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Growth, Hardness Parameters, Laser Damage Threshold and Thermal Analysis of L-Alanine Crystals Grown in Aqueous Solution of Hydrofluoric Acid (LAHF)

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Abstract - An attempt has been made to grow the NLO material viz. L-alanine in the medium of aqueous solution of hydrofluoric acid by employing slow evaporation solution method. Crystalline structure was investigated by single crystal XRD method. Nonlinear optical property was found by SHG test. Hardness parameters and laser damage threshold measurement (LDT) were carried out for the grown crystal. The thermal characteristics of the grown crystal were analyzed by thermogravimetric and differential thermal analysis (TG/DTA).The grown sample was characterized by Energy Dispersive Analysis by X-rays (EDAX).
Keywords: Single crystal; XRD; NLO; solution growth; LDT; TG/DTA;hardness

1. Introduction

The search and design of highly efficient nonlinear optical (NLO) crystals for visible and ultraviolet (UV) region are extremely important for laser processing. High quality organic NLO crystals must posses large NLO coefficient, transparency in UV region, high laser damage threshold power and ease of growth with improved dimension [1]. Organic materials draw more interest because of their superior performances involving fairly high NLO coefficient and ultrafast nonlinear response. Amino acids play vital role in nonlinear optical field. In this work, the amino acid like L- alanine was mixed with inorganic hydrofluoric acid to enhance its NLO efficiency, hardness and laser damage threshold. Many researchers focus their reputed interest in combining L-alanine with organic and inorganic materials to improve the nonlinear properties of L-alanine [2-4]. L-alanine crystal grown in aqueous solution of hydrofluoric acid (LAHF) was reported for the fist time by Jothi Mani and Selvarajan[5]. Hardness parameters, thermal analysis, EDAX spectrum and laser damage threshold studies of LAHF sample is discussed in this paper by the same authors.

2. Growth of LAHF crystal

The salt of L-alanine admixtured with hydrofluoric acid (LAHF) was synthesized by taking L-alanine (99% purity) and analar grade hydrofluoric acid (HF) in the molar ratio of 1:1 in double distilled water. The dissolved solution was heated at 50 ^{o}C for the synthesis of LAHF salt. The purity of the synthesized salt was further increased by repeated re-crystallization. The saturated solution of the re-crystallized salt of LAHF was prepared in accordance with the solubility data [5] and the calculated amounts of the reactants were thoroughly dissolved in double distilled water and stirred well for about 2 h using a magnetic stirrer to ensure homogeneous temperature and concentration over entire volume of the solution. The solution was filtered and transferred to a crystal growth vessel and crystallization was allowed to take place by slow evaporation method.

3. Characterization

3.1 Structural analysis

The structure of the grown LAHF crystal was analyzed by single crystal X-ray diffractometer. From the single crystal X-ray diffraction data, it is observed that the LAHF crystal belongs to orthorhombic structure with the lattice parameters a = 5.759(2) Å, b = 6.042(4) Å, c=12.358(3) Å, α = β = γ = 90° and V =430.01(1) Å^3 with non-centrosymmetric space group $P2_12_12_1$ and Z= 4. The obtained structural data for the grown crystal of this work are almost coincided with those of L-alanine crystal and therefore the crystal structure of LAHF crystal is not changed [6] and the slight changes in lattice constants may be due to incorporation of admixture material (HF).

3.2 Chemical composition analysis

Energy dispersive X-ray spectroscopy (EDAX) is an analytical technique used for the elemental analysis of a sample. The EDAX spectrum of the grown crystal of LAHF was taken using a computer controlled scanning electron microscope (Model: HITACHI S-3000H) and it is displayed in Fig. 1. From the diagram, it is confirmed that the elements such as carbon, oxygen, nitrogen and fluorine are present in the sample.

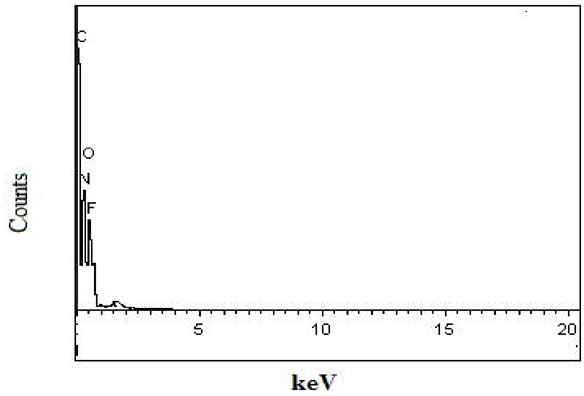

Figure 1: EDAX spectrum of LAHF sample.

3.3 Nonlinear Optical (NLO) studies

The NLO activity in reference to SHG of a sample can be checked using the Kurtz and Perry method [7]. A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 6 ns was passed through the powdered sample. The SHG behavior was confirmed from the output of the laser beam having the green emission (λ = 532 nm). It is noticed that the SHG efficiency of the grown LAHF sample is 1.05 times that of the standard KDP crystal. Comparing L-alanine crystal grown in water (SHG = 0.33), [6] LAHF crystal shows improved NLO efficiency.

3.4 Hardness test

Microhardness analysis was carried out using Vickers microhardness tester fitted with a diamond indenter. The well polished LAHF crystal was placed on the platform on the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time. The indentation time was kept as 10 s for all the loads. The hardness number was calculated using the relation given in the literature [8].Variation of hardness with load (figure 2) shows that hardness number increases with the increase of load obeying the reverse indentation size effect. The plot of log (P) verses log (d) is shown in figure 3 and it exhibits the value of the work hardening coefficient (n) as 3.994. According to Onitsch, 1.0 ≤ n ≤ 1.6 for hard materials and n >1.6 for soft materials [9]. Hence, it is concluded that LAHF crystal belongs to the category of soft material.Yield strength of the material can be found out using the relation, Yield strength (σ_y) = $(H_v/3)(0.1)^{n-2}$ where σ_y is the yield strength and H_v is the hardness of the material. It is observed from figure 4 that yield strength increases with increase of load and hence the grown LAHF crystal has relatively high mechanical strength. The elastic stiffness constant (C_{11}) for different loads was calculated [10] using Wooster's empirical formula $C_{11} = H_v^{7/4}$ and variation of stiffness constant with the load is given in figure 5 which gives an idea about the measure of resistance of plastic to bending and tightness of bonding between neighboring atoms.

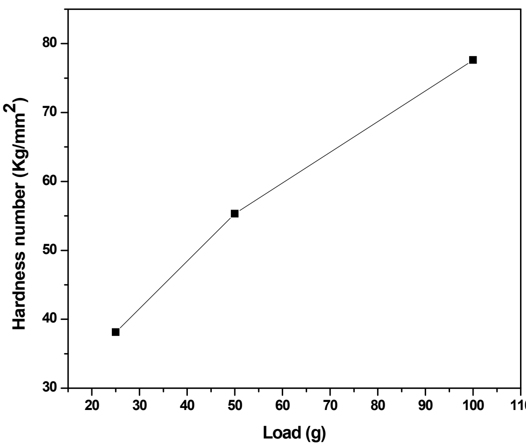

Figure 2: Dependence of microhardness with load for LAHF crystal

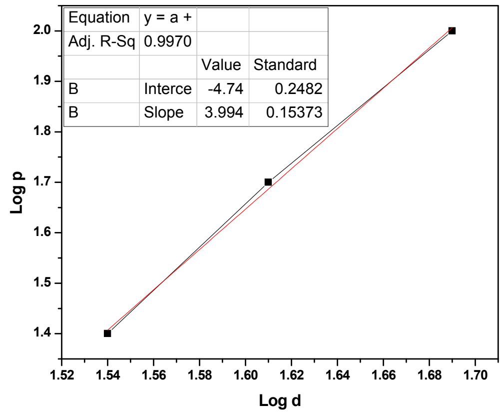

Figure 3: Plot of log (d) versus log (P) for LAHF crystal

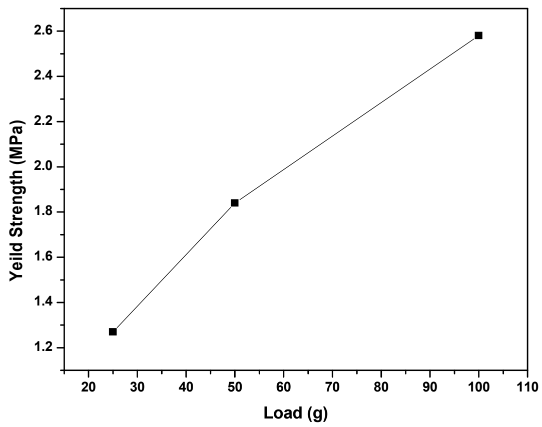

Figure 4: Dependence of yield strength with load for LAHF crystal

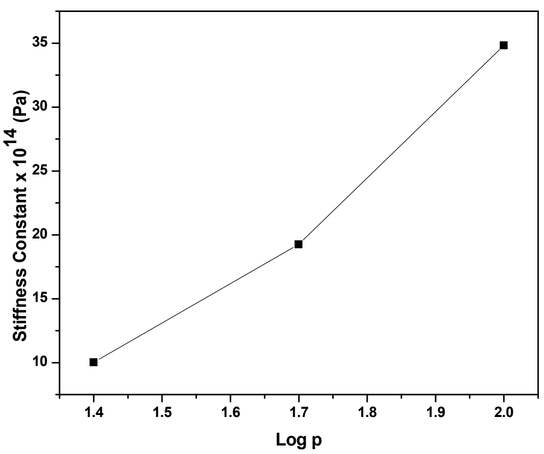

Figure 5: Variation of stiffness constant with load for LAHF crystal

3.5 Thermal analysis

The TG/DTA themal curves of LAHF crystal is shown in Fig. 6. The initial mass of the material was taken to be 7.631 mg and the final mass left out after the experiment was only 0.229 mg of initial mass. The LAHF sample was stable up to 220 ^{o}C. There is a major weight loss of sample between 220 ^{o}C to 310^{o}C which was assigned to decomposition of LAHF crystal. From the observation it was concluded that the crystal decomposes only at 298.57°C. The endothermic peak shows the good degree of crystallinity of the sample [11].

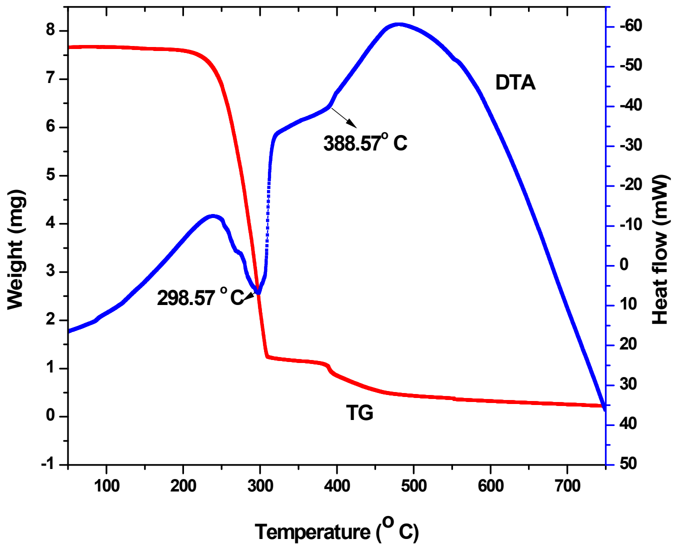

Figure 6: TG/DTA curves of LAHF sample

3.6 Laser damage threshold measurement

The laser damage threshod (LDT) was measured by coherent energy/power meter (Model No. EPM 200) and it is an important factor which affects the applications optical materials. If the material has low damage threshold it severely limits its applications even though it has excellent properties like high SHG [12]. The LDT value was determined using the formula $P = E/\tau r^2$ where E is the energy in mJ, τ is the pulse width in ns and r is radius of the spot in mm and the obtained value is 347 MW/cm^2. The value of LDT for LAHF is observed to be better than that of KDP (200 MW/cm^2) crystal.

3.7 Conclusion

Single crystals of LAHF have been grown by slow evaporation solution growth technique and the grown crystals were transparent with a well defined external appearance. The unit cell parameters for LAHF crystal have been evaluated by single crystal XRD method and the structure is confirmed to be orthorhombic. The NLO efficiency of LAHF sample is found to be 1.05 times that of KDP. The microhardness study reveals the mechanical strength of the material. Thermal behavior and laser damage threshold measurements were found to be good for LAHF sample.

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