International Journal of Applied and Advanced Scientific Research (IJAASR)
Impact Factor: 5.655, ISSN (Online): 2456 - 3080
(www.dvpublication.com) Volume 2, Issue 2, 2017

GROWTH AND STUDIES OF UREA CADMIUM SULFATE CRYSTALS

M. Andiappan*, P. Selvarajan & S. Perumal***
* Physics Research Centre, S.T Hindu College, Nagercoil, Tamilnadu
** Department of Physics, Aditanar College of Arts and Science, Tiruchendur, Tamilnadu

Cite This Article: M. Andiappan, P. Selvarajan & S. Perumal, "Growth and Studies of Urea Cadmium Sulfate Crystals", International Journal of Applied and Advanced Scientific Research, Volume 2, Issue 2, Page Number 257-263, 2017.

Abstract:

Nonlinear optical (NLO) materials have applications in harmonic frequency generation devices, hybrid bistable devices, modulators, parametric amplifiers and IR converters, optical bistability, phase conjugation, frequency tripling in deep UV conversion, optical communication, optical computing, optical data processing, photonics etc. Organic nonlinear optical (NLO) crystals have poor mechanical strength, poor thermal stability and highly volatile and these disadvantages can be avoided in inorganic and semiorganic NLO crystals. In this research work, a semiorganic crystal namely urea cadmium sulfate hydrate (UCSH) was considered for growth and characterization. Slow evaporation technique was adopted to grow the single crystals of UCSH. The grown crystals of UCSH are observed to be transparent, colourless and non-hygroscopic. The harvested UCSH crystals have been characterized by NLO studies, XRD studies, spectral studies, dielectric studies, thermal studies, LDT studies, EDAX studies and the results obtained from the various studies are analyzed and discussed.

Key Words: Single Crystal, Solution Method, Characterization, Spectroscopy, NLO, XRD, FTIR, Dielectrics, SHG & TG/DTA

1. Introduction:

Crystal growth plays a vital role in the modern technology and many crystals are useful in electro-optic devices, piezo-electric, accousto-optic, photo-refractive, photo-elastic, in radiation detectors, laser hosts, parametric amplifies, and transducers, harmonic generators, etc. Modern technology is based on single crystals of semiconductors, dielectric, ferroelectric, superconductor, acousto-optic, nonlinear optical and optoelectronic materials [1, 2]. Nonlinear optical (NLO) crystals have a lot of applications in the modern areas like optical communication, optical computing and laser technology. Cadmium sulfate hydrate crystal is found to be a third-order NLO crystal and it crystallizes in monoclinic structure with a centrosymmetric space group [3, 4]. The presence of water molecules in the crystal lattice and hence the hygroscopic property of cadmium sulfate crystals have been explained by Yun-Hong Zhang et *al*. [5]. Various studies of Tutton's salts like potassium cadmium sulphate and ammonium cadmium sulfate have been reported in the literature [6-8]. Urea is one of the simplest biological molecule and one of the simplest diamide used in organic chemistry because of its capability in forming transition metal complexes [9]. In search of compounds for better optical and mechanical properties many scientists have studied the derivatives of urea [10-13]. Some crystals under the combination of urea thiourea complexes are explored and studies have been carried out [14-16]. In this work, urea and cadmium sulfate were mixed to form urea cadmium sulphate hydrate (UCSH) crystals and various studies for UCSH crystals have been carried out to characterize them.

2. Synthesis and Crystal Growth:

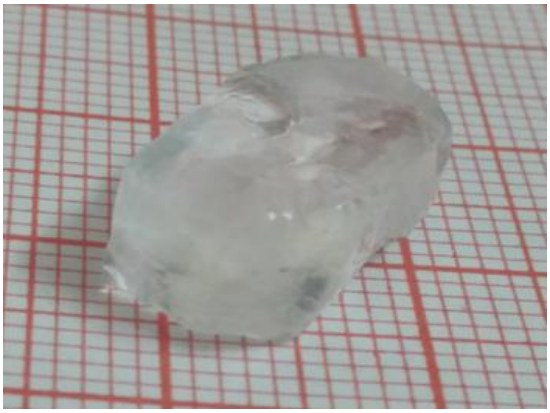

Figure 1: Photograph of the grown urea cadmium sulphate crystal

Urea cadmium sulphate hydrate (UCSH) salt was synthesized by taking AR chemicals of urea and cadmium sulphate hydrate in 1:1 molar ratio. The reactants were dissolved in double distilled water and saturated solution was prepared. This solution was heated at 50 ^{o}C for about 10 hours to obtain the salt of UCSH. The purity of this salt was improved by re-crystallization for twice. Using the aqueous solution of the synthesized salt of UCSH, seed crystals were prepared by evaporation method. To obtain big-sized crystals of

UCSH, seed immersion solution growth technique was adopted and it took about 25 days to harvest the required crystals. In the growth process, stirring of the solution was carried out by using a hot plate magnetic stirrer and in order to remove the undissolved solid substances in the solution, the prepared solution was filtered using the Whatmann filter papers. The harvested crystal of UCSH is shown in the Fig.1 and it is observed that the grown crystal is non-hygroscopic, transparent and colourless.

3. Identification of Functional Groups by FTIR method:

Fourier Transform Infrared (FTIR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all the infrared frequencies encoded into it and the signal can be measured very quickly [17, 18]. The recorded FTIR spectrum of UCSH crystal is shown in the Fig. 2. The broad peak centered at 3409 cm^{-1} corresponds to the presence of OH stretching vibration. NH_2 vibration occurs at 3150 cm^{-1}. OH and NH_2 bending vibrations are observed at 1628 cm^{-1}. S = O stretching vibration is noticed at 1451 cm^{-1}. SO_4^{2-} stretching and degenerate vibrations are observed at 1137 cm^{-1} and 618 cm^{-1}.The assignments to the absorption frequencies for UCSH crystal are given in table 1.

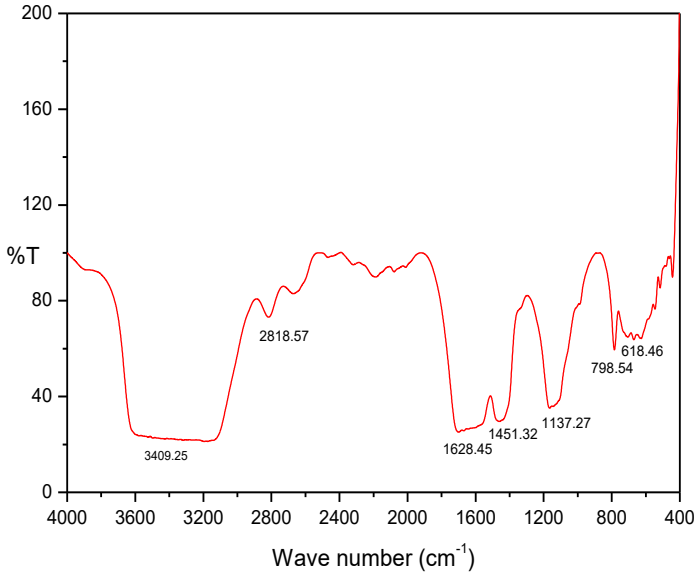

Figure 2: FTIR spectrum of UCSH crystal

Table 1: FTIR absorption frequencies and their assignments for UCSH crystal

Wave number (cm^{-1})	Assignments
3409	OH stretching
3150	NH_2 stretching
1628	Bending vibrations of OH and NH_2
1451	S = O stretching
1137	SO_4^{2-} and N-C-N stretching
798	SO_4^{2-} stretching
618	Degenerate vibrations of SO_4^{2-}

4. EDAX Method for Identifying the Elements:

EDAX or EDS method is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an elements atomic structure to be identified uniquely from one another. The EDS X-ray detector measures the relative abundance of emitted X-rays versus their energy. A SEM instrument with EDAX facility is used to record the EDAX spectrum of the sample. The EDAX spectrum of UCSH crystalline sample is presented in the figure 3. From the spectrum, the elements such as Cd, O, N, S and C are identified in UCSH

sample. Hence, from FTIR spectrum and EDAX spectrum, it is confirmed that urea cadmium sulphate hydrate crystal has been formed.

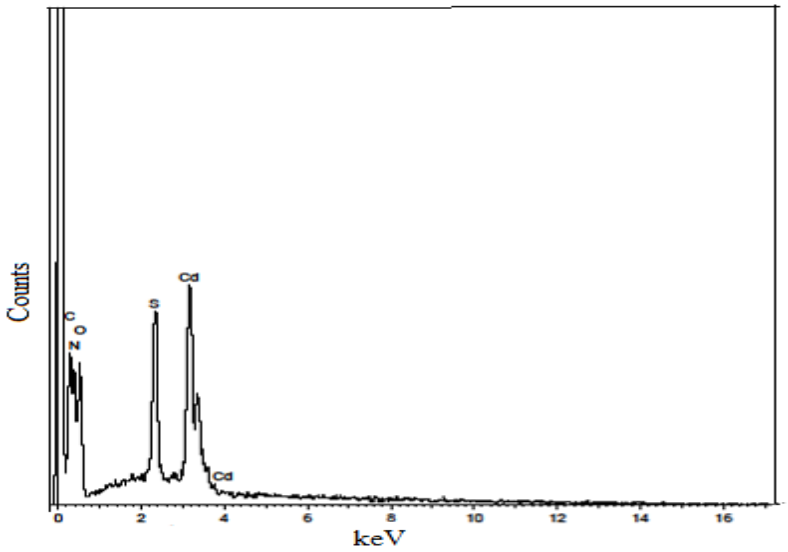

Figure 3: EDAX spectrum of UCSH crystal

5. Single Crystal X-Ray Diffraction Method:

X-ray diffraction (XRD) is an efficient analytical technique used to identify and characterize unknown crystalline materials and it is the most definitive one available for the determination of crystal and molecular structures and the results obtained are usually unambiguous and generally quite accurate. When Bragg's law is satisfied, X-ray diffraction will take place from crystals and from the XRD data, the crystal structure is analyzed [19, 20]. Since the sample here is a single crystal, single crystal XRD data were collected for UCSH crystal with the help of Bruker Kappa Apex II single crystal diffractometer and the obtained data are given in the table 2. From the lattice parameters of UCSH crystal, it is ascertained that this crystal has the orthorhombic crystal structure.

Table 2: Single crystal XRD data for UCSH crystal

X-Ray Diffraction Data	
a (Å)	7.813(4)
b (Å)	15.892(2)
c (Å)	12.471(3)
α, β and γ (°)	90°, 90°, 90°
Crystal System	Orthorhombic
V $(Å)^3$	1548.46

6. UV - Visible Spectral Studies:

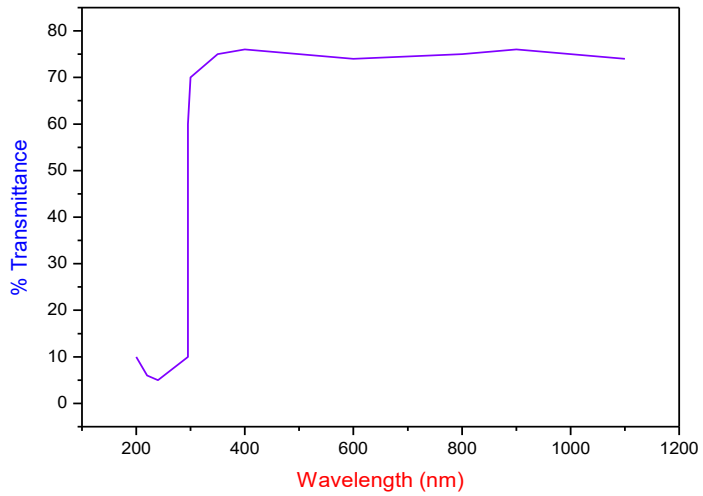

Figure 4: UV-visible transmittance spectrum of UCSH crystal

Ultraviolet and visible light have sufficient energy to excite the electrons in the occupied higher energy levels in complex ions and molecules. When a full range of wavelengths of UV-visible radiation is passed through a sample, an absorption spectrum is obtained. Each characteristic absorption corresponds to an electronic transition. The transmitted light is represented as transmittance $T = (I/I_o)$ and the absorbed light is represented as absorbance $A = \log_{10}(1/T)$ where I is the intensity of transmitted light and I_o is the intensity of incident light. In this study, both transmittance and absorbance spectra of a sample can be drawn[21-23]. The UV-visible transmittance spectrum is recorded and it is shown in the figure 4. The grown UCSH crystal has good transmittance in the visible region and the fundamental absorption observed for this sample is at 296 nm.

7. Second Harmonic Generation by Kurtz-Perry Powder Technique:

Second harmonic test was carried out for UCSH sample by Kurtz and Perry powder technique as given in the literature [24]. This technique has been considered as an authentic experimental method to verify the symmetry of a crystalline material. The microcrystalline powdered sample was packed in a capillary tube. The powder sample with an average particle size of 100-150 μm was illuminated using a Q-switched mode locked Nd:YAG laser of pulse width 8 ns at a wavelength of 1064 nm. When a laser input of 0.8 J was passed through the sample and KDP, the output signal energy obtained from UCSH sample was 9.9 mJ/pulse and signal energy from KDP sample was 8.8 mJ/pulse. The relative SHG efficiency of UCSH crystal is 1.12 times that of KDP.

8. Microhardness Studies:

The microhardness studies of the grown UCSH crystal were determined using the Vickers microhardness tester. The indentations were made on the polished crystal of UCSH for the loads of 25, 50, 75 and 100 g. The indentation time was kept as 10 s for all the loads. The Vickers microhardness number (H_v) was calculated using the relation $H_v = 1.8544\ P / d^2$ kg/mm^2 where H_v is the Vickers microhardness number, P is the applied load in kg, d is the mean diagonal length of the indentation in mm and 1.8544 is a constant for the geometrical shape of diamond pyramidal indenter. The variation of hardness number with the applied load for UCSH crystal is shown in the Fig. 5. From the obtained data, it is observed that the hardness number increases with increase of the applied load, showing the reverse indentation size effect (RISE). When low load is applied to the crystal, it seems that the crystal is hardened and it can withstand when high loads are applied until crack is formed in the crystal.

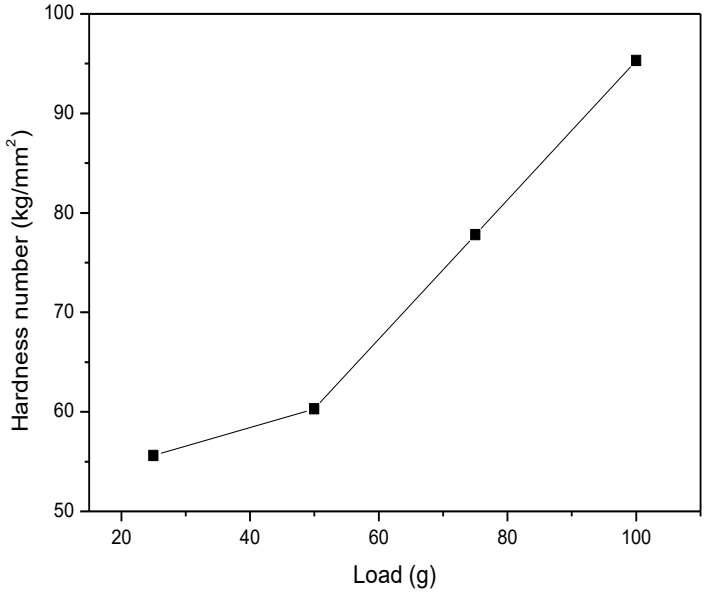

Figure 5: Variation of hardness number with load for UCSH crystal

9. TG/DTA Studies:

TG/DTA studies were carried out using a SDT Q600 V8.3 thermal analyzer in the temperature range from ambient temperature to 600 ºC at the heating rate of 20 ºC/min in nitrogen atmosphere. The recorded TG/DTA thermal curves for UCSH crystal are shown in the figure 6. From TG curve, it is seen that there is about 8 % of weight loss upto 200 ^oC and 40 % of weight loss is noticed in the temperature range from 200 ^oC to 375 ^oC. Only 22 weight% of the sample is left at 500 ^oC. Since there is a gradual weight loss upto 200 ^oC, the grown UCSH crystal has water of crystallization. The endothermic peak in the DTA curve at 145 ^oC corresponds to removal of water of crystallization and at 200 ^oC the sample is changed into the unhydrated sample. The endothermic peak at 247 ^oC corresponds to the decomposition point of the sample.

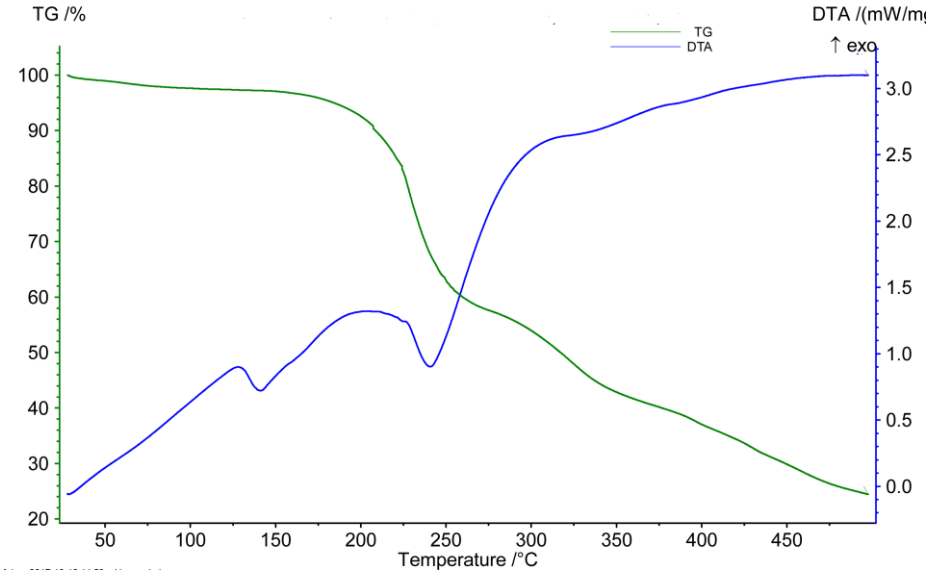

Figure 6: TG/DTA thermal curves of UCSH crystal

10. Dielectric Studies:

The dielectric properties of UCSH crystal were determined by using a multi-frequency LCR meter for various temperatures from 30 °C to 100 °C over a frequency range of 100 Hz to 1 MHz. The variation of dielectric constant with frequency at different temperatures is shown in Fig.7. As the temperature of the sample increases, the dielectric constant increases in a slow rate in low the temperature region and in a fast rate in the high temperature region. The dielectric constant remains high at frequencies and reduces rapidly in the high frequency region. Similar behaviour is observed in the case of dielectric loss factor of UCSH crystal (Fig.8). The high value of dielectric constant and loss factor at low frequencies may be due to the presence of space charge and other polarization phenomena. At low frequencies, the dipoles can easily switch alignment with the changing fields. As the frequency increases, the dipoles are able to rotate less and maintain phase with the field and thus they reduce their contribution to the polarization field and reduces the dielectric constant and dielectric loss. Variation of the dielectric parameters with temperature is generally attributed to the crystal expansion, the electronic, space charge and ionic polarizations and also attributed to the thermally generated charge carriers and impurity dipoles. As far as polarization is concerned, the increase in dielectric constant with temperature is essentially due to the temperature variation of ionic and space charge polarizations and not due to the temperature variation of orientational polarization. The low dielectric loss at high frequency implies that the grown crystal of UCSH is a good quality crystal less defects and this parameter is of vital importance for nonlinear optical materials in their applications [25-29].

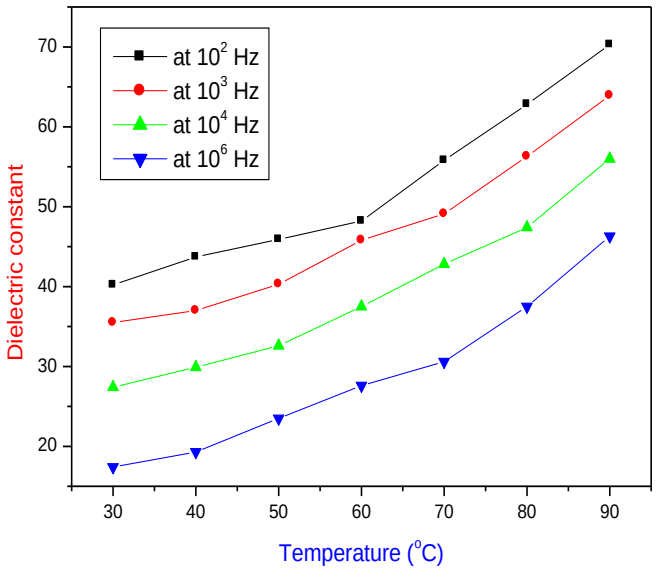

Figure 7: Temperature dependence of dielectric constant at different frequencies for UCSH crystal

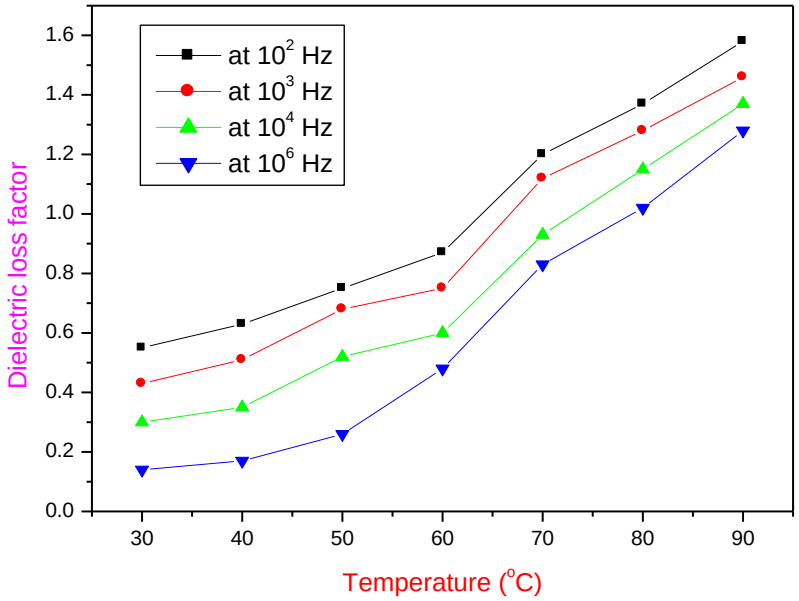

Figure 8: Temperature dependence of dielectric loss at different frequencies for UCSH crystal

11. Measurement of LDT Value:

The NLO materials must have high laser damage resistance because high optical intensities are involved in nonlinear process. In the present experiment, an actively Q-switched Nd: YAG laser source with 6 ns pulse width and 10 Hz repetition rate was used. The output intensity of the laser was controlled with variable attenuator and delivered to the test sample located at the near focusing of the converging lens. The energy density of the input laser beam was recorded using power meter till the crystal got damaged. As the procedure given in the chapter-IV, the energy of the laser beam was measured by Coherent energy/power meter (Model No. EPM 200) and LDT value was determined. The obtained value of LDT for UCSH crystal is 0.65 GW/cm^2 and this value is observed to be more than that of KDP crystal (0.20 GW/cm^2) [30].

12. Conclusions:

A big-sized crystal of urea cadmium sulphate hydrate (UCSH) of dimensions 16 x 10 x 7 mm^3 has been by slow evaporation solution growth technique. The crystal structure is found to be orthorhombic by XRD method. The various functional groups of the sample were confirmed by FTIR technique and the elements present in the crystal of UCSH were identified by EDAX spectroscopy. The lower cut-off wavelength is found to be at 296 nm and the value of LDT for the sample is evaluated to be 0.65 GW/cm^2. Dielectric constant and dielectric loss factor of UCSH crystal were determined at different frequencies and temperatures to understand the dielectric properties. From TG/DTA studies, it is observed that UCSH crystal has the decomposition point at 247^{o}C. Microhardness values have been measured for the grown crystal and it is confirmed that the sample has reverse indentation size effect.

13. Acknowledgement:

The authors like to thank the authorities and staff members of IIT (Chennai), SAIF (Cochin), Crescent Engineering College (Chennai), St. Joseph's College (Trichy), Karunya University (Coimbatore), VIT (Vellore) for providing the research facilities to carry out this work.

14. References:

1. B. R. Pamplin, Crystal Growth, Oxford Press, New York (1975).
2. P. Santhana Ragavan and P. Ramasamy, Crystal Growth Processes and Methods KRU Publications, Kumbakonam (2001).
3. E.G. Sauter, Nonlinear optics, John Wiley& Sons Inc, NewYork (1996).
4. H.E.Swanson, H.F.McMuride, M.C. Morris, E.H.Evans, X-ray diffraction Patterns, National Bureau of Standards, Monograph-25, Section 3, 20, 1964.
5. R.Caminity, G.Johansson, Acta Chem.Scand. Ser.A, 35(1981)451.
6. M. Andiappan, P. Selvarajan & S. Perumal, Int. J. Adv. Trends Eng. Tech, 2 (2017) 29-34.
7. Yun-Hong Zhang and Chak K.Chan, J.Phys. Chem. A, 106(2002) 285-292.
8. F. Bosi, G. Belardi, P. Ballirano, Am. Mineral. 94 (2009) 74.
9. H. Anandalakshmi, T.M. Rajendiran, R. Venkatesan, P. Sambasiva Rao, Spectrochim. Acta A 56 (2000) 2617.

10. L. Zeng, M. Zha, L. Zanotti, C. Razzetti, C. Paorici, J. Crystal Growth 147 (1995) 74–76.
11. M. Ardoino, L. Zeng, C. Razzetti, M. Zha, L. Zanotti, M. Curti, Mater. Chem. Phys. 66 (2000) 299-302.
12. F.Q. Meng, M.K. Lu, H. Zeng, Cryst. Res. Technol. 31 (1996) 33-36.
13. E.D.M. Gomes, V. Venkataramanan, E. Nogueira, M. Belsley, F. Proenca, A.Criado, M.J. Dianez, M.D. Estrada, S. Perez-Garrido, Synth. Met. 115 (2000)225-228.
14. R. Ravindiran, G. Madhurambal, M. Mariappan, J. Therm. Anal. Calorim. 104 (2011) 893–899.
15. Redrothu Hanumantha Rao, S. Kalainathan, Spectrochimica Acta Part A, 97 (2012) 456–463.
16. M. Mariappan, G. Madhurambal, R. Ravindiran, J. Therm. Anal. Calorim. 104 (2011) 915–921.
17. P.R.Griffths and J.A. De Hoseth , Fourier Transform Infrared Spectroscopy, Wiley, Chichester(1986).
18. G. Socrates, Infrared Characteristic Group Frequencies, Wiley- interscience, Chichester (1980).
19. H. P. Klug, L. E. Alexander, X-ray Diffraction Procedure for Poycrystalline and Amorphous materials, 2nd Edn., John Wiley and Sons, New York (1954)
20. L. V. Azaroff, Introduction to solids, McGraw-Hill, New York (1960).
21. H. H. Jaffe and M. Orchin, Theory and Applications of Ultraviolet Spectroscopy, John Wiley, New York (1962).
22. T. Dhanapal, M. Sethuram, G. Amirthaganesan, Samar K. Das, J. Molecular structure, 1045 (2013) 112-123.
23. S. Krishnan, C. Justin Raj, S. Dhinakaran, S.Jerome Das, Cryst. Res. Technol. 43 (6)(2008) 670-673.
24. J. Uma Maheswari, C. Krishnan, S. Kalyanaraman, P. Selvarajan, Physica B, 502(2016)32–38.
25. Selvarajan P, Glorium Arulraj J, Perumal S, Physica B, 405 (2010) 738.
26. Pattanaboonmee N, Ramasamy P, Manyum P, Ferroelectrics, 413 (2011) 96.
27. Rajesh P and Ramasamy P, Spectrochimica Acta Part A, 74 (2009) 210.
28. Balarew C and Duhlew R, J. Solid State Chem., 55 (1984) 1.
29. Sathaiah G, Ph. D. Thesis, Kakatiya University, Warangal (1988).
30. Redrothu Hanumantharao and S. Kalainathan, Optik, 124 (2013) 2204.