Synthesis, growth and optical properties of an efficient nonlinear optical single crystal: L-alanine DL-malic acid

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Abstract. Single crystals of L-alanine DL-malic acid (LADLMA) have been grown from aqueous solution by slow-cooling technique. Powder X-ray diffraction studies reveal the structure of the crystal to be orthorhombic. The nonlinear optical conversion efficiency test was carried out for the grown crystals using the Kurtz powder technique. The third order nonlinear refractive index and the nonlinear absorption coefficient where evaluated by Z-scan measurements. As the material have a negative refractive index it could be used in the protection of optical sensors such as night vision devices.

1. Introduction
Some organic compounds exhibit large NLO response than widely known inorganic materials. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. Among organic crystals for non linear optics (NLO) applications, aminoacids display specific features of interest such as (i) molecular chirality, which secures acentric crystallographic structures; (ii) absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions; (iii) zwitterionic nature of the molecule, which favours crystal hardness [1].

The title compound is the smallest molecule among the amino acids. Although its second harmonic generation (SHG) efficiency is about one-third that of potassium dihydrogen phosphate (KDP), the knowledge of studying the properties is very important since L-alanine can be considered as the fundamental building block of more complex amino acids [2]. Hence, it may be useful to synthesize the amino acid complexes with other carboxylic acids and study their properties. This paper discusses the growth of single crystals of LADLMA by slow cooling technique. Structural, second harmonic efficiency and Z-scan studies were carried out and the results were presented and discussed.

2. Synthesis and Growth
Stoichiometric amount of L-alanine and DL malic were taken with excess of water to synthesize L-alanine DL malic acid [3]. The solubility [4] of LADLMA was measured at 30, 35, 40, 45 and 50 °C. The variation of solubility with temperature is shown in Figure 1. Seed crystals, free from visible defects were used for bulk growth. The rate of cooling was 1 °C/day over a period of 22 days. Single crystal up to size of 11 x 8 x 9 mm$^3$ was grown and is shown in Figure 2.

3. Results
3.1 Powder XRD
In order to confirm the crystallinity and also to estimate the lattice parameter values, the grown crystals were subjected to powder X-ray diffraction analysis. X-ray powder patterns of the crystal were recorded on a SIEFERT X-ray Diffractometer using CuKα (Kα = 1.5408) radiation. The sample was scanned for a 2θ range of 10–50° and at a scan rate of 2°/ min$^{-1}$. All the observed reflections (figure 3) were indexed and the unit cell parameters were calculated. The XRD data of the crystal
indicates that it crystallizes in orthorhombic system with $P_2_1_2_1_2_1$ space group with $a=5.823$ Å, $b=6.030$ Å and $c=12.325$ Å which agrees well with the reported values [3].

**Figure 1.** Solubility curve of LADLMA

3.2 UV-Vis NIR Spectrum

To find the transmission range LADLMA the optical transmission spectrum of LADLMA for the wavelengths between 200-1200nm was recorded using Varian Cary 5E UV-Vis-NIR spectrophotometer. From the graph (figure 4), it is evident that LADLMA crystal has UV cutoff wavelength at 250nm. Moreover the absorption is minimum in the entire visible region and also in the near infrared region. The lower cut-off wavelength of LADLMA crystal is almost comparable to other analogs of L-alanine [2].

**Figure 3.** XRD patterns of the powder sample

**Figure 4.** UV-Vis NIR spectrum of LADLMA

3.3 SHG efficiency

Kurtz SHG test [5] was performed on LADLMA crystal to confirm the second harmonic signal generation efficiency. Microcrystalline material of KDP was used as a comparison with LADLMA, for the SHG experiments. For a laser input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 91.66 mV and 90.21 mV were obtained through KDP and LADLMA samples respectively. Thus the SHG efficiency of LADLMA is comparable to that of KDP.
3.4 Z-scan studies
The Z-scan technique is a simple and effective tool for determining the nonlinear properties. The third order nonlinear refractive index and the nonlinear absorption coefficient were evaluated by the Z-scan measurements. The crystals were cut and polished in the z direction and then subjected to Z-scan measurement. Figure 5 and Figure 6 show the open and closed aperture Z-scan for the crystal.

Z-scan parameters are presented in Table 1. As the material have a negative refractive index, it results in defocusing nature of the material, which is an essential property for the application in the protection of optical sensors such as night vision devices [6].

**Table 1. Z-Scan Data**

| Parameter                                      | Value                        |
|-----------------------------------------------|------------------------------|
| Laser beam wavelength (λ)                    | 532 nm                       |
| Lens focal length (F)                        | 10 cm                        |
| Spot size diameter in front of the aperture (ωa) | 2 mm                        |
| Aperture radius (ra)                         | 0.087 x 10⁻² m               |
| Incident intensity at the focus (z=0) (I₀)   | 2.3915 x 10⁵ m W             |
| Effective thickness of the sample (L_eff)    | 0.9938 mm                    |
| Linear absorption co-efficient (α)           | 0.0123                       |
| Non-linear refractive index (n₂)             | -8.1064 x 10⁻¹² cm²/W       |
| Non-linear absorption co-efficient (β)       | 1.1662 x 10⁻⁴ cm/W          |
| Real part of the third-order susceptibility (Reχ(3)) | 3.6466 x 10⁻¹⁰ esu          |
| Imaginary part of the third-order susceptibility (Imχ(3)) | 2.222 x 10⁻⁸ esu          |
| Third-order non-linear optical susceptibility | 2.2222 x 10⁻⁴ esu          |
4. Conclusions
Single crystals of L-alanine DL-malic acid (LADLMA) have been grown from aqueous solution by slow-cooling technique. Powder X-ray diffraction studies reveal the structure of the crystal to be orthorhombic. The nonlinear optical conversion efficiency test was carried out for the grown crystals using the Kurtz powder technique. The third order nonlinear refractive index and the nonlinear absorption coefficient were evaluated by the Z-scan measurements. The results strongly suggest that the material could be used in optical device fabrication.

5. References
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