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Growth, structural, optical, thermal and dielectric properties of L-asparagine monohydrate admixtured L-thiomalic acid single crystal

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ABSTRACT

Single crystal of L-asparagine monohydrate admixtured L-thiomalic acid (LAMTM) has been grown by slow evaporation solution growth technique using water as solvent at room temperature. Single crystal X-ray diffraction analysis reveals that LAMTM crystal crystallizes by orthorhombic system with space group of $P2_12_12_1$. The physical phase of the product was confirmed by powder X-ray diffraction analysis. The chemical composition of grown crystal was confirmed using elemental analysis. Functional groups present in the grown LAMTM crystals were identified from FTIR and FT-Raman analyses. The optical parameters, such as optical band gap energy, transparency, reflectance, refractive index were calculated using UV–vis transmittance data in the spectral range 200–800 nm. Thermal stability of material is determined using TGA and DTA thermal analyses. Further the kinetic parameters, such as activation energy (E), entropy (ΔS), enthalpy (ΔH) and Gibbs free energy (ΔG), were calculated using Coats–Redfern method. The variation of dielectric properties of the grown crystals as a function of frequency has been investigated at different temperatures.

1. Introduction

Nonlinear optics plays a vital role in the emerging photonic and optoelectronic technologies in recent scenario [1]. Organic materials are gaining more attention due to their fast response in electro-optic effect, high non-linear coefficient and more stability in physical, chemical properties. Organic materials have found to be superior due to their high electronic susceptibility (χ) through molecular hyperpolarisability (β) relatively over the conventional inorganic substances [2]. Organic materials have another advantage over inorganic materials, in that the properties of organic materials can be optimized by modifying the molecular structure using molecular engineering and chemical synthesis [3]. Amino acids are suitable organic materials for nonlinear optical application devices, since they contain donor carboxylic ($COOH^-$) group and proton acceptor amino (NH_2) group known as zwitterions which create hydrogen bonds [4]. L-Asparagine monohydrate (LAM) is an interesting amino acid material which crystallizes in a structure exhibiting a complex network of hydrogen bonds among asparagine molecules and between asparagine and water molecules [5]. L-asparagine monohydrate $C_4H_8O_3N_2{\cdot}H_2O$ (LAM) single crystal has orthorhombic structure [6]. On the account of this, asparagine compound materials such as L-asparagine, L-tartaric acid (LALT) [7], L-asparaginium picrate (LASP) [8], L-asparagine cadmium chloride monohydrate [9], L-asparaginium nitrate (LAN) [10], are proved to be potential materials for NLO application.

In the present work, efforts have been made to grow a single crystal of LAMTM by slow evaporation solution growth technique at room temperature. The physical phase and cell parameters were identified by powder and single crystal X-ray diffraction analyses. Chemical composition of grown crystal was confirmed by elemental analysis. FTIR and FT-Raman analyses were subjected to identify the functional groups present in the grown crystal. DRS-UV–vis spectrum analysis was carried towards optical properties. Thermal and dielectric properties used to study thermal and electrical behaviour of the material.

2. Experimental

2.1. Materials and crystal growth

L-Asparagine monohydrate (SRL) and L-thiomalic acid (LOBA) were taken as starting materials in equimolar ratio (1:1). The calculated amount of L-asparagine monohydrate and L-thiomalic

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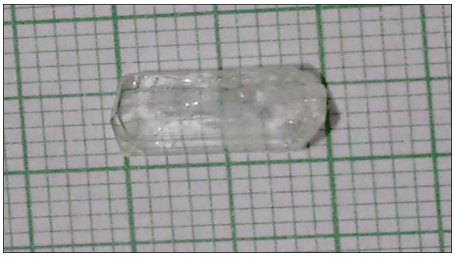

Fig. 1. As grown LAMTM crystal.

acid were dissolved in deionized water at room temperature. The solution was stirred well using of Ultrasonicator for 1 h, further continued in magnetic stirrer about 2 h to improve the homogeneity of the solution. The saturated solution was filtered using Whatman filter paper and kept in a beaker covered with perforated polythene to avoid contamination and fast evaporation of the solvent. Optically transparent and well shaped crystals of 10 mm × 5 mm × 3 mm size have been harvested after 40 days of growth as depicted in Fig. 1.

2.2. Characterization techniques

A single crystal (0.50 mm × 0.40 mm × 0.20 mm) was selected to measure the cell parameters of LAMTM crystal using a Bruker APEX II CCD diffractometer. Powder X-ray diffraction pattern was recorded by JEOL JDX services instrument with Cu$K\alpha$ (1.5406 Å). The chemical composition of LAMTM was analysed using Vario EL III Elemental instrument. The FTIR spectrum was recorded using Perkin Elmer Fourier transform infrared spectrophotometer using KBr pellet technique. Fourier Transform Raman (FT-Raman) spectrum was recorded with FRA-106 attachment to Bruker IFS-88 spectrometer equipped with Ge detector cooled to liquid nitrogen temperature. The scattered light was collected in the region of 4000–50 cm^{-1}. The diffuse reflectance ultraviolet visible spectral (DRS-UV–vis) analysis was carried out by Shimadzu (UV-2450) instrument to study the optical behaviour of grown crystal. The thermal behaviour of the grown crystal was investigated using NETZSCH STA 449F3 thermal analyzer. Sample of mass 2.516 mg was heated in a crucible between 20 °C to 800 °C heating rate of 20 °C min^{-1} under nitrogen atmosphere. The frequency dependent dielectric constant and dielectric loss of LAMTM have been measured using HIOKI 3532-50 LCR HI-TESTER for various temperatures (313, 333, 353 and 373 K). A sample of dimension 5 × 3 × 2 mm^3 having high quality silver coating on the opposite faces were placed between the two iron electrodes to form a parallel plate capacitor. The capacitance of the sample noted for the applied frequency (50 Hz to 5 MHz).

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction analysis for the grown LAMTM crystals has been carried out to identify the unit cell parameters. The calculated lattice parameter values are, a = 5.582 Å, b = 9.806 Å, c = 11.785 Å, and V = 648 $Å^3$. LAMTM crystal belongs to orthorhombic crystal system with space group of $P2_12_12_1$.

3.2. Powder X-ray diffraction analysis

Powder X-ray diffraction analysis carried out to confirm the physical phase of the product. Crushed powder of LAMTM crystal was subjected to analysis in order to determine the crystal phases by XRD. From the powder X-ray diffraction pattern of grown LAMTM, the different planes of reflection were indexed using XRDA program (Fig. 2). The observed d values for different 2θ with ($h\,k\,l$) indices of the corresponding planes are presented in Table 1.

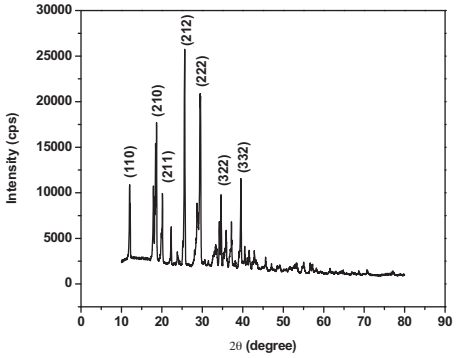

Fig. 2. Powder X-ray diffraction of LAMTM crystal.

Table 1
Indexed X-ray powder diffraction data of LAMTM crystal.

H	K	L	d cal (Å)	2θ cal (Å)
1	1	0	7.53	11.99
2	1	0	4.76	18.77
2	1	1	4.35	20.00
2	1	2	3.55	25.70
2	2	2	3.07	29.70
3	2	2	2.58	34.50
3	3	2	2.27	39.50

3.3. Elemental analysis

The chemical composition of LAMTM was analyzed using Vario EL III Elemental instrument and the obtained result is presented in Table 2. The experimental values of C, H, N, O and S have good agreement with theoretical values.

3.4. FTIR and FT-Raman spectral analyses

The various functional groups present in LAMTM crystal were identified from FTIR and FT-Raman spectra are shown in Figs. 3 and 4, respectively. The broad and strong bands observed at 3112, 2147 cm^{-1} in FTIR spectrum and 3102 cm^{-1} in FT-Raman spectrum are attributed to NH_3 stretching. The broad peak observed at 3383 cm^{-1} in FTIR is corresponds to NH_2 stretching. The broad peak observed at 2946 cm^{-1} in FTIR, 2963 and 2931 cm^{-1} in FT-Raman is attributed to C–H stretching. A peak observed at 2001 cm^{-1} in FTIR is exhibiting to N–H stretching. The sharp peaks observed at 1072 cm^{-1} in both FTIR and FT-Raman spectrum are corresponds to C–N stretching. Sharp peaks observed at 836 cm^{-1} in FTIR and 837 cm^{-1} in FT-Raman spectrum are assigned to C–C vibration. Sharp peaks observed at 1358 cm^{-1} in both FTIR and FT-Raman spectrum is corresponds to CH bending. A sharp peak observed at 1231 cm^{-1} in FTIR and at 1234 cm^{-1} in FT-Raman is attributed to NH_2 rocking. Sharp peaks observed at 1147 cm^{-1} in FTIR, at 1142 cm^{-1} in FT-Raman are attributed to NH_3 rocking. A peak observed at 1431 cm^{-1} in FTIR and at 1424 cm^{-1} in FT-Raman

Table 2
Elemental analysis of LAMTM crystal.

Element (%)	Experimental	Theoretical
C	38.09	38.39
H	5.24	5.64
N	11.01	11.19
O	31.72	31.96
S	12.59	12.81

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