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Structural, mechanical, optical, dielectric and SHG studies of undoped and urea-doped γ-glycine crystals

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ABSTRACT

Single crystals of undoped and urea-doped γ-glycine (gamma-glycine) were grown from aqueous solutions by slow evaporation technique. Morphological changes were noticed in γ-glycine crystals when urea was added as dopant. Single crystal X-ray diffraction (XRD) studies were carried out to find crystal structure and lattice parameters of the grown crystals. UV-Visible transmittance spectra were recorded for the samples to analyze the transparency in visible and near infrared (NIR) region and UV cut-off wavelength observed for the samples to be at 257 nm. Nonlinear optical (NLO) activity of the grown crystals was studied using a Q-switched and pulsed Nd:YAG laser and second harmonic generation (SHG) efficiency was found. Values of work hardening coefficient were determined from microhardness studies and confirmed that the grown crystals belong to the category of soft materials. Measurements on values of dielectric constant, dielectric loss, AC conductivity and activation energy of the samples were carried out to understand the electrical phenomena that are taking place in pure and urea-doped γ-glycine crystals.

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1. Introduction

Organic and semi-organic nonlinear optical (NLO) materials formed from amino acids have potential applications in second harmonic generation (SHG), optical storage, optical communication, photonics, electro-optic modulation, optical parametric amplifiers, optical image processing etc. [1–5]. It is known that glycine, the simplest and non-essential amino acid, exhibits in three different polymeric forms viz. α-glycine, β-glycine and γ-glycine. Among the three forms, γ-glycine exhibits strong piezoelectric and NLO effect [6–8]. Iitaka reported the details of γ-glycine in 1958 and analyzed the crystal structure [9]. Growth of γ-glycine crystals in the mixture of water with various sodium compounds was reported by Narayan Bhat et al. [10] and Srinivasan et al. has reported the growth of α-glycine and γ-glycine and made detailed studies on the effect of sodium chloride (NaCl) on morphology of the grown crystals [11]. Recently, growth and various studies of γ-glycine crystals have been reported by many authors and it is observed that γ-glycine single crystals have been grown using additives such as potassium chloride, sodium chloride, lithium chloride, potassium bromide, sodium fluoride etc. [12–15]. In our work, γ-glycine crystals have been grown by solution method using ammonium chloride as an additive. It has been reported that doping NLO crystals with organic impurities can alter various physical and chemical properties and doped-NLO crystals may find wide applications in opto-electronic devices compared to pure NLO crystals [16,17]. Since no work has been noticed in the literature on doped γ-glycine crystals, an attempt has been made to introduce urea into the lattice of γ-glycine crystal to alter its physical and chemical properties. Urea is a well known simple organic NLO material and if it is added as a dopant, it is expected to occupy the interstitial positions of the lattice, which may disturb the lattice of γ-glycine crystal and in turn this may lead to alter the various properties γ-glycine [18]. The aim of this paper is to report the growth and various studies such as UV-Visible-NIR transmittance

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studies, XRD studies, SHG, measurement of microhardness and hence work hardening coefficient, measurement of dielectric constant, loss, AC conductivity and activation energy of undoped and urea-doped γ-glycine crystals.

2. Experimental methods

2.1. Synthesis and growth

Initially, pure and urea-doped γ-glycine salts were synthesized. Analar reagent (AR) grade of glycine and ammonium chloride in the molar ratio of 3:1 were used for synthesis of γ-glycine salt. The calculated amounts of glycine and ammonium chloride were dissolved in de-ionized water and stirred well using a magnetic stirrer for about 2 h. The solution was heated until the synthesized salt of pure (undoped) γ-glycine was obtained. To obtain urea-doped sample, 1 mol% of urea was added to the solution of γ-glycine. Solubility of the synthesized salts of undoped and urea-added γ-glycine in de-ionized water at room temperature (30 °C) was found to be 22.5 and 23.8 g/100 ml, respectively. The method of finding solubility was already reported in the literature [19]. In accordance with the solubility data, saturated solutions of the synthesized salts of undoped and urea-doped γ-glycine were prepared separately and the crystals were grown by solution method with slow solvent evaporation technique at room temperature (30 °C). The crystals were harvested after a period of 25–30 days.

2.2. Characterization techniques

X-ray diffraction (XRD) provides an efficient and practical method for the structural characterization of crystals. This method helps in determining the arrangement and the spacing of atoms in a crystalline material. The grown single crystals of undoped and urea-doped γ-glycine were subjected to single crystal X-ray diffraction (XRD) studies using an ENRAF NONIUS CAD4 diffractometer with Mo K_α radiation (λ=0.71073 Å) to identify the crystal structure, to find lattice parameters, space group and number of molecules per unit cell (Z).

UV-Visible-NIR transmittance spectra of the samples were recorded using a Varian Cary 5E UV-Visible-NIR spectrophotometer in the range 200–1100 nm covering the near, visible, near infrared region to find the transmission range to know the suitability for optical applications. A crystal thickness of about 2 mm was used for transmission studies. The sample absorbs a portion of the incident radiation and the remainder is transmitted on to a detector. Mechanical property was studied by measuring microhardness of the grown crystals and this was carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. Smooth, flat surface was selected and subjected to this study on the (1 0 0) plane of both undoped and urea-doped γ-glycine crystals. Indentations were made for various loads from 10 to 65 g. Several trials of indentation were carried out on the (1 0 0) plane and the average diagonal lengths were measured for an indentation time of 10 s. The Vickers microhardness number was calculated using the relation $H_v = 1.8544P/d^2$ kg/mm^2 where P is the applied load and d is the diagonal length of the indentation impression [20,21].

Measurements of dielectric parameters like capacitance, dielectric constant (ε_r) and dielectric loss ($\tan\delta$) of crystals carried out using an LCR meter (Agilent 4284A) at various frequencies in the range 10^2–10^6 Hz and at different temperatures ranging from 30 to 80 °C. Temperature was controlled to an accuracy of ±0.1 °C and it was measured using a digital thermometer. Crystals with high transparency and large surface defect-free (i.e. without any pit or crack or scratch on the surface, tested with a traveling microscope) size were selected and used. The sample crystals were cut, polished and silver-electroded. The observations were made while cooling the sample. Since the area of the crystal was smaller than that of the plate area of the cell, the dielectric constant of the crystal was calculated using the relation

$$\varepsilon_r = \left\{\frac{C_{crys} - C_{air}(1 - A_{crys}/A_{air})}{C_{air}}\right\}\int \frac{(A_{air})}{(A_{crys})}$$

where C_{crys} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of the electrode. Inaccuracy involved in the measurements of dielectric parameters was within ±5%. AC electrical conductivity of the grown crystals was determined using the data available from dielectric measurements [19,22].

Second Harmonic Generation (SHG) test for the grown undoped and urea-doped γ-glycine crystals was performed by the powder technique of Kurtz and Perry [23] using a pulsed Nd:YAG laser (Model: YG501C, λ=1064 nm). Pulse energy of 4 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz were used. The grown crystals were ground to powder of grain size 1500–1800 μm and the input laser beam was passed through IR reflector and directed on the powdered sample packed in a sample cell. Microcrystalline material of Potassium Dihydrogen Phosphate (KDP) was used as reference in this experiment. Second Harmonic Generation (SHG) from the samples was detected using a photomultiplier tube (PMT).

3. Results and discussion

3.1. Result of crystal growth

The harvested single crystals of undoped and urea-doped γ-glycine grown by slow solvent evaporation technique are displayed in Fig. 1. The grown crystals are found to be polyhedron in shape and are stable, do not decompose in air and non-hygroscopic at ambient temperature. The grown crystals are observed to be transparent, colourless and the crystal faces and edges are well formed. The morphology of the crystal is found to be different when γ-glycine is doped with urea and this is due to adsorption of the urea onto the surface of the crystal. The value of dipole moment of urea is 4.587 Debye units and this could influence of solvent-solute interactions in the solution. It is reported that urea acts as an immobile impurity that is usually adsorbed at the terrace of the crystal during the growth. Adsorption of urea on the surface of the crystal take place during the growth and hence the dopants have been introduced into the lattice of γ-glycine crystal. It is possible that adsorption of

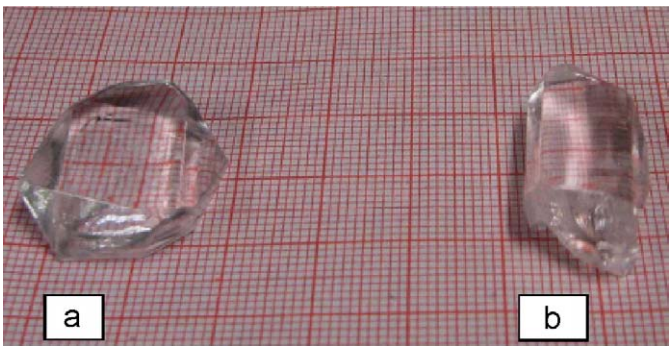

Fig. 1. Harvested crystals of (a) pure and (b) urea-doped γ-glycine crystals.

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