CHAPTER 6

GROWTH OF TRIGLYCINIUM CALCIUM NITRATE CRYSTAL AND ITS CHARACTERIZATION

6.1 INTRODUCTION

The research field of non-linear optics (NLO) investigates new materials that can be used to build optical devices like frequency doublers and optical modulators. Recent investigations focus on the design of new materials that attain second order optical processes, as well as the strong interaction with the oscillating electric field of light. Materials based in a mixture of amino acids with ionic salts have been investigated in the NLO field and have been recognized as materials that have good nonlinear optical properties (Hernandez-Paredes et al 2008). Glycinium sodium nitrate (GSN) has proven to have characteristics to be a candidate for nonlinear optic applications. Semi-organic compounds based on aminoacids mixed with inorganic complexes have been found useful for second harmonic generation (SHG) process. The purpose is to achieve the construction of useful devices such as: frequency doublers, active optical interconnects, and switches. These devices have great applications in telecommunications and signal processing (Hernandez-Paredes et al 2008).

Within the last decade much progress has been made in the development of these NLO organic materials having large nonlinear optical coefficients. However, most of the organic NLO crystals are constituted by weak van der Walls and hydrogen bonds with conjugated π electrons. So they are soft in nature and difficult to polish and these materials also have intense absorption in UV region. In view of these problems, new types of hybrid NLO materials have been explored from organic-inorganic complexes with stronger ionic bond. Many semiorganic nonlinear optical 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 semiorganic nonlinear optical material whose single crystal exhibits more NLO properties than that of inorganic crystals like KDP, BBO, and LBO (Sinha et al 2009). Presently, inorganic and organic materials are being replaced by semi-organics. 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 inorganics has been found to be successful in the recent past.

6.2 PRESENT WORK

The semiorganic compounds such as glycinium lithium nitrate (Michel Fleck and Ladislav Bohaty 2005), glycinium sodium nitrate (Krishnakumar et al 2001), glycinium silver nitrate (Mohana Rao and Viswamitra 1972) and glycinium magnesium nitrate tetra hydrate (Fleck and Bohaty 2005) have been synthesized and studied. Calcium nitrate, also called Norgessalpeter (Norwegian saltpeter), is the inorganic compound with the formula $Ca(NO_3)_2$. This colourless salt absorbs moisture from the air and is commonly found as a tetra hydrate. In this chapter we are presenting the growth of triglycinium calcium nitrate (TGCN) single crystals and their characterization.

6.3 GROWTH OF TRIGLYCINIUM CALCIUM NITRATE

Triglycinium calcium nitrate single crystals were grown from the aqueous solution of glycine (Merck) and calcium nitrate tetrahydrate (Merck) in equimolar ratio, with millipore water as a solvent by slow solvent evaporation method. A homogeneous aqueous solution of glycine and calcium nitrate tetrahydrate was prepared by mixing calcium nitrate tetrahydrate with saturated solution of glycine little by little. The pH value of the prepared solution was 4.8. Then the prepared solution was kept for evaporation at room temperature. After a month, good optically transparent triglycinium calcium nitrate crystals were harvested with a dimension of 29 x 19 x 4 mm^3. The as grown crystals are shown the Figure 6.1. The possible reason for growing triglycinium calcium nitrate crystal is due to more lattice energy benefit than 1:1 coordination of glycine and calcium nitrate.

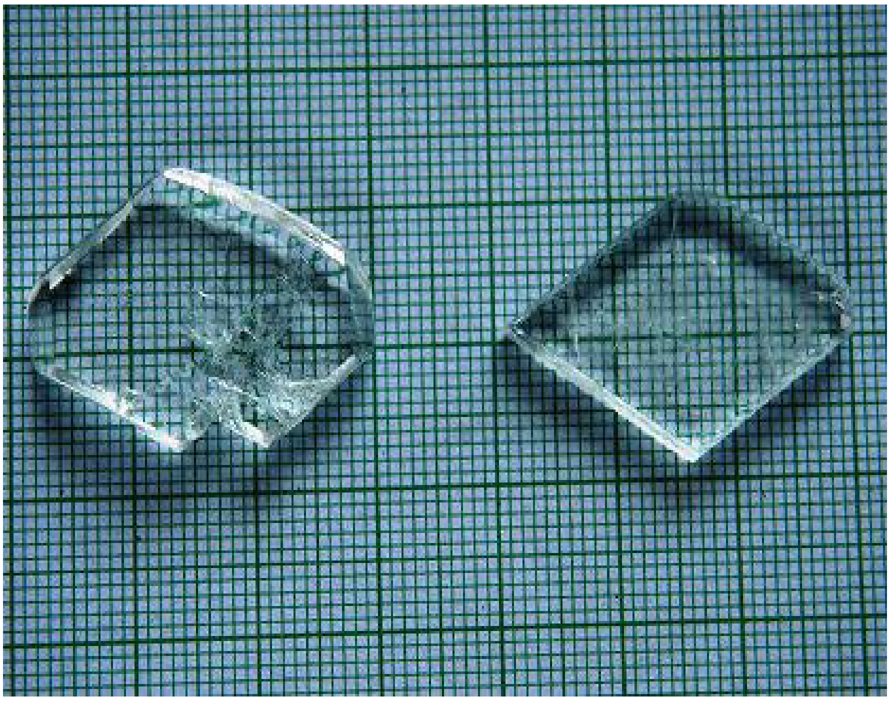

Figure 6.1 Photograph of as grown triglycinium calcium nitrate crystal

6.4 STRUCTURE DETERMINATION AND REFINEMENT

Triglycinium calcium nitrate crystal was subjected to single crystal X-ray analysis using ENRAF NONIUS CAD4 single crystal X-ray diffractometer to determine the crystal structure, unit cell and hydrogen bonds parameters. The compound, $[H_3N^+CH_2COO^-]_3.[Ca(NO_3)_2]$, crystallizes in the noncentrosymmetric space group $Pna2_1$ with six glycinium switterions and four calcium nitrate in the asymmetric unit. Among 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 switterions 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 Figures 6.2 and 6.3 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 6.1.

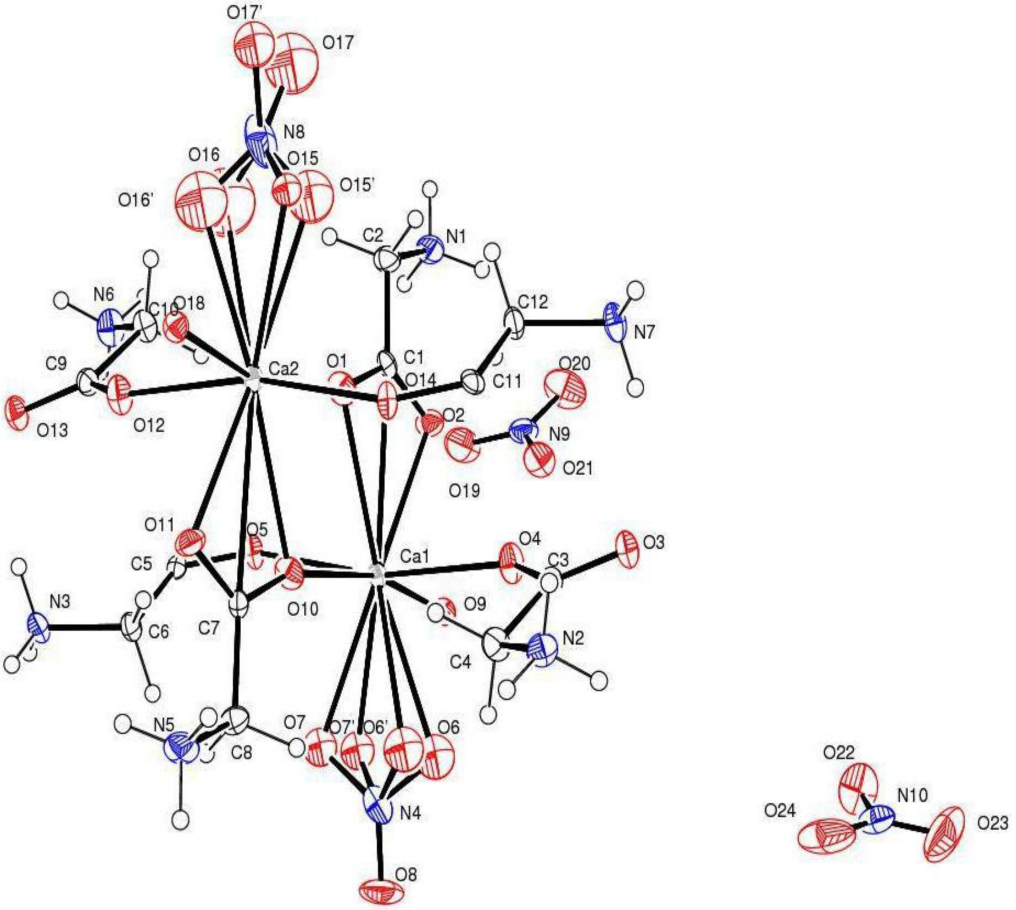

Figure 6.2 Molecular structure of triglycinium calcium nitrate crystal

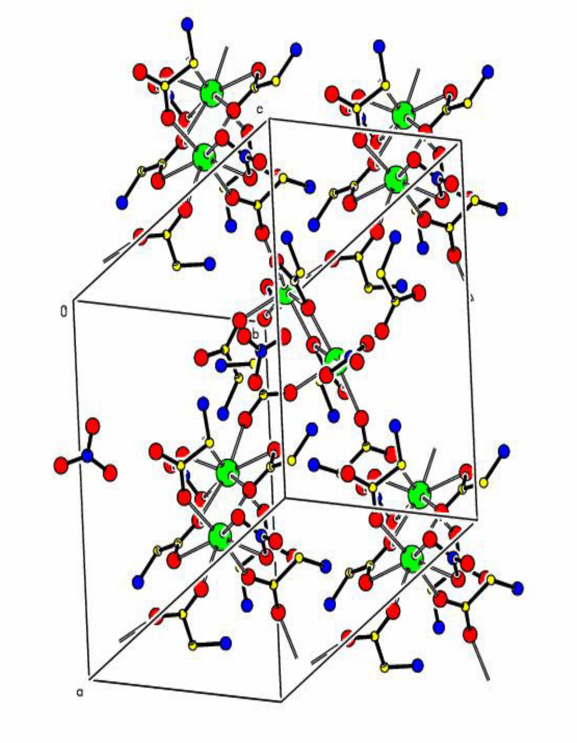

Figure 6.3 Packing diagram of triglycinium calcium nitrate crystal

In the compound, $C_{12}H_{30}Ca_2N_{10}O_{24}$, bond angles and lengths are in close agreement with the reported value (Allen et al 1987) except for the disordered atoms. The atoms O6, O7, O15, O16 and O17 are disordered over two positions with site occupancy factors for the major and minor conformers 0.667 (2) and 0.333 (2); 0.656 (2) and 0.344 (2); 0.730 (4) and 0.274 (4); 0.840 (3) and 0.160 (3); 0.725 (1) and 0.275 (1) respectively. The bond length N4-O7' = 1.111 (2) Å is relatively shorter and N4-O7 = 1.358 (1) Å is longer due to the delocalized electrons arising because of the thermal vibration of the disordered atoms. The hydrogen bonds parameters of triglycine calcium nitrate crystal are shown in the Table 6.2.

The sum of bond angles around N8 [354.30°] indicate Sp^2 hybridisation. In the plane made by the atoms Ca2/O10/C7/O11, the atom C7 has got a maximum deviation of 0.0438 as indicated by the least-squares plane calculation (Cremer and Pople 1975). In the crystal packing, the molecule is stabilized by N-H··· intermolecular interactions. The packing is further facilitated by C-H···O intermolecular interactions by the contribution of atoms C4, C10, O6 and O23 along with weak van der Waals forces.

Table 6.1 Crystal data and structure refinement for triglycinium calcium nitrate crystal

Identification code	TGCN
Empirical formula	C12 H30Ca2 N10 O24
Formula weight	768.54
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Space group	Pna21
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<=h<=13, -10<=k<=10, -24<=l<=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
GooF (F^2)	1.067
Final R indices [I>2sigma(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}

Table 6.2 Hydrogen bonds in triglycinium calcium nitrate crystal

D-H...A	d(D-H)	d(H...A)	d(D...A)	(DHA)
N(1)-H(1A)...O(8)	0.89	2.31	3.004(7)	135.0
N(1)-H(1A)...O(24)	0.89	2.35	2.974(8)	127.0
N(1)-H(1B)...O(21)	0.89	2.34	3.100(7)	143.3
N(1)-H(1B)...O(19)	0.89	2.52	3.339(9)	153.5
N(6)-H(6C)...O(21)	0.89	2.45	2.994(6)	120.3
N(1)-H(1C)...O(13)	0.89	2.16	2.931(6)	144.0
N(3)-H(3A)...O(4)	0.89	1.97	2.817(5)	157.9
N(5)-H(5B)...O(3)	0.89	2.12	2.903(6)	145.6
N(3)-H(3B)...O(14)	0.89	1.95	2.818(5)	166.4
N(2)-H(2C)...O(22)	0.89	2.39	2.997(8)	125.3
N(2)-H(2E)...O(20)	0.89	2.16	2.869(7)	136.3
N(5)-H(5A)...O(19)	0.89	1.95	2.822(7)	168.1
N(6)-H(6D)...O(8)	0.89	2.37	3.214(7)	157.6
C(8)-H(8B)...O(17’)	0.97	2.28	3.139(8)	147.0
C(10)-H(10A)...O(23)	0.97	2.45	3.058(1)	120.0

6.5 CHARACTERIZATION STUDIES

6.5.1 FTIR Spectral Analysis

Near-infrared (NIR) spectroscopy can be an attractive option for certain organic systems because of ease of sampling. Generally, the infrared bands for inorganic materials are broader, fewer in number and appear at lower wavenumbers than those observed for organic materials. A slightly more complex inorganic, such as $CaCO_3$, contains a complex anion. These anions produce characteristic infrared bands (Barbara stuart 2004). The NIR region of the spectrum, by convention taken to be the range between 4000 cm^{-1} and visible radiation, principally records much weaker overtones and combinations of the vibrational fundamentals. These mostly involve the overtones of bond-stretching modes of XH, XH2 or XH3 groups (X = C,N,O, etc.)

or these in combination with the angle-deformation modes of the same group (Barbara stuart 2004). In order to analyze the presence of functional groups in triglycinium calcium nitrate crystals qualitatively, Fourier transform infrared spectrum was recorded between 4000 and 450 cm^{-1} using Perkin Elmer spectrum one FT-IR spectrometer. The obtained spectrum is shown in the Figure 6.4. In this spectrum, a broad and strong band is obtained at 3044 cm^{-1}, which is due to the NH_3^+ asymmetric stretching vibration (Sharma 2007, John Coats 2000). Nitrite (NO_2) asymmetric stretching band occurs at 1626 cm^{-1} (Barbara stuart 2004). A fairly strong symmetrical NH_3^+ 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 NH_2 wagging and twisting and 1384 cm^{-1} identifies NO_3 stretching vibration. The absorption peaks characterizing different functional groups for triglycinium calcium nitrate are shown in the Table 6.3 (Robert Silverstein and Francis Webstar 1998).

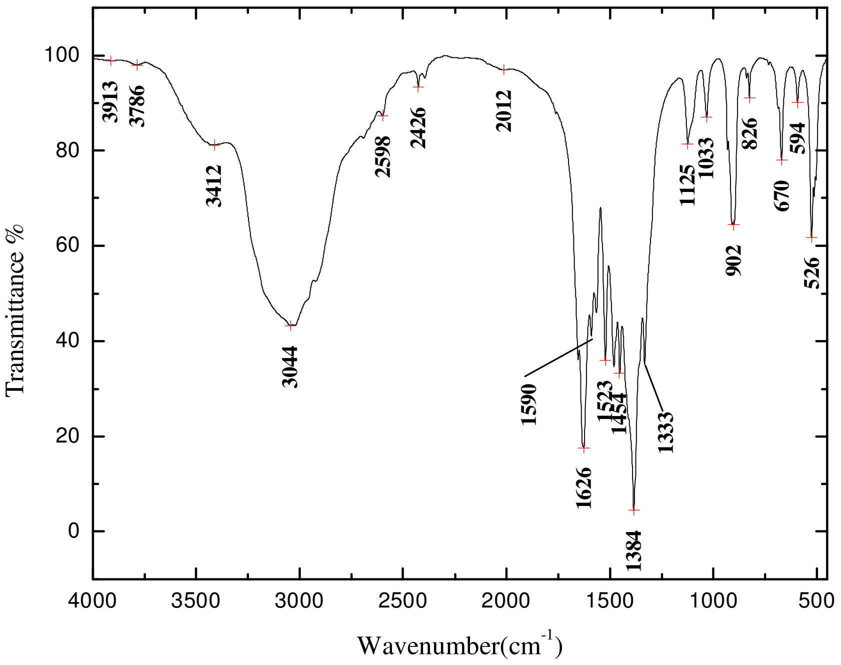

Figure 6.4 FTIR spectrum of triglycinium calcium nitrate crystal

Table 6.3 Frequencies of the fundamental vibrations of triglycinium calcium nitrate crystal

Frequency in wavenumber (cm^{-1})	Assignment of vibrations
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	$C(\overset{\cdots}{-}O)_2$ bending
526	torsional oscillation

6.5.2 UV-Vis-NIR Studies

To determine the transmission range and hence to know 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 Lamda 35 UV/VIS spectrometer. The crystal of 2 mm thickness was used for recording the spectrum. Figure 6.5 shows the resultant transmittance curve, in which it is observed that the transmittance increases gradually from 40 % to 50 % transmittance 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 worth noting that the transparency range for triglycinium calcium nitrate is larger and so it can be used for generation and mixing of frequencies over a wide range of electromagnetic spectrum including the UV.

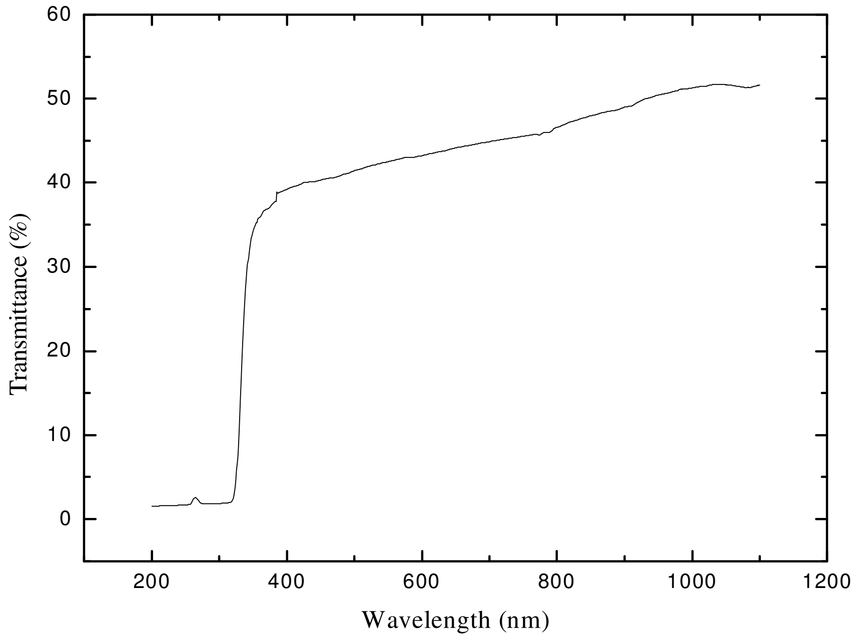

Figure 6.5 UV-Vis-NIR spectrum of triglycinium calcium nitrate crystal

6.5.3 NLO Studies

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. Typically, only laser light is sufficiently intense to modify the optical properties of a material system (Robert Boyd 2007). The Kurtz and Perry technique was used to investigate the efficiency of second harmonic generation (SHG). A high intensity Nd:YAG laser with fundamental radiation of 1064 nm and beam energy 1.95 mJ/pulse was used as the optical source. The grown triglycinium calcium nitrate crystalline sample was ground into very fine powder and tightly packed in a microcapillary tube. Then it was kept in the path of Nd:YAG laser beam. KDP crystal was used as a reference material, whose transmitted beam voltage was 62 mV. But it was observed that the output voltage was 32 mV for the triglycinium calcium nitrate crystal. Its SHG behaviour was confirmed from the output of green light from the crystal. The SHG efficiency of triglycinium calcium nitrate crystal is half that of KDP crystal.

6.5.4 Thermal Studies

Thermal properties of triglycinium calcium nitrate crystal were studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), which were carried out between 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. The corresponding curves are presented in Figure 6.6. From the thermogravimetric analysis, 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. The material starts to melt at 250 °C and is found to dissociate from 266 °C, which is confirmed by the sharp endothermic peak obtained in differential thermal analysis curve at the same temperature. It is observed from the thermogravimetric analysis curve that the grown triglycinium calcium nitrate material decomposed about 57 % 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 triglycinium calcium nitrate compound is thermally stable up to 250 °C.

6.5.5 Dielectric Studies

In order to find dielectric constant of the grown triglycinium calcium nitrate crystal, capacitance of the crystal was studied at various temperatures and frequencies using Precision LCR meter AGILENT 4284A model. For this the crystal polished to 1 mm thickness was used. Typical area of the sample for the experiment was 49 mm^2. Both the crystal surfaces were coated with fine graphite powder to make a contact with the electrodes. 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 annealed in the thermostat itself. The dielectric parameters such as capacitance and dielectric loss were measured as a function of temperature for the range of frequencies from 100 Hz to 1 MHz.

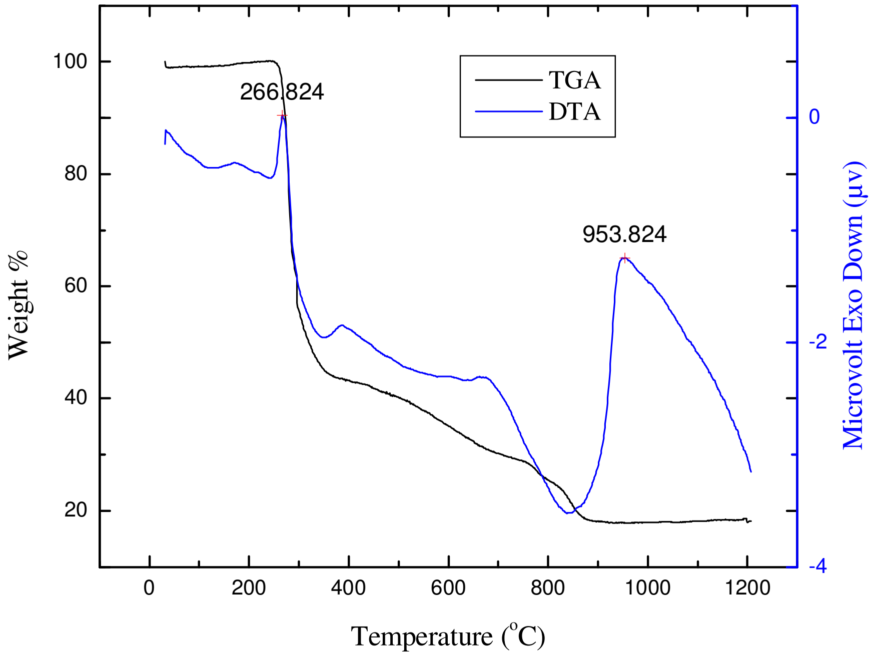

Figure 6.6 TGA and DTA thermogram of triglycinium calcium nitrate crystal

Figure 6.7 shows the plot of dielectric constant versus temperature for different frequencies. It is observed that the dielectric constant increases with the increase of temperature and it is 9 at 180 °C. Figure 6.8 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 also is corresponding to the dielectric constant plots at the given experimental frequencies ranging from 100 Hz to 1 MHz. From the experimental observation made on the crystal, dielectric loss is very less and the magnitude of dielectric constant increases with the decrease of frequencies.

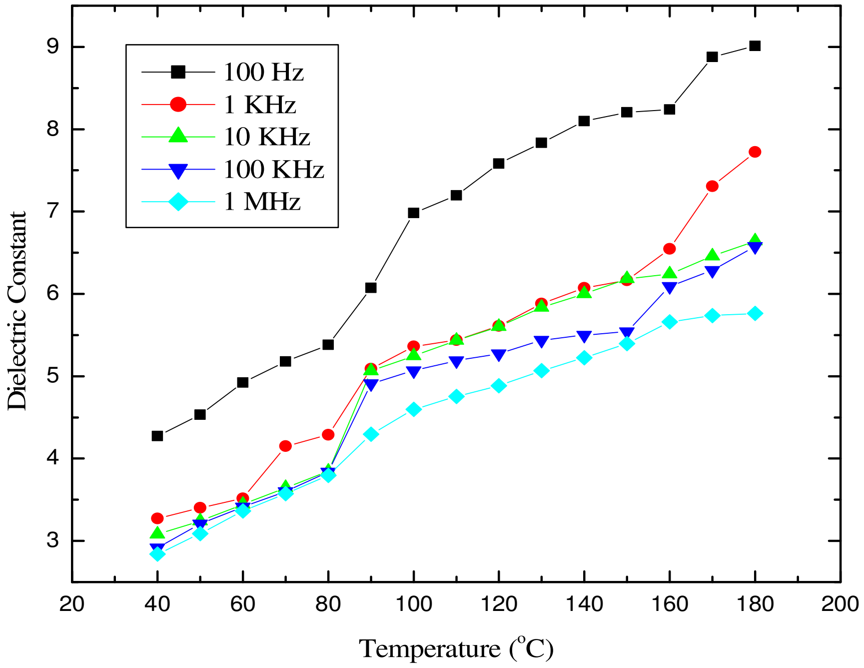

Figure 6.7 Dielectric constant of triglycinium calcium nitrate crystal

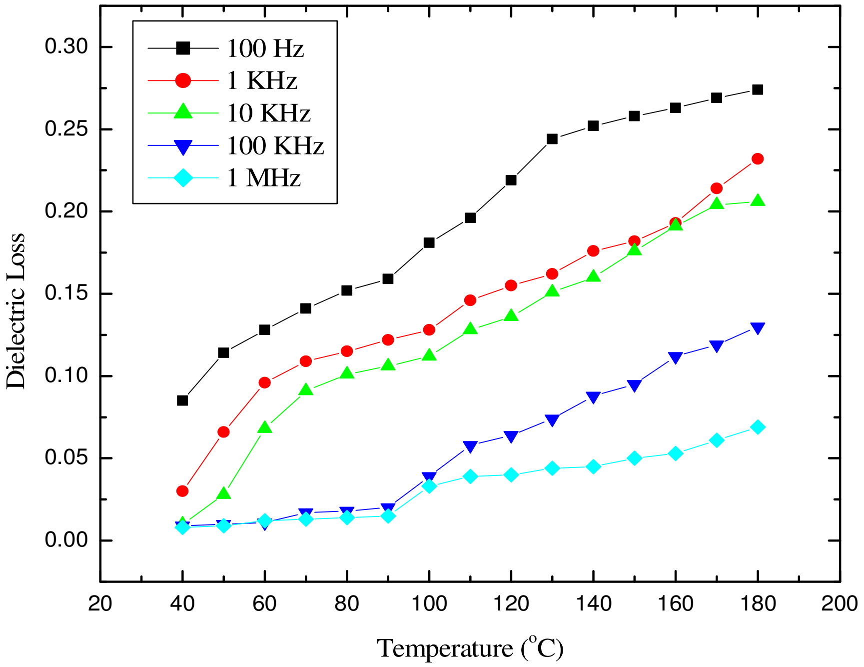

Figure 6.8 Dielectric loss of triglycinium calcium nitrate crystal

6.5.6 Mechanical Studies

In order to find the surface hardness of the grown triglycinium calcium nitrate single crystal, Vicker's microhardness was analyzed using Reichert-jung MICRO-DUROMAT 4000 E Microhardness tester. The Vicker's microhardness number was calculated from the standard formula $H_v = 1.8544\ P/d^2\ \text{kg/mm}^2$, where P is the applied load, d is the average diagonal length of the indentation and 1.8544 is a constant of a geometrical factor for the diamond pyramid. Figure 6.9 shows the variation of Vicker's microhardness as a function of applied load ranging from 5 g to 60 g. 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/mm^2.

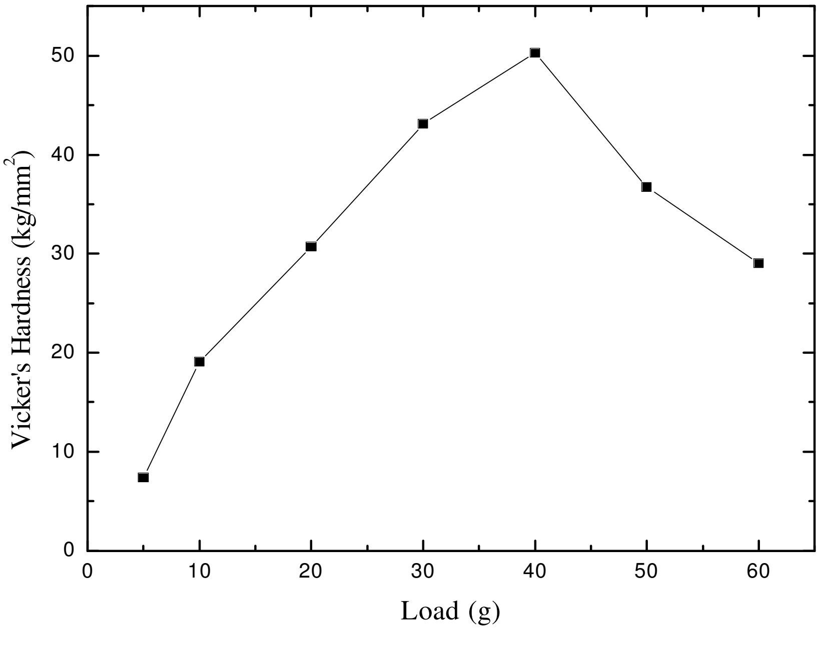

Figure 6.9 Mirohardness Vs load graph of triglycinium calcium nitrate crystal

Work hardening is when a material is strained beyond the yield point. An increasing stress is required to produce additional plastic deformation and the material apparently becomes stronger and more difficult to deform. Work hardening coefficient (n) was calculated using the Meyer's relation P = ad^n, where P is the applied load, d is the diagonal length of the indentation and 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. Figure 6.10 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. As seen in the previous chaptor, it is suggested that the grown triglycinium calcium nitrate crystal comes under the category of soft material. Yield strength (σ_y) of the triglycinium calcium nitrate crystal was calculated using the formula $\sigma_y = (H_v/3)(0.1)^{n-2}$, where H_v is the Vicker's micro hardness and n is the logarithmic exponent. The calculated yield strength was 3.33 MPa.

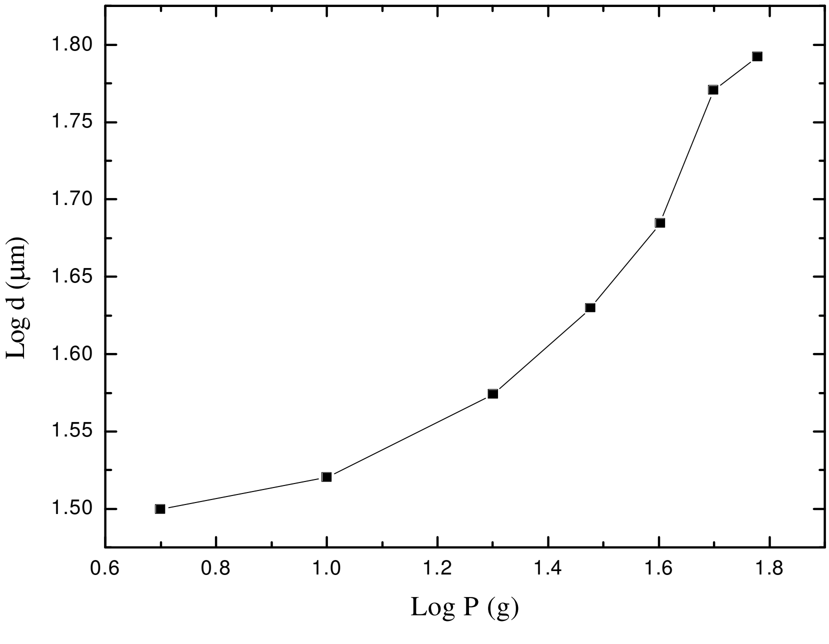

Figure 6.10 Plot of log P and log d of triglycinium calcium nitrate crystal

Fracture toughness (K_c) is a property which describes the ability of a material containing a crack to resist fracture and is one of the most important properties of any material for virtually all design applications. It was calculated using the formula $K_c = P/\beta C^{3/2}$, 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 Vicker's indenter (Krishnan et al 2008). The crack length developed in the grown triglycinium calcium nitrate crystal with the applied load 40g was 95 μm, 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 (Monita Bhat et al 2004). Brittleness index was calculated using the formula $B_i = H_v/K_c$ [20] as 8.1 x 10^{-3} m$^{-1/2}$.

6.5.7 Etching Studies

In single crystals, fluctuations in growth rates during the growth process are recorded as variations in perfection and homogeneity, such as growth sectors. The growth rates may vary for various reasons, resulting in fluctuations in impurity concentration and point defect density. Such fluctuations are recorded in single crystals in the form of "growth banding," which arises due to fluctuating concentrations of point defects, impurities, and inclusions. The three properties of a crystal, external form, perfection, and homogeneity, are directly related to how the crystal grows (Ichiro Sunagawa 2005).

The symmetry of the crystal face from the shape of the etch pits and the distribution of structural defects of the crystals can be investigated by etching (Ramesh Babu et al 2006). The study of microstructural imperfections or defects presents in the as grown crystal for producing good quality single crystal for nonlinear optical devices is essential (Sudeshna Mukerji and Tanusree Kar 1999). So, etching studies were carried out on the as grown triglycinium calcium nitrate single 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 one second, two seconds, three seconds and four seconds 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.

The microphotographs of the triglycinium calcium nitrate crystal before etching and the etch pattern produced in the on-growing surface of the crystal were taken and analysed. It is observed very precisely that the etch pit formed in the surface is hexagonal in shape. More over when etching time increases, the size of the etch pits gets enlarged. Figure 6.11 is the microphotograph of the on-growing surface of the triglycine calcium nitrate crystal before etching.

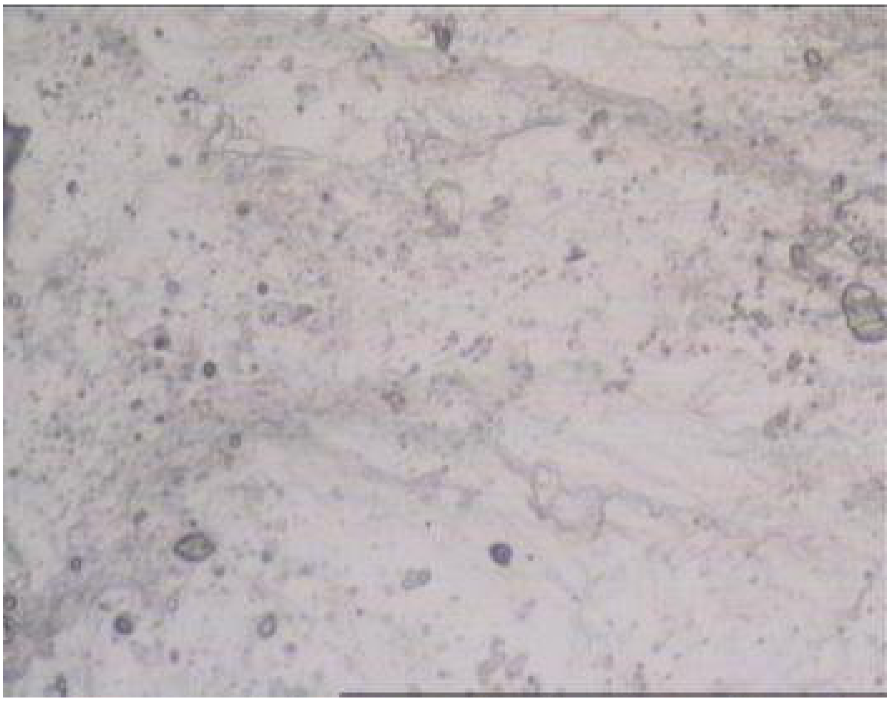

Figure 6.11 Surface of the as grown triglycinium calcium nitrate crystal

When the etching time is one second, it is observed in the microphotograph that many small hexagonal shaped etch pits of size 22 µm are formed in the crystal (Figure 6.12). Etching time 2 seconds and 3 seconds lead to the development of bigger sized etch pits of size 65 µm and 100 µm respectively, which is shown in the Figures 6.13 and 6.14. But when it is 4 seconds, it leads to the development of hexagonal etch steps (Figure 6.15). The etch pits disappear on prolonged etching. The possible reason for the formation of these etch pits is incorporation of impurity in the crystal which introduces strain in the crystal lattice and serves as sites of dissolution (Sudeshna Mukerji and Tanusree Kar 1999).

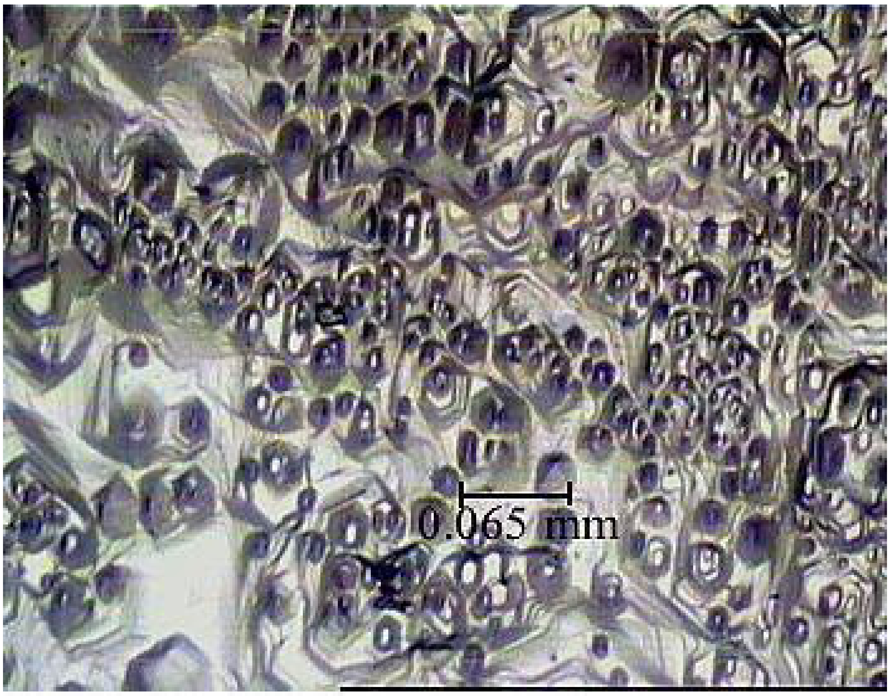

Figure 6.12 Microphotograph of the etch patterns produced on the crystal for one second

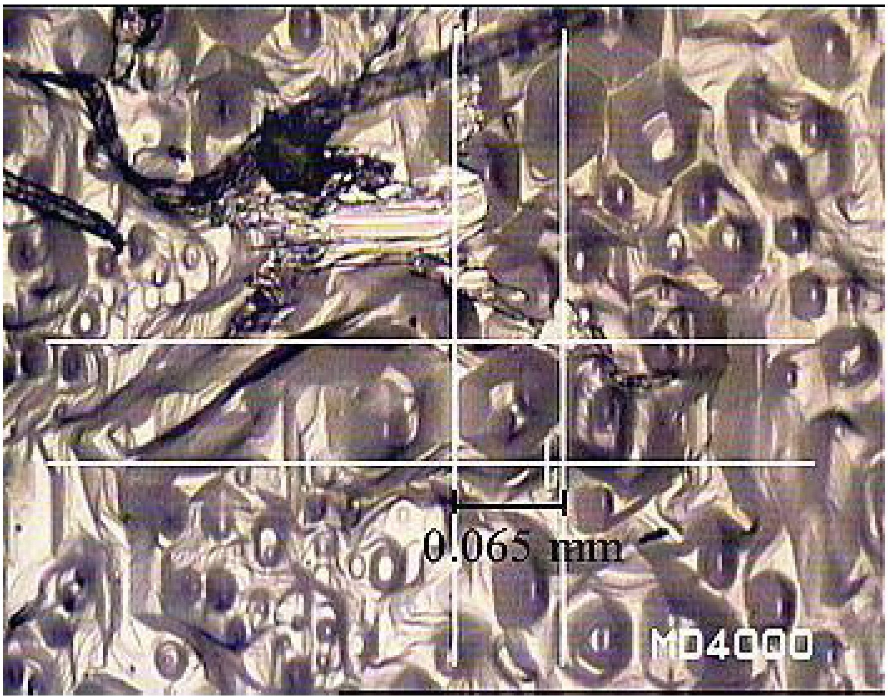

Figure 6.13 **Microphotograph of the etch patterns produced on the crystal for 2 seconds**

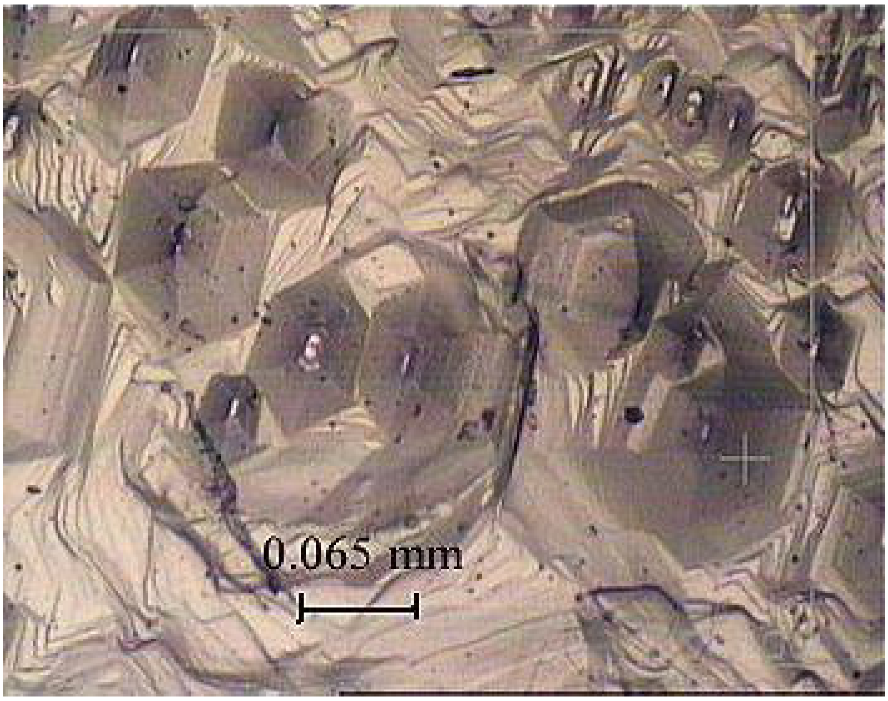

Figure 6.14 **Microphotograph of the etch patterns produced on the crystal for 3 seconds**

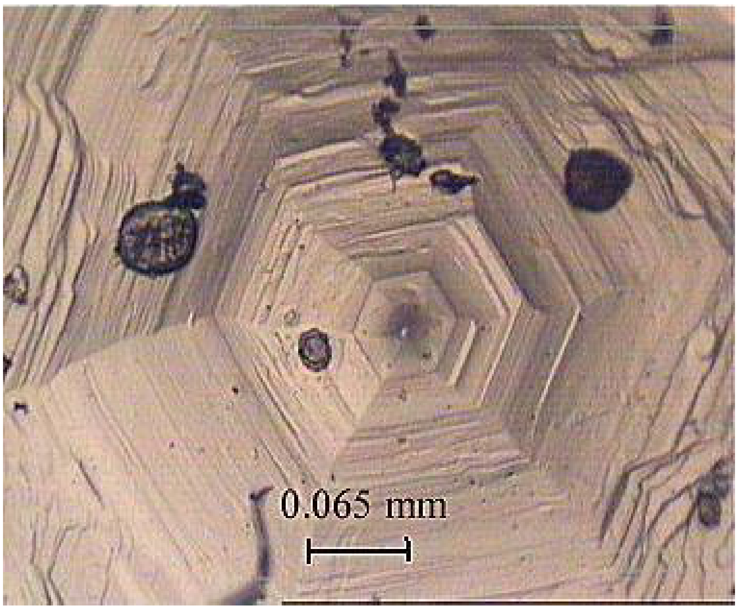

Figure 6.15 Microphotograph of the etch patterns produced on the crystal for 4 seconds

6.6 CONCLUSION

Triglycinium calcium nitrate, a semiorganic nonlinear optical material, has been grown by slow solvent evaporation technique from the aqueous solution of glycine and cacium nitrate tetrahydrate at room temperature. The cell parameters estimated by single crystal X-ray diffraction analysis agree with the reported values. Its various functional groups present in the crystal 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. Triglycinium calcium nitrate crystal melts at 250 °C and starts to dissociate from 266 °C, hence the thermal stability of the crystal is relatively higher. Dielectric constant is 9 at 180 °C. The Vicker’s microhardness of the triglycinium calcium nitrate is maximum of 50 kg/mm^2 at 40 g load. It is concluded from the etching studies that the formation of etch pits is incorporation of impurity in the crystal.