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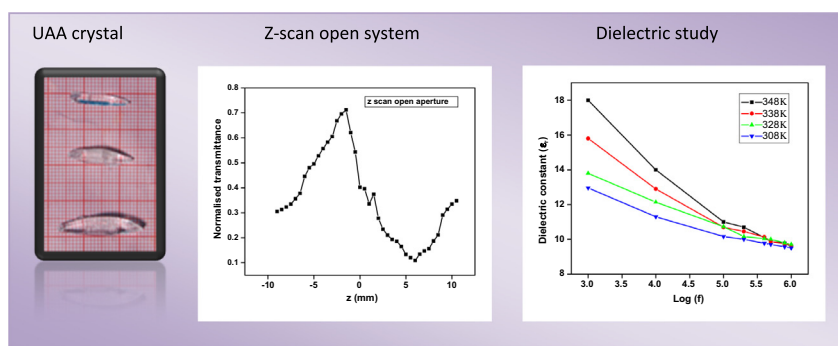
Growth and characterization of a single crystal of Urea Adipic acid (UAA) – A third order nonlinear optical material

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HIGHLIGHTS

- The various properties of urea-adipic acid (UAA) crystals are reported for the first time.
- The UAA crystal was grown in methanol solvent.
- From the UV–visible spectral studies, various optical constants were determined.
- Z-scan measurements reveal the aptness of crystal for third order NLO application.

GRAPHICAL ABSTRACT



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ABSTRACT

An organic single crystal of Urea Adipic acid (UAA) was successfully grown in methanol solvent by slow solvent evaporation technique at room temperature (30 °C). The structure of grown crystal was elucidated from the X-ray diffraction study and it belongs to monoclinic system with centrosymmetric space group $P2_1/c$. The optical transmission spectrum of UAA has been recorded and its theoretical calculations were carried out to determine the linear optical constants such as linear absorption coefficient, extinction coefficient, refractive index and reflectance etc. The third-order nonlinearities of UAA crystal have been investigated by Z-scan method. The values of nonlinear refractive index (n_2), the absorption coefficient (β) and third-order nonlinear susceptibility ($\chi^{(3)}$) are found to be the order of $0.96 \times 10^{-10} \text{ cm}^2/\text{W}$, $1.248 \times 10^{-4} \text{ cm/W}$ and $6.44 \times 10^{-8} \text{ esu}$ respectively. Fourier Transform Infra Red and Raman spectroscopy studies reveal the intermolecular interactions present in the UAA sample. The dielectric and mechanical measurements of the title compound are also reported.

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Introduction

Organic crystals are found to possess high nonlinear optical efficiencies and additionally offer large number of design possibilities. Some of them show extremely fast optical nonlinearities compared to that of inorganic crystals [1,2]. Optical nonlinearity of organic molecules can be enhanced by adding strong electron

donating and withdrawing entities and it generates highly polarizable charge transfer compound with an asymmetric electron distribution. This is mainly due to the asymmetric molecules carry a dipole moment in their ground electronic state, and in order to reduce the dipole–dipole interaction, which is dominant over the Van der Waals interaction in the lattice. This configuration will be favored for forming a crystal in centrosymmetrical crystalline structure. All the centrosymmetrical crystals have the third-order nonlinear properties and the third-order nonlinear susceptibilities are indispensable for all optical switching, modulating, and

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computing devices [3]. The third-order nonlinear optical materials have weak nonlinear absorption [NLA] but strong nonlinear refraction [NLR] and have considerable attention of their potential use in the optical signal processing devices [4].

Urea is one of the most promising materials for nonlinear optical application in UV region and it has a high birefringence and a high laser-damage threshold [5–8]. However, the growth of high quality and large-sized urea crystals is difficult due to unfavorable growth habits. It is an important chemical used in the fertilizer industries and it also serves a better crystal compared to KDP for its NLO efficiency [9–14]. From the molecular point of view, alkyl derivatives of urea are expected to show comparable nonlinear parameters, due to the fact that the low-lying electronic states are ruled by the same amino-carboxylic group. Harries and Thomas [15] have reported that the urea molecule forms an extensively hydrogen bonded host structure and Chadwick et al. [16] have reported the phase diagram of a related urea-dicarboxylic acid and Jerome Das et al. have reported urea – succinic acid crystal which possesses ferroelectric properties [17].

The combination of both organic materials such as urea with tartaric acid and urea with L-malic acid form non-centrosymmetric crystal structure with interesting nonlinear optical properties [18,19]. Hanumantharao et al. [20] has reported the growth and characterization of organic nonlinear optical crystals of urea thiosemicarbazone monohydrate. The nonlinear organic materials have attracted great attention and are gaining enormous demand due to their wide applications in the recent technologies like optoelectronics, areas of optical switching, optical data storage for the developing technologies in telecommunications and signal processing [21,22]. With this reported background, we have ventured into growth and characterization of Urea Adipic acid (UAA) crystal and it is expected that this would be a non-centrosymmetric complex, but to our surprise it has been formed in a centrosymmetric structure in which third order nonlinearity is more favorable and prominent. Similar results of third-order nonlinear optical properties have been reported earlier [23,24]. In this paper, we report the growth and characterization of single crystals of UAA and it is to be mentioned here that for the first time the results of various studies such as solubility, XRD, linear optical constants, third-order NLO studies, dielectric studies, FT-IR and FT-Raman studies are reported and discussed.

Synthesis, solubility and growth

Urea Adipic acid (UAA) salt was synthesized by taking high purity (AR) grade sample of urea and adipic acid in the molar ratio of 1:1 and dissolved in methanol solvent. Tanaka and Matsuoka [25] proposed that the crystal habits are influenced by the two factors such as the heat of crystallization and the solvent of growth. Based on this view, to select a suitable solvent for the growth of UAA crystal, solubility test was performed in different solvents such as de-mineralized water, methanol, ethanol and other organic solvents. Finally it is found that UAA sample has high solubility in methanol compared to that of de-mineralized water and other solvents, hence methanol was used as a solvent in the growth process. A beaker with 10 ml of methanol solvent was placed on a hot plate magnetic stirrer and the UAA salt was added in small amount at successive stages and subsequent stirring was continued till the small precipitate was formed at the bottom of beaker. After attaining the saturation, 5 ml of saturated solution was pipetted out and the same was poured into a clean, dry and empty petri dish. The solvent was completely evaporated by warming the solution. The amount of salt present in 5 ml solution was measured by subtracting the empty dish's weight. From this, the amount of the salt present in 100 ml of solution was calculated at 30 °C. In this manner,

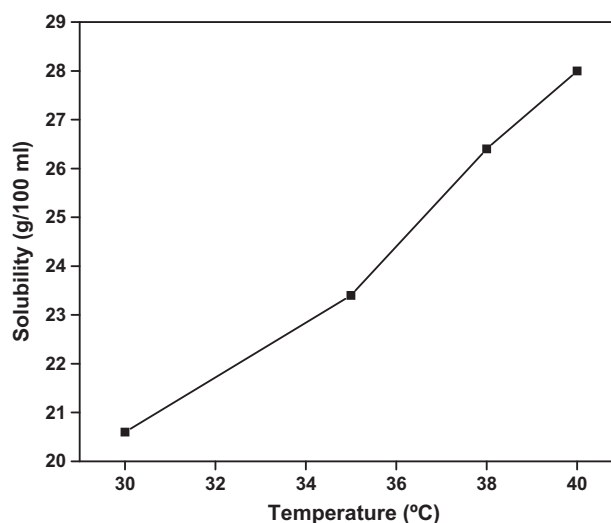


Fig. 1. Solubility curve for UAA sample.

the solubility of UAA salt at other temperatures (35, 38 and 40 °C) was measured. A graph of solubility versus temperature is shown in Fig. 1.

In order to grow single crystal of UAA, in accordance with the solubility data, saturated solution was prepared and it was continuously stirred about two hours to ensure homogeneous concentration and temperature throughout the volume of the solution. Then the solution was filtered using a high quality 4 micro Whatmann filter paper to remove extraneous solid colloidal particles. To obtain big single crystals, the bottom seed growth technique was adopted. The prepared saturated solution was taken in a beaker and covered by perforated cover for controlled evaporation and kept in an undisturbed condition. The seed crystals of UAA were obtained by spontaneous nucleation. The supersaturation of the solution was found by observing the first crystal formed at the bottom glass beaker due to slow evaporation of the solvent. The supersaturated solution of UAA was carefully transferred into another glass beaker and kept at 30 °C in the constant temperature bath. The defect-free seed crystals were placed in the supersaturated solution and the solution was allowed to evaporate the solvent slowly into the atmosphere. After a typical period of 13–15 days, colorless and transparent UAA crystals were obtained. The size of the big one is $24 \times 6 \times 4 \text{ mm}^3$. The photograph of the grown crystals is shown in Fig. 2.

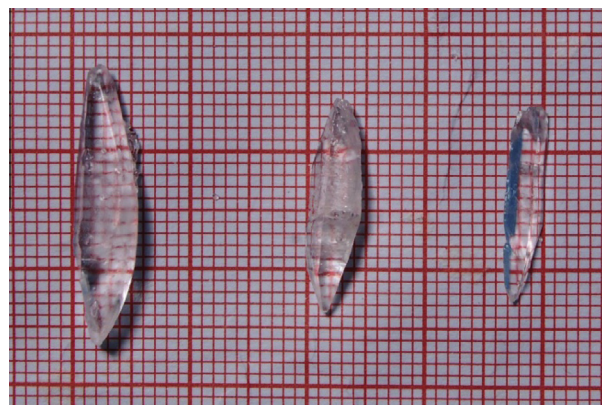


Fig. 2. Photograph of UAA crystals.

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