ULTRASOUND ASSISTED SYNTHESIS, CHARACTERIZATION AND NONLINEAR OPTICAL PROPERTY OF ZWITTERION L-GLYCINE

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Abstract : Experimental study of nonlinear optical (NLO) property of 25 kHz ultrasonic assisted crystallized zwitterion L-glycine (USALG) and non-assisted crystallized zwitterion L-glycine (LG) are reported. Good-quality single crystals of LG and USALG were successfully grown by a slow evaporation technique at room temperature. They were characterized by powder X-ray diffraction technique and both crystals were found to crystallize in the monoclinic system. The ultrasonic (US) assisted crystal possessed better transparency and crystalline perfection. The electrolytic conductivity (κ) of aqueous solutions of the crystals was measured using a conductivity meter at room temperature, and USALG exhibited high electrolytic conductivity. The second harmonic generation (SHG) efficiency was evaluated by the Kurtz and Perry method, and USALG was found to be 1.53 times more efficient than standard potassium di-hydrogen phosphate (KDP). The experimental result showed that USALG exhibited good second order nonlinear optical property.

L-Glycine, ultrasound, X-ray diffraction, conductivity, NLO property.

1. INTRODUCTION

Researches on the influence of US on crystallization processes has revealed that the nucleation of solid crystals from a number of liquids ranging from organic fluids to metals is affected by the presence of US waves. The US waves are reason for easy, faster primary nucleation, initiation of secondary nucleation and production of smaller, uniform sized pure crystals. The excellent mixing conditions created by the US which reduces agglomeration through control of the local nucleus population. US plays a role on crystallization by altering the principal variables such as induction period, super-saturation concentration and metastable zone width involved in this physical process. These effects vary in strength with the nature of the US source and its location; also, their influence is a function of the particular medium to which this form of energy is applied [1]. The literature contains a number of reports that establish empirical control over sonocrystallization parameters to achieve monodisperse crystals of a minimal size [2]. The continued expansion of sonocrystallization applications will be greatly benefited by the development of new technologies, including processes that couple atomization and ultrasound to produce crystals with well-defined size distributions and surfaces [3, 4].

Glycine (C2H5O2N), a white crystalline amino acid, is a widely used material for crystallization experiments [5]. Unlike other amino acids, it has no asymmetric carbon and it is optically inactive [6]. It exists as zwitterions (+NH3CH2COO–) in aqueous solution (at pH $\approx$ 6) and in a solid state [7]. Louhi-Kultanen et al. studied crystallization of glycine with ultrasound at 20 kHz [8]. Amino acids and peptides are used as probe molecules to understand the complex nature of the protein. In aqueous solution they ionize and act as acids or bases. Knowledge of acid-base properties of amino acids is extremely important in understanding many properties of proteins [9]. There has been no study reported on the effect of ultrasonic on the conductivity of aqueous solutions of L-glycine and SHG property of USALG.

NLO applications demand quality single crystals having a large NLO coefficient with improved physical parameters [10]. Investigations on organic NLO materials have subsequently produced very good materials with highly attractive characteristics. They have a wide range of practical applications [11], such as optical limiting [12-13], optical data storage [14] and terahertz wave generation [15]. Amino acid family crystals have been subjected to extensive investigation during the recent decades for their nonlinear optical properties [16]. Even though varieties of nonlinear optical materials are available, their applications are limited due to physical and chemical properties [17]. Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid (–COOH) group and the proton acceptor amino (–NH_2) group. They are widely utilized because they possess zwitterionic nature favoring crystal hardness [18]. The present study deals with the effect of ultrasonic on the conductivity of the aqueous solution of LG and SHG property of USALG.

2. Materials and methods

2.1. Materials

L-Glycine (G.R. Grade, purity > 99.7%, HiMedia Laboratories, Mumbai, India) and laboratory double deionized water were used for solution preparation.

2.2 Experimental Procedure

2.2.1 Crystallization of zwitterion L-glycine crystals (LG)

For crystallization the supersaturated solution was prepared by weighing a certain quantity of solid L-glycine in double deionized water. The obtained saturated solution was allowed to evaporate at room temperature, which yielded crystals of the glycine. Crystallized material was purified by repeated the crystallization process. The colourless, transparent, non-hygroscopic and stable crystals were obtained due to spontaneous nucleation. Among them, the defect free crystals were selected and stored for further analysis.

2.2.2 Ultrasound assisted Crystallization of zwitterion L-Glycine crystals (USALG)

Saturated solution (100 ml) of glycine was prepared at room temperature in a 250 ml round bottom flask. The solution was subjected to ultrasonic waves for 30 min and it was allowed to crystallize. The colourless, transparent, non-hygroscopic and stable crystals were obtained. The defect free crystals were selected and stored for further analysis.

2.3 Characterization by Powder X-ray diffraction (PXRD)

Crystalline nature was verified by measuring the X-ray powder diffraction patterns of crystallized samples using a powder x-ray diffractometer (XRD 3003 TT, GE Inspection Technologies, Germany). The experiments were performed in the symmetrical reflection mode with Cu Ka radiation (λ = 1.5406 Å). The scattered intensities were measured with a Våntec-1 line detector. The angular range was from 0 to 50° in steps of 0.005°. Other measurement conditions were as follows: target, Cu; filter, Ni; voltage, 40 kV; current, 40 mA; measuring time, 0.02 s per step.

2.4 Electrolytic Conductivity

0.05, 0.1, 0.15, 0.2 and 0.3 g of LG were separately dissolved in 100 ml deionised water. The conductivity of each solution was measured using ELICO conductivity meter (conductivity cell, 0.5 m^{-1} cell constant) at room temperature. The same set of prepared solutions were subjected to ultrasonic waves for 30 min and then conductivity measurements were made.

2.5 Kurtz powder second harmonic generation capacity of USALG

The second harmonic generation efficiency of USALG in comparison with KDP standard was measured by Kurtz and Perry method [19]. A collimated Nd:YAG Q-switched laser (YAG is yttrium aluminum garnet; duration of pulses 8 ns, repetition rate 10 Hz) operating at 1064 nm was used as a light source. A finely powdered crystal of USALG was densely packed in a microcapillary and exposed to a laser beam. The generated second harmonic wave of 532 nm was detected by a photomultiplier tube (Hamamatsu R5109, visible PMT) and converted into electrical signals.

3. Result and discussion

Over the past decades crystallization has been augmented by a lot of methods, techniques and recently ultrasound have evolved as a powerful tool in inducing and investigating the crystallization mechanism in various systems. Though ultrasound has been reported to influence every aspect of the crystallization process its effect on the phenomenon of nucleation is highly significant. The effect of ultrasound in the diagnostic frequency range of 1–10 MHz on the nucleation and growth characteristics of glycine has been reported [20]. In order to identify the advantages of sonication on crystallization, electrolytic conductivity and NLO property of L-glycine, the crystallization was first carried out in the absence of ultrasound. The crystals obtained under sonication were more transparent than that produced in the absence of ultrasound.

3.1 Powder X-ray diffraction pattern of LG and USALG

For structural confirmation and lattice parameter determination, the PXRD pattern of a homogeneously powdered LG and USALG was recorded and shown in figure 1 with hkl indexing.

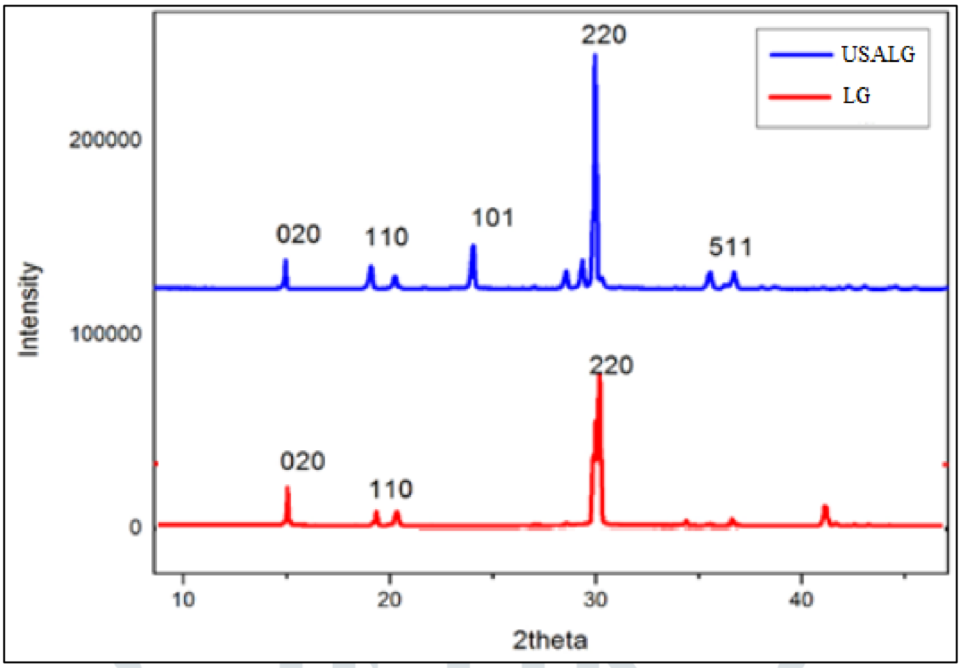

Figure 1. Powder X-ray diffraction pattern of ultrasound treated zwitterion L- glycine (USALG) and zwitterion L- glycine (LG).

The high crystallinity of the grown crystals of USALG was confirmed from the observed sharp and intense peaks of the diffraction pattern. The crystallographic data of LG and USALG were obtained using Xpowder software (table 1).

Table 1. Crystallographic data of the LG and USALG.

Zwitterion L-glycine (LG)	**ultrasound assisted zwitterion L-glycine (USALG)**
a = 7.065Å	a = 6.3071 Å
b = 12.1909 Å	b = 17.5273 Å
C = 5.4848 Å	c = 4.1301 Å
α=90.0000°	α=90.0000°
β=112.0000°	β=93.7627°
γ=90.0000°	γ=90.0000°
volume=472.56	volume=455.58
monoclinic	monoclinic

3.2 Electrolytic Conductivity of LG and USALG

Most of the chemical and biological functions of biomolecules take place in aqueous medium. Electrolytes are expected to influence the water structure, and the importance of contribution from structural changes of the solvent to the thermodynamic properties of aqueous solutions of biological molecules has often stressed. The information on the zwitterionic nature of amino acids in water is given in the literature [21-22].

The measurements were made using a commercial conductivity cell with platinum black electrodes. The cell was calibrated using two commercially available conductivity standards (aqueous potassium chloride solutions) with κ = (0.1 ± 0.0005) Sm^{-1} and κ = (1.0 ± 0.0025) Sm^{-1} at room temperature. An amino acid, when dissolve in water, perturbs the arrangement of water molecules with the strong electric field of its ions. The observed electrolytic conductivity measurements of aqueous solutions of LG and ultrasonic treated solutions were shown in figure 2. The US waves weaken the solute-solvent, ion-ion, dipole-dipole and ion-solvent interactions and hence the electrolytic conductivity of US treated aqueous solutions of LG is larger than that of the LG.

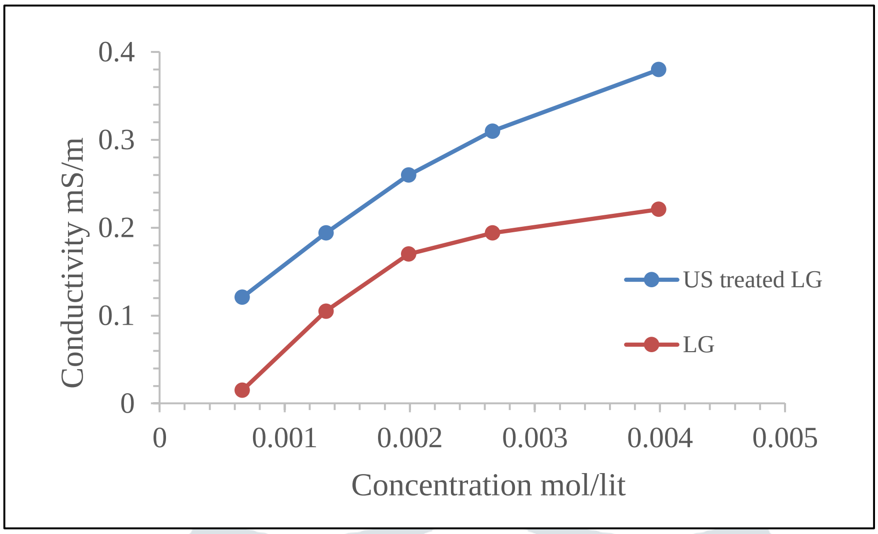

Figure 2. Conductivity plot of aqueous solutions of ultrasound treated zwitterion L- glycine (USALG) and zwitterion L- glycine (LG).

3.3 Kurtz powder second harmonic generation

The most widely used technique for confirming the SHG efficiency of NLO materials to identify the materials with noncentrosymmetric crystal structures is the Kurtz Powder technique [13]. The grown single crystal of glycine was crushed into powder with a uniform particle size and then packed into a microcapillary tube with a uniform pore size and exposed to laser radiation. Q-switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm was used. The input laser energy incident on the sample was 6.2 mJ/pulse and a pulse width of 8 ns with a repetition rate of 10 Hz was made to fall normally on the sample. A KDP crystal was used as a reference material in the SHG measurement. The second harmonic radiation generated by the randomly oriented microcrystals was detected by a photomultiplier tube. The generation of the second harmonic radiation was confirmed by a bright green emission emerging from the powdered sample. The emission of green light from the ultrasound treated zwitterion Glycine crystals confirmed their noncentro symmetric crystal structure.

The relative conversion efficiency was calculated from the output power of ultrasound treated zwitterion L-Glycine crystals with reference to KDP crystals. The standard KDP crystal produced 62 mV as output beam voltage while the ultrasound treated zwitterion L-Glycine produced about 95 mV as output beam voltage. Hence, it is confirmed that the material has NLO efficiency of about 1.53 times that of the KDP crystal, whereas the SHG efficiency of the crystal γ-glycine had been reported as 1.5 times higher than that of KDP [23].

4. Conclusion

In this study, the electrical conductivity and the nonlinear optical property of USALG were investigated. Colourless and transparent with and without ultrasonic assisted crystals of zwitterion L-glycine has been grown successfully in deionized water by the slow evaporation method. Crystallization with ultrasound proved to be a good tool to optimise, control nucleation and crystallization of glycine. Ultrasound assisted crystallization technique enhanced the behaviour of the zwitterion L-glycine crystals. It is because of the reduction in the impurity content in the grown crystals. The nonlinear optical study confirms the SHG property of the material is 1.53 times higher than that of the standard. The good second harmonic generation efficiency indicates the use of USALG crystals for application in nonlinear optical devices.

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