

Structural, growth and characterizations of NLO crystal: Triglycinium calcium nitrate

M. Esthaku Peter^{1*}, P. Ramasamy²

¹Department of Physics, Easwari Engineering College, Chennai 600089, Tamilnadu, India

²Centre for Crystal Growth, SSN College of Engineering, Kalavakkam 603110, Tamilnadu, India

*Corresponding author. Tel: (+91) 9841305008; Fax: (+91) 44-22491130; E-mail: mesthakupeter@gmail.com, esthaku1603@gmail.com

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ABSTRACT

Single crystals of triglycinium calcium nitrate, a semiorganic nonlinear optical (NLO) material, have been grown by slow solvent evaporation technique at room temperature. The size of the grown crystal is up to the dimension of 29×19×5 mm³. The structure of the crystal was analyzed by single crystal X-ray diffraction and the functional groups present in the sample were identified by FTIR spectral analysis in the range 4000-450 cm⁻¹. The UV-vis-NIR studies was undertaken to find the transmittance in the ultraviolet and visible region. The efficiency of second harmonic generation was analyzed by Kurtz-Perry powder technique and compared with standard KDP crystal. Thermogravimetric and differential thermal analysis have been performed to determine the thermal stability of the crystal. Dielectric properties such as dielectric constant and dielectric loss were studied at various temperatures and frequencies. Vickers microhardness testing was carried out on the as grown crystal surface to reveal the mechanical properties of the crystal. Etching studies were made on the as grown crystal to analyze the structural imperfection of the crystal. Copyright © 2016 VBRI Press.

Keywords: Crystal growth; crystal structure; etching; X-ray diffraction.

Introduction

Materials, which are capable of generating the second harmonic frequency, play an important role in the domain of optoelectronics and photonics. Crystals possessing nonlinear optical properties with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for several device applications. Nonlinear optical materials efficiently exhibit nonlinear optical phenomena, which are conversion of amplification of light, and conversion of the refractive index depending on optical intensity. Research is being performed periodically in the development of NLO organic and semi organic crystals which possess large nonlinear optical coefficients. Slow solvent evaporation, Slow cooling of the solution and Temperature gradient techniques are the conventional and simple methods to grow organic, inorganic and semi organic crystals. Crystals such as KDP, ADP, group of amino acid compounds and mixing of amino acid with inorganic compounds such as Triglycine calcium dibromide, Triglycine zinc chloride, L-Hystidine Tetra-Fluoro-Borate have been grown by solution growth method. Among them L-Hystidine Tetra-Fluoro-Borate crystal has considerable SHG efficiency which may be suitable as a frequency converter in Lasers. Organic materials possess better SHG efficiency due to highly movable π -electrons. Glycine is a simple compound

of amino acid and amphoteric in nature, it reacts chemically either as an acid or a base with other compounds to produce large number of possible glycine compounds. When glycine is mixed with other compounds, which results large number of compounds with NLO properties. To increase the mechanical properties of organic crystals, inorganic compounds are added. In view of that point glycine with calcium nitrate has been attempted to grow single crystal and studied its properties.

New types of hybrid NLO materials have been grown from organic-inorganic complexes with stronger ionic bond [1]. Many semi organic nonlinear optical crystalline materials have been grown by slow solvent evaporation technique, which are attracting a great deal of attention in the nonlinear optical field from application point of view. L-Hystidine Tetra-Fluoro-Borate (L-HFB) is a semi organic nonlinear optical material whose single crystal exhibits more NLO properties than that of inorganic crystals like potassium dihydrogen phosphate, beta barium borate, and lithium triborate crystals [2]. Presently, inorganic and organic materials are being replaced by semi-organic crystal. They share the properties of both organic and inorganic materials. Recent interest is concentrated on metal complexes of organic compounds owing to their large non-linearity. The approach of combining the high nonlinear optical coefficients of the organic molecules with the excellent physical properties of the inorganic compounds has been found to be successful in the recent past.

Crystal growth

TGCN single crystals were grown from the aqueous solution of glycine and calcium nitrate tetrahydrate in equimolar ratio, with millipore water of resistivity 18.2 M Ω .cm as a solvent by slow solvent evaporation technique. A homogeneous aqueous solution of glycine and calcium nitrate tetrahydrate was prepared by mixing calcium nitrate tetrahydrate with saturated solution of glycine. The pH value of the prepared solution was 4.8. Then the prepared solution was taken in a borosilicate beaker and kept for evaporation at room temperature. After a month, good optically transparent triglycinium calcium nitrate crystals were obtained with a size of 29×19×5 mm³. The photograph of the as grown crystals is shown in the **Fig. 1**.

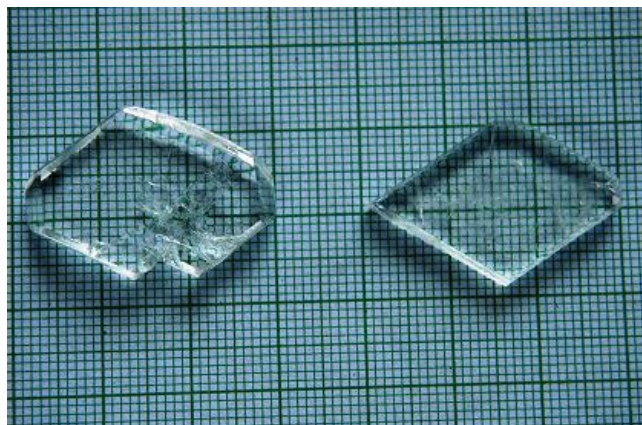


Fig. 1. Photograph of as grown Triglycinium calcium nitrate crystal.

Experimental

In order to reveal the properties of the crystal, the TGCN single crystals were subjected to various tests. Single crystal X-ray diffraction studies were carried out using a Bruker AXS Kappa APEX II single crystal CCD diffractometer coupled with graphite-monochromated MoK α ($\lambda = 0.7107\text{\AA}$) radiation. The goniometer equipped with the diffractometer is four circle goniometer with ϕ , χ , ω and 2θ axes by which the crystal is rotated. The crystals of size $0.30 \times 0.20 \times 0.20$ mm³ were cut and mounted on a glass fiber using cyanoacrylate. The structure was solved by direct method with the aid of SHELXS97 (Sheldrick, 2008) and refined using SHELXL97 (Sheldrick, 2008) by the methods of full-matrix least squares refinement. Functional groups such as hydrogen bonds and ammonia group play a very important role in crystallization and nonlinear optical performances according to both Phillips-Van Vechten-Levine-Xue bond theory and chemical bonding theory [3-5]. In order to analyze the presence of functional groups in triglycinium calcium nitrate crystals qualitatively, FT-IR spectrum was recorded between 4000 and 450 cm⁻¹ using Perkin-Elmer spectrum one FTIR spectrometer. To find the transmission range and the suitability of triglycinium calcium nitrate single crystals for optical applications, the UV-vis-NIR transmission spectrum was recorded in the range of 200 to 1100 nm using Perkin-Elmer Lambda 35 UV-vis spectrometer. A polished crystal of thickness 2 mm was used for recording the spectrum. Since triglycinium calcium nitrate crystallized in a noncentrosymmetric space

group, it was thought that there is a possibility for second harmonic generation. The Kurtz and Perry powder technique was used to find the efficiency of second harmonic generation (SHG). A high intense Nd: YAG laser beam of wavelength 1064 nm with beam energy 1.95 mJ/pulse was used in this investigation.

Thermal properties of triglycinium calcium nitrate crystal were analyzed by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) between the temperature 25 °C and 1200 °C in nitrogen atmosphere at a heating rate of 10 °C/min using NETZSCH STA 409 C/CD TG/DTA instrument. To find dielectric constant of the crystal, capacitance of the crystal using Precision LCR meter AGILENT 4284A model by varying temperature. A polished crystal of 1 mm thickness was used to analyze the dielectric properties. In order to make a good contact with the electrodes, the surface of the crystal was coated with fine graphite powder. Then the prepared sample was placed in between the two electrodes and heated from 40 °C to 180 °C using thermostat. After reaching 180 °C, the sample was subjected to the process of annealing in the thermostat itself. The dielectric properties such as capacitance and dielectric loss were measured at different temperatures and frequencies from 100 Hz to 1 MHz. The grown TGCN single crystal was subjected to Vickers microhardness testing using Reichert-Jung MICRO-DUROMAT 4000 E microhardness tester to find the surface hardness of the crystal.

The three properties of a crystal, external form, perfection, and homogeneity, are directly related to the crystal growth [7]. Etching studies were carried out in the as grown (011) plane of the crystal at room temperature using deionized water as an etchant. It was performed by soaking the surface of the sample by wet tissue paper at room temperature for 1, 2, 3 and 4 sec respectively. Then the etched surface was dried by gently pressing the crystal between two filter papers and its surface micromorphology was photographed using REICHERT POLYVAR 2-Metallurgical microscope.

Results and discussion

The triglycinium calcium nitrate crystallizes in the Pna2₁ space group with six glycinium zwitterions and four calcium nitrate in the asymmetric unit. Among the four nitrate groups two nitrate ions exist in the lattice separately in resonance condition and two of them have made strong covalent bond with calcium metal ion. Moreover, these six glycinium zwitterions and two calcium nitrate groups run along the c-axis repeatedly. The molecular structure and packing diagram of the triglycinium calcium nitrate are shown in the **Fig. 2** and **Fig. 3** respectively. Within these chains, strong hydrogen bonds bind neighbouring molecules together. Crystal data, details of the measurements and the refinements are given in the **Table 1**. In the FTIR spectrum shown in the **Fig. 4**, a broad and strong band is obtained at 3044 cm⁻¹, which is due to the NH₃⁺ asymmetric stretching vibration [8, 9]. Nitrate (NO₂) asymmetric stretching band occurs at 1626 cm⁻¹ [6]. A fairly strong symmetrical NH₃⁺ bending vibration occurs at 1523 cm⁻¹. The carboxylate ion group absorbs strongly at 1590 cm⁻¹. The absorption at 826 cm⁻¹ belongs to NH₂

wagging and twisting and 1384 cm^{-1} belongs to NO_3 stretching vibration.

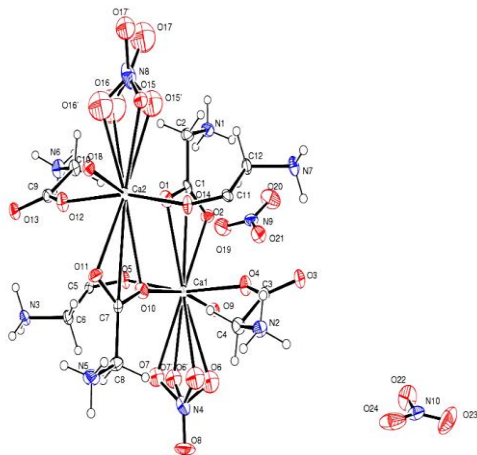


Fig. 2. Molecular structure diagram of Triglycinium calcium nitrate crystal.

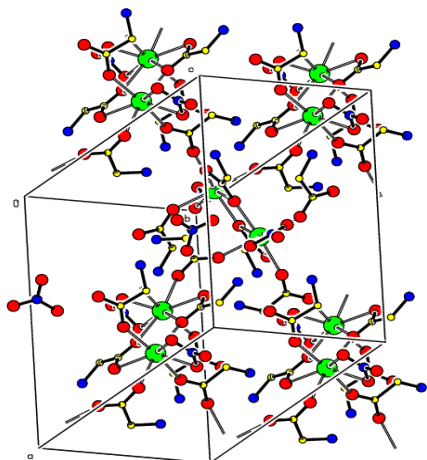


Fig. 3. Packing diagram of Triglycinium calcium nitrate crystal.

Table 1. Crystal data and structure refinement for Triglycinium calcium nitrate crystal.

Identification code	TGCN
Empirical formula	$\text{C}_{12}\text{H}_{30}\text{Ca}_2\text{N}_{10}\text{O}_{24}$
Formula weight	768.54
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Space group	$\text{Pna}2_1$
a, Å	14.6554(13)
b, Å	9.2349(9)
c, Å	21.382(2)
Volume, Å ³	2893.9(5)
Z	4
Calculated density, Mg/m ³	1.764
Absorption coefficient, mm ⁻¹	0.512
F(000)	1576
Crystal size, mm ³	0.30 x 0.25 x 0.20
Theta range for data collection, deg.	1.90 to 25.00
Limiting indices	$-17 \leq h \leq 13$, $-10 \leq k \leq 10$, $-24 \leq l \leq 25$
Reflections collected / unique	14358 / 4671 [R(int) = 0.0263]
Completeness to theta	25.00 98.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9045 and 0.8215
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4671 / 14 / 434
GoF (F ²)	1.067
Final R indices [I > 2σ(I)]	R1 = 0.0483, wR2 = 0.1361
R indices (all data)	R1 = 0.0534, wR2 = 0.1446
Absolute structure parameter	-0.02(5)
Largest diff. peak and hole	1.537 and -0.484 e. Å ⁻³

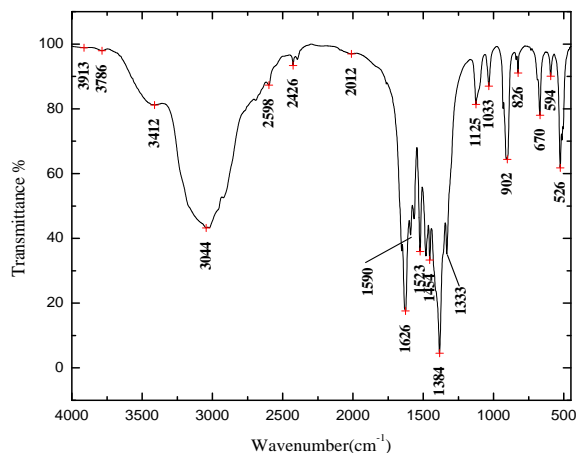


Fig. 4. FTIR spectrum of Triglycinium calcium nitrate crystal.

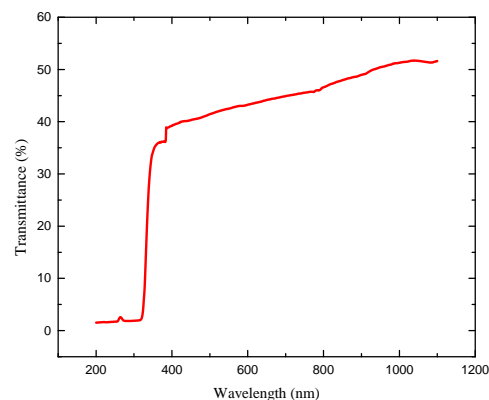


Fig. 5. UV-Vis-NIR spectrum of Triglycinium calcium nitrate crystal.

The absorption peaks for different functional groups are shown in the **Table 2**. The resultant transmittance of the crystal is shown in the **Fig. 5**, in which it is observed that the transmittance increases gradually from 40 % to 50 % in the visible region. The spectrum indicates that, the cut-off wavelength is about 340 nm and the maximum transmittance of the grown crystal is 51 % at 980 nm wavelength. It is noted that the transparency range for triglycinium calcium nitrate is moderate and so it can be used for generation and mixing of frequencies over a wide range of electromagnetic spectrum including the UV. The grown TGCN crystalline sample was tightly packed in a micro capillary tube in the form of fine powder and mounted in the path of Nd: YAG laser beam.

Table 2. Frequencies of the fundamental vibrations of Triglycinium calcium nitrate crystal.

wavenumber (cm ⁻¹)	Assignment [6],[8-10]
3044	NH_3^+ stretching
2426	C-H stretching
2012	N-H stretching
1626	NO_2 asymmetric stretching
1523	symmetric NH_3^+ stretching
1454	C-H deformation
1384	NO_3^- stretching
1333	asymmetrical N=O stretching
902	O-H out of plane bending
826	NH_2 wagging and twisting
670	$\text{C}(\cdots\text{O})_2$ Bending
526	torsional oscillation

It was observed that the crystal emitting green light with the output voltage of 32 mV. But while using KDP crystal as a reference material, the transmitted beam voltage was 62 mV. The nonlinear optical property of the crystal Second Harmonic Generation of the crystal was confirmed from the output of the green light. Hence the SHG efficiency of TGCN crystal is half that of KDP crystal.

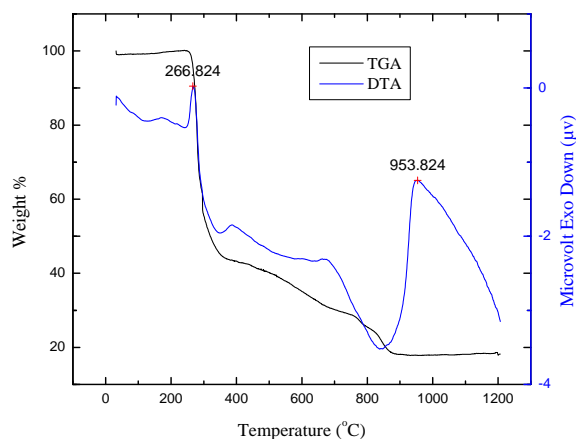


Fig. 6. TGA and DTA thermogram of Triglycinium calcium nitrate crystal.

The TG-DTA curves are shown in the **Fig. 6**. In TGA graph it is observed that there is no weight loss up to 250 °C. Hence it is confirmed that the crystal is devoid of any physically adsorbed water on it and the material starts to melt at 250 °C. The dissociation temperature is confirmed by the sharp endothermic peak obtained in differential thermal analysis curve at 266 °C. From the thermogravimetric analysis curve it is observed that the grown TGCN crystal decomposed upto 57 % when the temperature is increased from 266 °C to 400 °C. This is due to the complete decomposition of glycine molecule and the nitrate ions present separately in the compound. There is another endothermic peak at 953°C, which starts from 838 °C, corresponds to the melting point of calcium. While comparing thermogravimetric analysis curve, 82 % of the compound gets decomposed completely. The grown TGCN crystal is thermally stable up to 250°C.

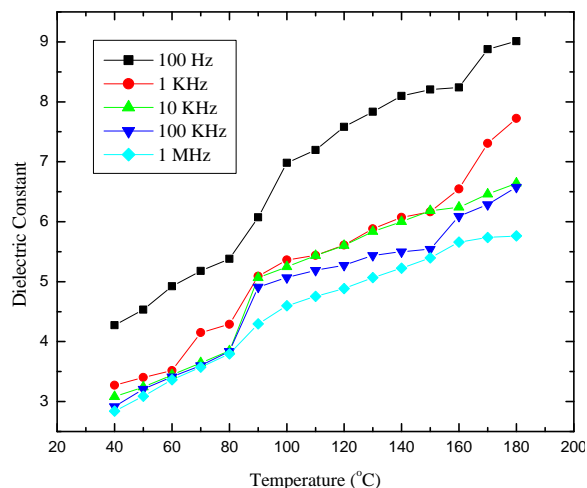


Fig. 7. Dielectric constant of Triglycinium calcium nitrate crystal.

A graph was drawn for the measurement of dielectric constant with respect to various frequencies which is shown in the **Fig. 7**. It is observed that the dielectric constant increases with the increase of temperature and it is found to be 9 at 180 °C.

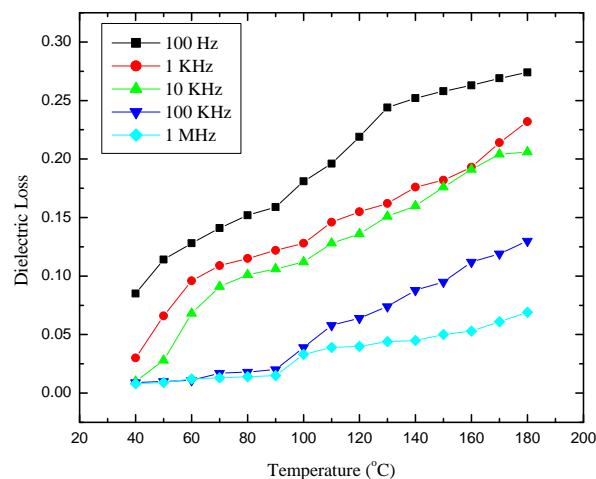


Fig. 8. Dielectric loss of Triglycinium calcium nitrate crystal.

Fig. 8 shows the variation of dielectric loss with the effect of temperature at various frequencies. It is also observed that the dielectric loss factor is less at higher frequency and more at lower electrical frequency. This corresponds to the dielectric constant graph of frequency range from 100 Hz to 1 MHz. From the experimental observation made on the crystal, dielectric loss is very less. Due to the inertia of the molecules and ions at high frequencies, the orientation and ionic contribution of polarization are small [11]. So, the magnitude of dielectric constant increases with the decrease of frequencies.

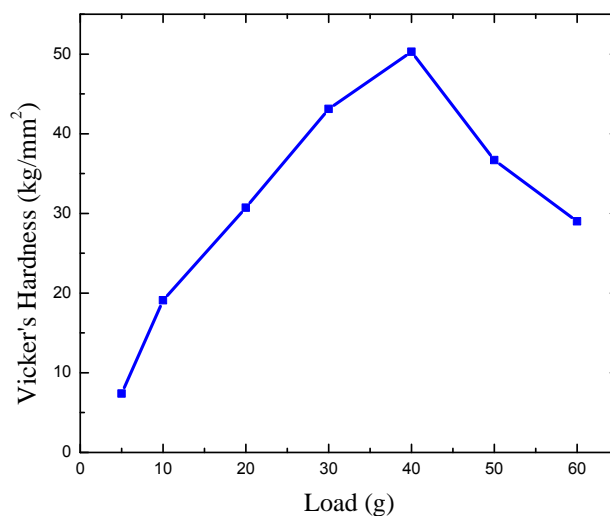


Fig. 9. Microhardness V_s load graph of Triglycinium calcium nitrate crystal.

The Vickers microhardness number was calculated from the standard formula $H_v = 1.8544 P/d^2$ kg/mm², where P is the load applied, d is the average diagonal length of the indentation made on the crystal and 1.8544 is a geometrical factor for the diamond pyramid. Vickers microhardness was

noted by changing the load from 5 g to 60 g and the variation of microhardness is represented in the **Fig. 9**. In this plot, it is observed that the value of microhardness increases with the increase of load up to 40 g, thereafter it decreases. The maximum microhardness obtained is 50 kg/mm².

Work hardening coefficient (*n*) was calculated using the Meyer's relation $P = ad^n$, to find the increase in strength that accompanies plastic deformation of the grown crystal, where *a* is the constant for the given material. A graph was drawn between logarithmic values of the applied load and average diagonal length of the indentation formed on the crystal. **Fig. 10** shows the plot of log *P* and log *d*, from which a slope was taken from a straight line. The calculated work hardening coefficient was 2.7. According to Onitsch [12], if the value of *n* lies between 1 and 1.6, the grown crystal will be a harder material and if it is more than 1.6, the material will be soft [13, 14]. As the work hardening coefficient "*n*" is more than 1.6 in the grown crystal, the crystal comes under the category of soft material. Yield strength (σ_y) of the grown crystal was calculated using the formula [15] $\sigma_y = (H_v/3)(0.1)^{n-2}$, where H_v is the Vickers microhardness and *n* is the logarithmic exponent. The calculated yield strength was 3.33 MPa.

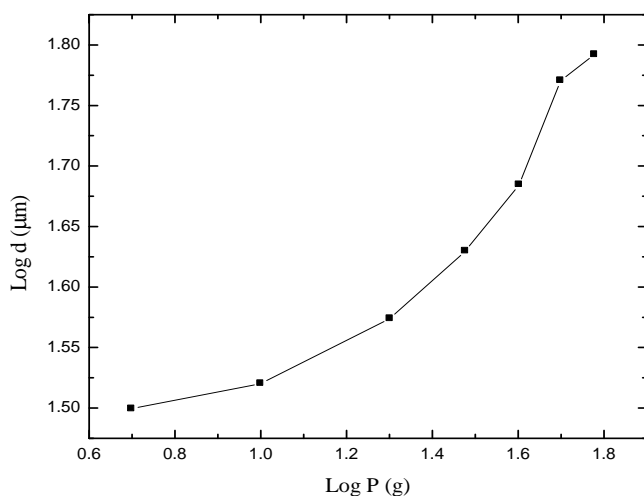


Fig. 10. Plot of log *P* and log *d* of Triglycinium calcium nitrate crystal.

Fracture toughness (K_{Ic}) is one of the mechanical properties describing the ability of a material containing a crack to resist fracture and it is one of the most important parameters for design applications. It was calculated using the formula $K_{Ic} = P/\beta C^{3/2}$, where *C* is the crack length from the center of the indentation, *P* is the applied load and β (≈ 7) is the geometrical constant for Vickers indenter [16]. The crack length developed in the grown triglycinium calcium nitrate crystal with the applied load 40g was 95 μ m, from which the fracture toughness was calculated as 6171 kg/m^{3/2}. Brittleness is an important property of the crystal which determines its fracture without any appreciable deformation. It is expressed in terms of brittleness index [17]. Brittleness index was also calculated using the formula $B_i = H_v/K_{Ic}$ [18] as $8.1 \times 10^{-3} \text{ m}^{-1/2}$.

The surface photograph of the triglycinium calcium nitrate crystal before etching and the etch pattern produced in the (011) plane of the crystal is shown in **Fig. 11**. It is

observed very clearly that the etch pit formed in the surface is hexagonal in shape. Moreover, when etching time increases, the size of the etch pits gets enlarged. **Fig. 11(a)** is the microphotograph of the (011) plane of the triglycinium calcium nitrate crystal before etching. When the etching time is given 1sec, it is observed in the microphotograph that many small hexagonal shaped etch pits of size 22 μ m are formed in the crystal (**Fig. 11(b)**). There is no change found in the shape of etch pits and morphology on successive etching from 4 s to 10 s, which suggest that the etch pits are due to dislocations. The etch pit density for one second was calculated as 185/mm². Etching time 2 seconds and 3 seconds lead to the development of bigger sized etch pits of size 65 μ m and 100 μ m respectively, which is shown in the **Fig. 11(c)** and **(d)**. The calculated etch pit density for 2 second and 3 seconds etching time is 46/mm² and 15/mm² respectively. But when it is 4 seconds, it leads to the development of hexagonal etch steps (**Fig. 11(e)**). The etch pits disappear on prolonged etching.

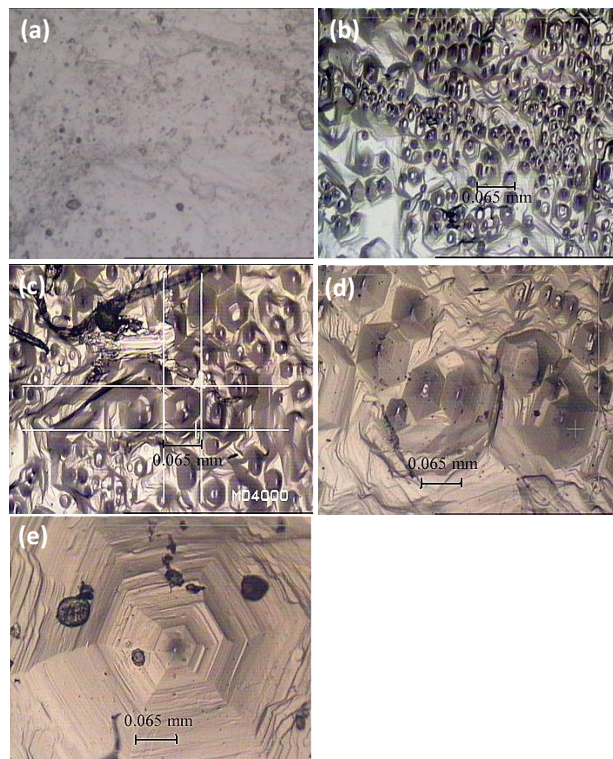


Fig. 11. (a) Surface of the as grown Triglycinium calcium nitrate crystal and Etch patterns produced in the (011) plane of the crystal for (b) 1 second (c) 2 seconds (d) 3 seconds and (e) 4 seconds.

Conclusion

Triglycinium calcium nitrate is a semiorganic nonlinear optical crystal, which can be grown by slow solvent evaporation technique from the aqueous solution of glycine and calcium nitrate tetrahydrate in 1:1 molar ratio at room temperature. The unit cell parameters estimated by single crystal X-ray diffraction agree with the reported values. The various functional groups present in the crystal confirm triglycinium calcium nitrate crystal, which were identified using FTIR spectrum. The maximum transmittance of the grown crystal under UV-vis-NIR radiation is 51 % at

980 nm wavelength and 45 % in the visible region. The nonlinear optical efficiency of the grown crystal is half that of KDP crystal. It melts at 250 °C and starts to dissociate from 266 °C, hence the thermal stability of the crystal is relatively higher. Dielectric constant increases with the increase of temperature and is 9 at 180 °C. The Vickers microhardness of the triglycinium calcium nitrate is 50 kg/mm² at 40 g load. From the microhardness studies made on the as grown crystalline material, mechanical properties such as yield strength, fracture toughness and brittleness index were studied. The defects present in the crystal were investigated using etching studies.

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