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Synthesis, growth, optical and mechanical studies of ferroelectric urea-oxalic acid single crystals

R. Ezhil Vizhi [a,*], R. Dhivya [a,b], D. Rajan Babu [a]

[a] Materials Research Laboratory, Department of Physics, School of Advanced Sciences, VIT University, Vellore 632014, Tamilnadu, India
[b] Voohrees College, Vellore 632014, Tamilnadu, India

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ABSTRACT

A single crystal of urea oxalic acid was grown by slow evaporation method. The lattice parameters are $a=5.13$ Å, $b=12.48$ Å, $c=7.07$ Å, $\beta=98.13^\circ$ with $V=448.5$ Å^3 which belongs to monoclinic system with space group $P2_1/c$ obtained from single crystal X-ray diffraction analysis. UV–visible spectrum was recorded from the wavelength region of 200–800 nm and its cutoff wavelength was found to be 270 nm. Optical energy band gap of 4.57 eV was determined using Tau's plot relation. Fourier transform infrared vibrational spectrum confirmed the presence of N–H asymmetric stretching which occurs at 3444 cm^{-1} and 1853 cm^{-1} arising due to the amide C=O symmetric stretching. The emission was observed at 364 nm from the photoluminescence spectrum. The mechanical stability of the grown crystal was estimated by Vickers microhardness studies and it is evident that the grown crystal belongs to soft material category. Hardness related parameters such as elastic stiffness constant, fracture mechanics, brittleness index and yield strength were also evaluated. The dielectric constant and dielectric loss of the grown crystal were carried out as a function of frequency for different temperatures.

1. Introduction

Polar materials possess an effective electric dipole moment in the absence of an external electric field. Ferroelectricity, which enables the electric changing of electric polarization, is attractive for versatile technical applications, such as ferroelectric random-access memories, ferroelectric field-effect transistors and infrared detectors etc. [1]. The important applications of ferroelectric materials are mostly in optoelectronics such as capacitors, non-volatile memory devices, high-performance gate insulators etc. [2]. The ferroelectric crystal is a phase-transforming material and there exists a critical temperature, called the curie temperature (T_c). Below the Curie temperature, ferroelectric and pyroelectric polar materials exhibits spontaneous polarization, but above T_c, they are paraelectric with nonpolar structures. Ferroelectric crystals have attracted attention for applications in various actuator and sensor applications due to their high frequency response [3]. Some compounds of oxalates are technologically important on account of their luminescent, ferroelectric and ferroelastic behavior [4,5]. The ferroelectric properties of several oxalates have wide applications in electro and acousto optical devices [6,7] and are used as precursors for many technologically important ferromagnetic and superconducting materials [8]. Oxalic acid is the only possible compound where two carboxyl groups are joined directly and for this reason oxalic acid is one of the strongest acids in organic compounds [9]. It also has high hydrolysis efficiency [10] and it is biodegradable and relatively inexpensive, and are found to occur naturally on earth [11]. Though urea has some undesirable chemical properties, it is used in various practical applications [12,13]. In the present work urea-oxalic acid single crystals are grown at room temperature by slow evaporation solution growth technique. The grown crystals were characterized using single crystal X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectrum analysis. The UV–visible NIR spectrum provided the information regarding the energy band gap value of the material. Vicker's indentation test was carried out to determine the mechanical strength of the crystal. Fracture toughness, brittleness index and yield strength for the grown crystal were also estimated. The dielectric constant and the dielectric loss were determined as a function of frequency. To cover the phase transition, measurements were carried out in the temperature range 293–413 K.

* Corresponding author.
E-mail addresses: rezhilvizhi@vit.ac.in, revizhi@gmail.com (R.E. Vizhi).

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2. Experimental

2.1. Material synthesis and crystal growth

Urea oxalic acid was synthesized by taking commercially available (AR grade E-Merck) urea and oxalic acid in the stoichiometric ratio of 2:1 and dissolved in water (resistivity of 18.2 MΩ cm at 25 °C) at room temperature. The saturated solution was filtered using Whatmann filter paper. The filtered solution was then transferred into 100 ml beaker. To control the evaporation of the solution, it was covered with a perforated polythene sheet. After 15 days, good quality crystals were harvested with dimensions of $10 \times 4 \times 2.23$ mm^3. Fig. 1(a) shows optically clear UOA crystal grown by the slow evaporation method.

2.2. Solubility and metastable zonewidth

Saturated solution was prepared at 35 °C and to ensure homogeneous concentration, the solution was stirred continuously. Solubility of UOA was determined gravimetrically using a constant temperature water bath, with an accuracy of ±0.01 °C. The equilibrium concentration of the solution was analyzed gravimetrically after achieving supersaturation. The same procedure was repeated at 40 °C, 45 °C and 50 °C and the resultant graph is presented in Fig. 1(b). It is clear from the figure that the crystal has positive temperature coefficient of solubility. Metastable zonewidth is the difference between the saturated temperature and nucleation temperature and it was determined by polythermal method [14].

In this method, the equilibrium saturated solution was cooled from the overheated temperature until the first nuclei was observed. In accordance with the solubility data, the saturated solution was prepared at 35 °C and it was heated upto 40 °C. The temperature of the bath was gradually cooled using an ultra cryostat. The first speck of the particle was observed when the bath temperature reached 24.86 °C which corresponds to the nucleation temperature. The same procedure was adopted when the saturated solution was prepared at 40 °C, 45 °C, 50 °C and the nucleation curve was drawn (Fig. 1(b)).

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The grown crystals of UOA were subjected to single crystal X-ray diffraction analysis using the BRUKER ADVANCED X-ray diffractometer to determine the cell parameters. X-ray diffraction studies confirmed that, the UOA crystallizes in the monoclinic system with space group $P2_1/c$ and the lattice parameters are found to be $a=5.048$ (3) Å, $b=12.398$ (3) Å, $c=6.960$ (2) Å, $\beta=98.13$ (7) Å and $V=448.5$ Å^3 which is in very good agreement with that of the reported values [15].

3.2. FT-IR spectrum analysis

In order to analyze the presence of functional groups qualitatively in a grown crystal of UOA, the FT-IR spectrum was recorded between 500 and 4000 cm^{-1} using the IFS BRUKER spectrometer and the resultant spectrum is shown in Fig. 2. From the spectrum it is evident that the absorption at 1720.50 cm^{-1} is due to amide C=O stretching of –COOH group and the N–H stretching mode was observed at 3327.21 cm^{-1}. The NH_2 bending is present in the urea molecule at 1494 cm^{-1}. The N–H and C–N stretching of vibrations are due to the peaks at 3444.87 cm^{-1} and 1024 cm^{-1} respectively. The CH_2 wagging is revealed by the peak at 1207 cm^{-1}. The vibrational peak at 779 cm^{-1} is due to the O–H plane bending vibration [16].

3.3. Optical studies

3.3.1. UV–vis-NIR spectrum analysis

Optical absorption studies for the urea oxalic acid were recorded in the range 200–800 nm and the resultant spectrum is shown in Fig. 3(a). From the graph it is clear that a low absorption is observed throughout the visible and IR region. The cut off wavelength of the UOA crystal is found to be 270 nm. The optical absorption coefficient (α) was calculated using the relation [17]

$$\alpha = \frac{2.303}{d} \log\left(\frac{1}{T}\right) \quad (1)$$

where T is the transmittance and d is the thickness of the crystal. The direct band gap of UOA has an absorption coefficient (α)

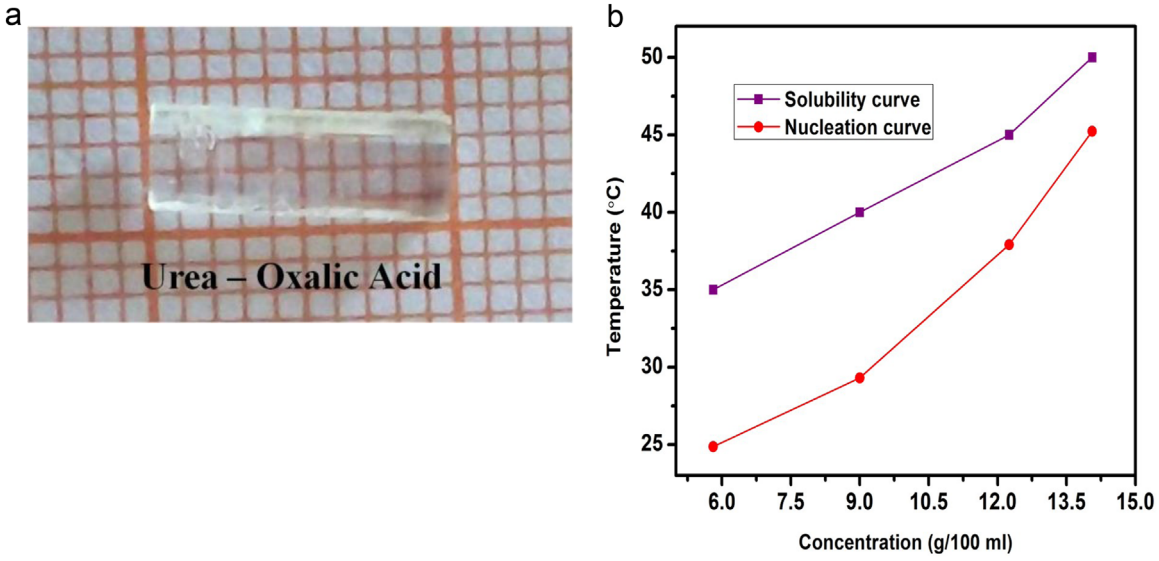

Fig. 1. (a) As grown crystal of UOA and (b) metastable zonewidth of UOA.

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