, cracks were developed on the smooth surface of the crystal due to the release of internal stress generated locally by indentation.



Load (P)

Fig 6. Hardness vs. Load of the LAOM crystal.

5. Conclusion

The second harmonic generation test on the LAOM crystal was performed by the Kurtz powder SHG method [18]. The fundamental beam of 1064 nm with 10 ns pulse width from Q-switched Nd:YAG laser is used as the source and directed on the powdered sample through a visible blocking filter. The doubling of frequency was confirmed by the emission of green radiation of wavelength 532 nm collected by a monochromator after separating the 1064 nm pump beam with an IF blocking filter. A photomultiplier tube was used as detector. It is seen that the SHG efficiency of LAOM is about 1.3 times higher than that of KDP.

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