Growth and characterization of DL-Alanine — A new NLO material from the amino acid family

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Abstract

Single crystals of DL-Alanine (C₃H₇NO₂), one among the rare amino acid racemates crystallizing in a non-centrosymmetric space group and a new NLO material, were grown from aqueous solution by slow evaporation method. They were characterized by single crystal X-ray diffraction. Fourier transform infrared spectroscopy (FTIR) showed the presence of the different functional groups. The thermal stability and decomposition of the sample was studied by thermal analysis (TGA/DTA). The optical transparency was studied by UV–Vis–NIR spectral analysis. The above experimental results showed that DL-Alanine is stable up to 280 °C and transparent in the region of 220 nm–1100 nm. The second harmonic generation (SHG) efficiency was determined using Kurtz and Perry method and found to be 1.7 times higher than that of standard KDP.

Keywords: Optical materials; Crystal growth; Fourier transform infrared (FTIR); Thermal property

1. Introduction

In the last decade, second order nonlinear optical (SONLO) crystals have attracted much attention because of their potential applications in many fields. Advanced laser-based imaging, optical communication and data storage systems require improved nonlinear optical materials. Coherent blue and green light are important for many applications such as display, high-resolution printing, and signal processing [1–3]. A number of such crystals, especially from the amino acid family, have recently been reported [4–8].

DL-Alanine is one among the rare amino acid racemates crystallizing in a non-centrosymmetric space group. The structure of DL-Alanine was elucidated from our laboratory by Subha Nandini et al. [9]. The crystal structure is stabilized by a network of characteristic head-to-tail hydrogen-bond sequences. The structure contains three types of such sequences: straight sequence along the c-axis with O₂ of the carboxylate as acceptor, zigzag sequence along the 2₁ screw axis with O₁ of the same carboxylate group as acceptor and zigzag DL-sequence among the glide-related molecules with O₂ of the carboxylate group as acceptor. Fig. 1 shows the molecular structure of DL-Alanine. The carboxyl group is present as a carboxylate ion and amino group as ammonium ion. The structural arrangement (head-to-tail hydrogen-bond sequence) and the occurrence of the π→π* transition in the carboxylic group account for the nonlinearity in this crystal. In the present investigation, single crystals of DL-Alanine were grown and characterized by single crystal X-ray diffraction. Fourier transform infrared (FTIR) spectroscopic studies, thermo gravimetric analysis (TGA/DTA), UV–Vis–NIR spectral analysis and second harmonic generation (SHG) studies were also carried out for the first time, on this useful material.
2. Experimental

2.1. Crystal growth

Commercially available DL-Alanine (Analar grade, SRL, India) was further purified by repeated recrystallization processes. The solubility of purified DL-Alanine was estimated by the gravimetric analysis in the temperature region between 25 °C and 75 °C. Since it is insoluble in acetone, ethanol and methanol, solubility experiment was done only for water. Solubility of this compound increases with temperature (Fig. 2). A saturated solution of DL-Alanine was prepared and allowed to evaporate at a controlled temperature of 30 °C. Small needle-shaped, transparent crystals of size: 2.0×1.0×0.5 mm³ were obtained within a period of 20 days. Attempts are being made to grow the crystals of DL-Alanine in larger sizes.

2.2. Characterization

The grown crystals were subjected to single crystal X-ray diffraction using Nonius CAD-4/MACH 3 Diffractometer, with MoKα radiation (λ=0.71073 Å). The cell data were obtained from the least-squares refinement of the setting angles of 25 reflections. Density of DL-Alanine was found to be 1.39 kg/m³ using the floatation method. The FTIR spectra of the sample were recorded in KBr phase in the frequency region of 400–4000 cm⁻¹ using a Jasco Spectrometer (FTIR, model 410), at a resolution of 4 cm⁻¹ and with a scanning speed of 2 mm/s. Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out for the crystals, using a NETZSCH-Gerätebau STA 409 PC thermal analyzer. A powder sample was used for the analysis in the temperature range of 26 °C to 800 °C with a heating rate of 10 °C/min. The crucible used was of alumina (Al₂O₃), which served as a reference for the sample. The transmission spectrum was recorded using VARIAN (Cary 500), UV–Vis–NIR spectrophotometer in the range of 200–1100 nm covering the entire near ultraviolet, visible and NIR regions. The nonlinear optical conversion efficiency was tested using a modified setup of Kurtz and Perry [10]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was used with an input power 2.0 mJ and pulse width of 10 ns, the repetition rate being 10 Hz. The crystals of DL-Alanine were ground to a uniform particle size of about 125–150 μm and then packed in a capillary of uniform bore and exposed to laser radiations. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation (λ=532 nm) by the crystal. The intensity of the green light was measured using a photomultiplier tube.

3. Results and discussions

3.1. Single crystal X-ray diffraction analysis

It was found that the crystals belong to the orthorhombic system with four molecules in the unit cell of dimensions: a=12.0263 (2) Å, b=6.0320 (9) Å, c=5.827 (17) Å and the space group Pna21. These values agreed well (within the standard deviations) with those reported in the structural investigation.

3.2. Fourier transform infrared spectroscopic (FTIR) studies

The recorded FTIR spectra (Fig. 3) were compared with the standard spectra of the functional groups [11]. The carboxylic acid group present in the molecule of DL-Alanine donates its proton to the amino group to form the structure: NH₃⁺CHCH₃COO⁻. Thus, in the solid state, DL-Alanine exists as a dipolar ion in which carboxyl group is present as a carboxylate ion and amino group is present as an ammonium ion. Due to this dipolar nature, DL-Alanine has a high melting point (280 °C). The bands due to hydrogen bonding modes appear just below 3000 cm⁻¹. The bands at 2803 and 2602 cm⁻¹ are assigned to C–H stretching. The sharp peak at 2114 cm⁻¹ is due to the combination of NH₃⁺ asymmetrical stretching and its torsional oscillation. The symmetrical NH₃⁺ stretch is observed at 1518 cm⁻¹. The C=O stretching of COO⁻ gets overlapped with the NH₃⁺ asymmetric stretching mode. The C–COO⁻ vibrations produce strong peaks at 1306, 1236, 1149 and 1115 cm⁻¹.

3.3. Thermal analysis

In the TGA/DTA spectra (Fig. 4), an endothermic peak observed at 280 °C in DTA corresponds to the melting point of DL-Alanine.
The melting of the crystal and the decomposition of the molecule occurred simultaneously. CO₂ and NH₃ molecules are liberated at 280 °C and 288 °C, respectively in sequence and contributes to the loss of mass of 49.4% and 19.1%, respectively. The loss of 18% of mass around 295 °C is attributable to the release of CH₄ molecule. The exothermic peak observed at 473.3 °C is due to the phase transition expected to happen in the carbon residue [12]. The small dip around 100 °C in the DTA curve is not due to any phase transition. It may be due to the release of adhered water molecules used as the solvent.

3.4. UV–Vis–NIR analysis

From the UV–Vis–NIR spectrum, it is seen that the UV transparency cutoff occurs around 200 nm and there is no remarkable absorption in the entire region of the spectra. The presence of chromophores, namely amino group and carboxyl groups in the DL-Alanine structure, makes it transparent in the UV–Vis region. The useful transmission extends from 200 to 1100 nm which makes it valuable for those applications requiring blue/green light. It is an important requirement for NLO materials having nonlinear optical applications [13].

3.5. Second harmonic generation analysis

A second harmonic signal of 75 mV was obtained, while the standard KDP crystal gave a SHG signal of 45 mV/pulse for the same input energy. This observation showed that the SHG conversion efficiency of DL-Alanine is about 1.7 times higher than that of KDP. The SHG efficiency will vary with the particle size of the powder sample [14].

4. Conclusions

Small needle-shaped crystals of DL-Alanine were grown by solvent evaporation method at 30 °C. The grown crystals were characterized by single crystal X-ray diffraction studies, FTIR, TGA/DTA, UV–Vis–NIR and SHG studies were also carried out. The occurrence of the π–π* transition in the carboxylic group accounts for the nonlinearity in this crystal. Since the crystal is stable up to 280 °C without any phase transition, transparent in the UV–Vis region and possesses higher SHG efficiency than that of standard KDP DL-Alanine may be useful for the NLO applications.

Fig. 3. FTIR of DL-Alanine.

Fig. 4. TGA/DTA of DL-Alanine.
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References