International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 4 Issue 08, August-2015

Thermal And Dielectric Studies on Beta Alanine Thiourea Oxalate Nlo Single Crystals

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***Abstract* - A novel NLO single crystal Beta Alanine Thiourea Oxalate was grown using slow evaporation solution growth method. The structure of the BATO was analyzed using X-ray diffraction and FTIR spectrum. The thermal stability and other temperature dependant phenomena were elucidated using TG-DTA and DSC techniques. The dielectric studies of the crystal were carried out using which ac conductivity and activation energy were estimated.**

Key words - TG-DTA, DSC, ac conductivity, activation energy

1. INTRODUCTION

Because of the increasing demand of NLO single crystals in the fields of high speed information processing, frequency conversion, optical communication and high optical disc storage, the art of growing new crystals has been offered a new shape and dimension. Researchers in the universe are working tirelessly to introduce novel crystals with excellent optical, thermal and electrical properties. Amino acids play a key role in the growth of NLO crystals and they also provide wide range of choice in the selection of their counterparts. Thiourea serve as a matrix modifier because of its large dipole moment. One of the dicarboxylic acids, oxalic acid dihydrate together with beta alanine and thiourea yields a new single crystal with nonlinear optical activity. This research article throws light into the thermal and electrical properties of the grown crystal.

2. EXPERIMENTAL WORK

Beta Alanine Thiourea Oxalate single crystals were synthesized by dissolving beta alanine , thiourea and oxalic acid dihydrate in equimolar ratio in deionized water. The solution was stirred well for four hours with magnetic stirrer. This highly homogeneous mixture of uniform composition was filtered and kept in dustfree atmosphere at room temperature. Tiny seed crystals formed by spontaneous nucleation were collected and suspended in the mother solution which was allowed to evaporate. Large size single crystals were obtained due to collection of monomers at the seed crystal sites from the mother solution. They were colourless and optically transparent whose photograph is shown in fig.1

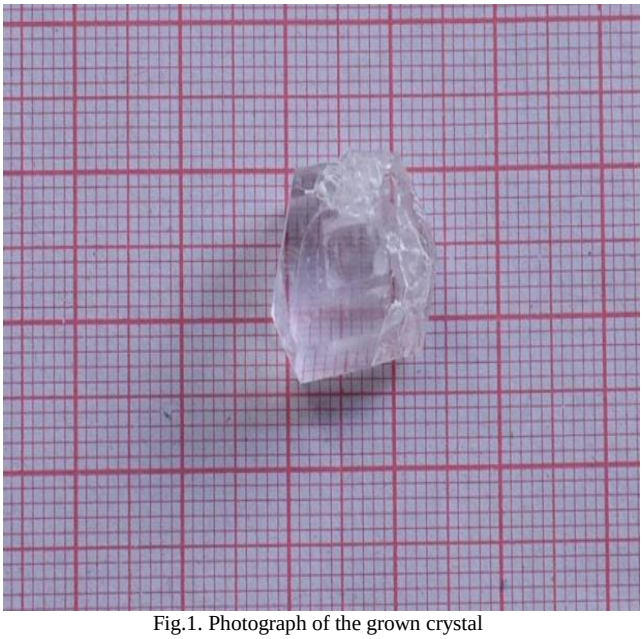

Fig.1. Photograph of the grown crystal

3. RESULTS AND DISCUSSION

3.1.SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES

The title crystal has been subjected to single crystal XRD employing Brucker-Nonius MACH3/CAD4 crystal X-ray diffractometer. It reveals that the grown crystal belongs to monoclinic crystal system with lattice parameters were a=22.325 A^0 , b= 5.679 A^0,C= 14.001 A^0 , β=115·12^0 and the volume of the unit cell =1607.5(A^0)^3 .

3.2. POWDER X-RAY DIFFRACTION ANALYSIS

Powder X-Ray diffraction pattern was recorded using BRUKER AXS D8 advance diffractometer with CuKα (λ=1.5418A0) radiation after crushing the sample into fine powder. The sample was scanned over the range 10-100 ^{0} at the rate of 2 ^{0} per minute. The powder XRD pattern obtained is shown in the fig.2.It was indexed using least square fit method to identify the reflecting planes .The sharp and well defined peaks at specific 2θ values testify the excellent crystalline nature and purity of the grown crystal. Crystalline size was estimated using Scherrer formula

$$D=K\lambda / \beta COS\theta$$

and it lies in the nanoregion (24nm- 74nm).

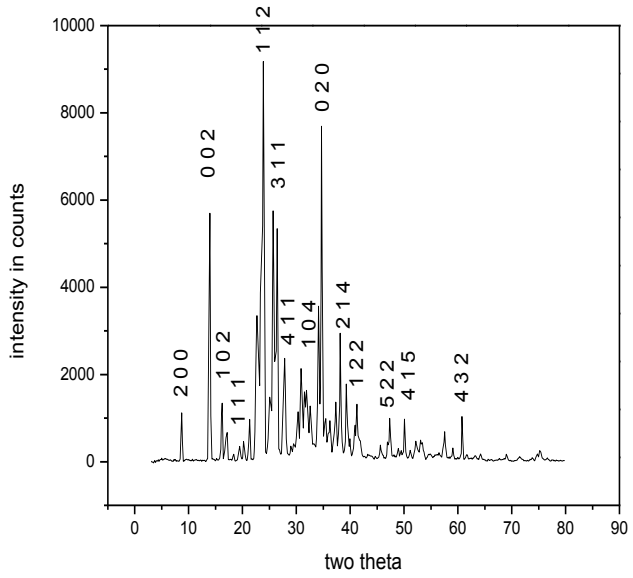

Fig. 2. PXRD Pattern

3.3. FTIR SPECTRAL ANALYSIS

The FTIR spectrum of the grown crystal given in fig. 3 was recorded in the range 400-4000cm^{-1} employing BRUKER IFS 66V FT-IR Spectrometer .The N-H stretching vibrations of amino group are found at 1526 , 1402 and 1024cm^{-1}. The absorption at 3085cm^{-1} is due to O-H stretching vibrations of carboxylic group. The strong absorption at 1713cm^{-1} indicates the existence of carbonyl stretching vibration. N-H bending vibrations gives the peak at 1617cm^{-1}. C-N stretching vibrations and NH_2 rocking vibrations appear at 1203 and 1124cm^{-1} respectively. The peaks at 801 and 701 cm^{-1} indicate the existence of NH_2 wagging and CH out of plane bending vibrations respectively. N-C-N stretching vibrations due to thiourea gives the peak at 478 cm^{-1}.

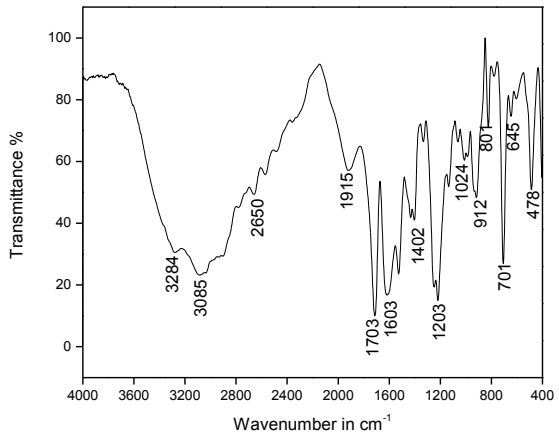

Fig.3. FTIR Spectrum

3.4. DIELECTRIC STUDIES

The study of dielectric constant of a material gives an outline about the nature of atoms , ions , and the bonding in the material. From the analysis of dielectric constant and dielectric loss as a function of frequency and temperature, the different polarization mechanisms in solids can be understood. The dielectric constant and dielectric loss of BATO were studied at different temperatures using Agilent Precision 4284A LCR meter in the frequency region 100Hz to 1MHz.The dielectric constant was calculated using the relation

$$\varepsilon_r = Cd / \epsilon 0A$$

Where d is the thickness of the crystal and A is the area of the same.[1] Fig.4 shows the plot of dielectric constant as a function of frequency for different temperatures.

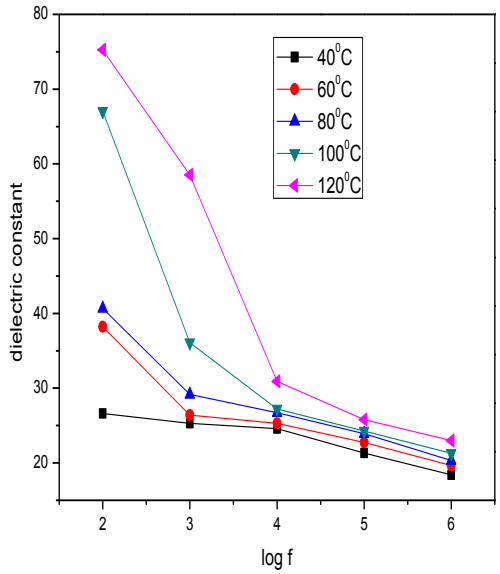

Fig.4.Variation of dielectric constant with frequency at different temperatures

It is seen that the value of dielectric constant is high in the low frequency region and then it decreases with increase in frequency. The high value of dielectric constant at low frequency is attributed to space charge polarization due to charged lattice defects. When the electric charge carriers cannot follow the variations in the applied ac electric field beyond a certain critical frequency, the dielectric constant decreases with increase in frequency and thereafter it remains almost constant. [2].Fig.5 illustrates how dielectric constant depends on temperature at different frequencies.

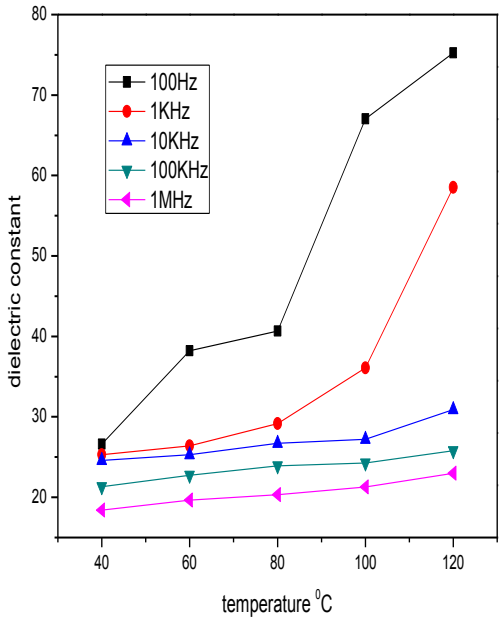

Fig.5 .Plot of dielectric constant versus temperature

The hopping of the charge carriers in the lattice sites is thermally activated by increasing temperature. Because of this, dielectric polarization increases causing an increase in dielectric constant. The relation between dielectric loss and frequency at various temperatures is plotted in fig.6. Dielectric loss is low in the high frequency region which reveals the good optical quality of the grown crystals . Hence there is a chance for less number of defects in the crystal. This is preferred for NLO material to be used in opto electronic,acousto optic and electro optic device fabrication.

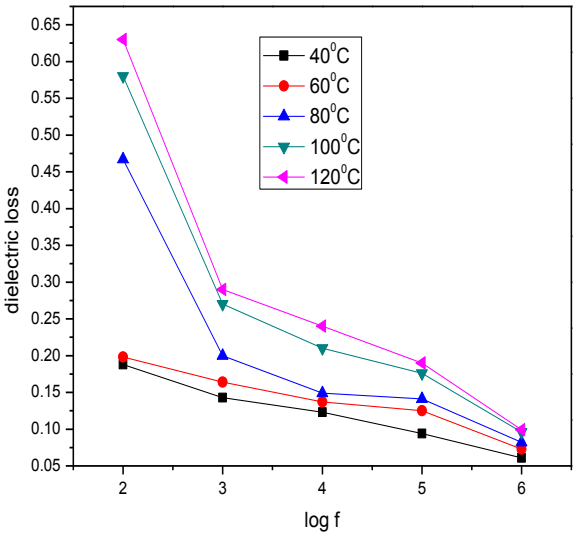

Fig.6.Dielectric loss versus frequency at various temperatures

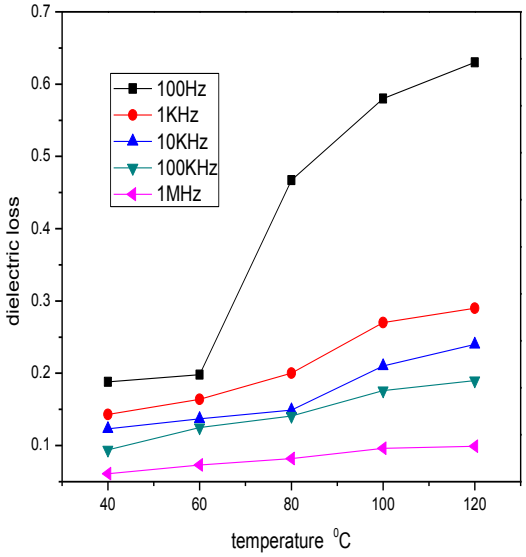

Fig.7.Dielectric loss versus temperature at different frequencies

Fig.8.shows the frequency dependence of ac conductivity at different temperatures. It is observed that ac conductivity increases with increase in temperature which is explained in terms of power law. [3-5].The power law dependence of frequency is of universal nature and corresponds to short ranges which are separated by energy barriers of varying heights. This regime is attributed to hopping conduction which sets in high frequency . As temperature increases, more and more defects are created and hence conductivity increases. [6-7].

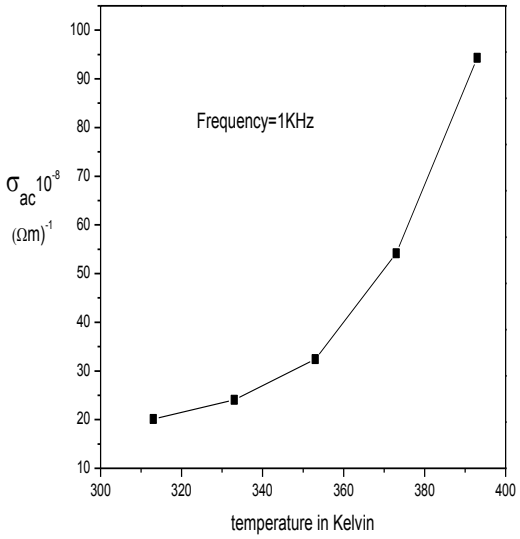

Fig.8.Variation of ac conductivity with temperature

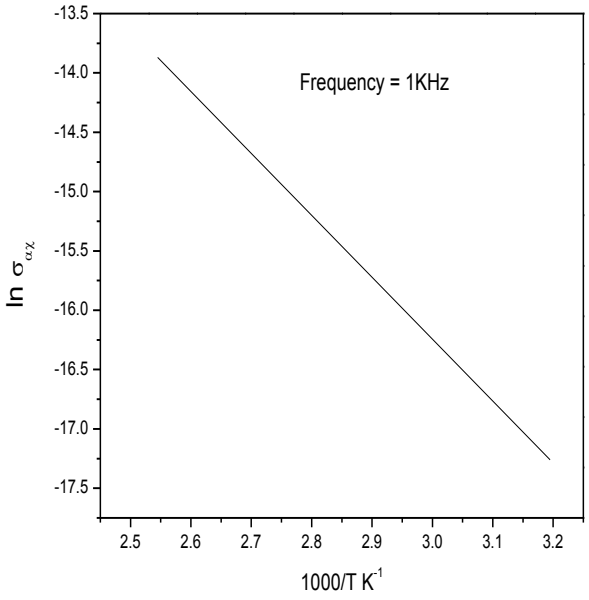

Fig.9.Graph between 1000/T and ln σ_{ac}

The graph between ln(σ_{ac}) and 1000/T(i.e) fig.9. is found to be linear. From the slope of the graph, activation energy E_{ac} can be estimated using the relation

$$E_{ac} = -(\text{slope})1000K$$

Where K is Boltzmann's constant.[8-9]. Thus the calculated value of activation energy of the crystal at frequency 1KHz = 0.23 e V.

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3.5. THERMAL ANALYSIS

3.5.1. TG-DTA ANALYSIS

Perkin Elmer Diamond instrument was used to record the thermograms under nitrogen atmosphere. The material was heated from 40^0 C to 730 ^{0}C at the rate of 10^0 C per minute. The initial mass of the material taken in the form of powder was 11.438mg and the final mass left after the experiment was zero. There are three stages of weight loss in the entire course of the analysis. No weight loss was seen in the material till 125^{0}C. A small weight loss of 8% between 125^{0}C and190^{0}C .Major loss of 51% occured in between 190^{0}C and 240^0 which implies that melting point of the crystal lies in this region. Another weight loss 32% is noted between 240^0 and 350 ^{0} C. Thereafter the material started decomposing completely.[10].The corresponding thermograms are given in fig.10 and 11.

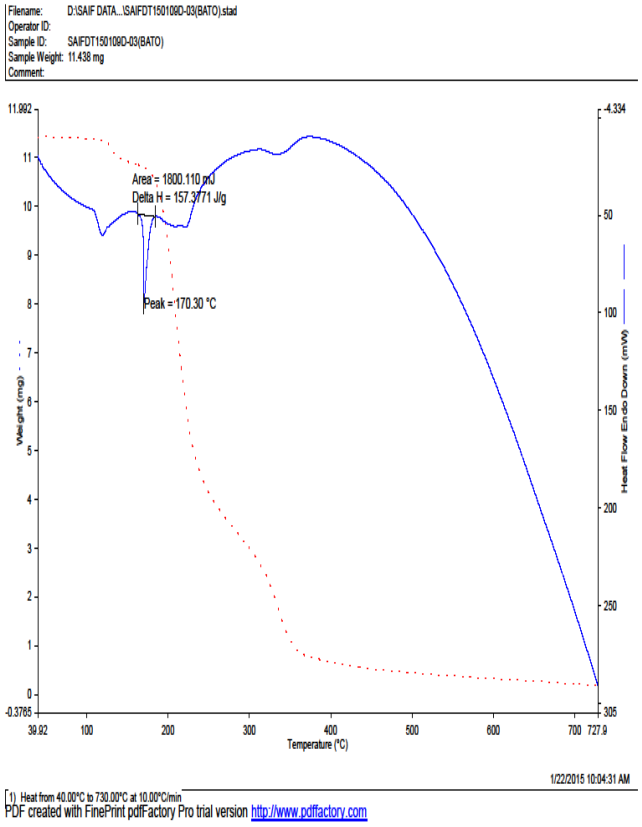

Fig.10.TG-DTA Curve of the crystal

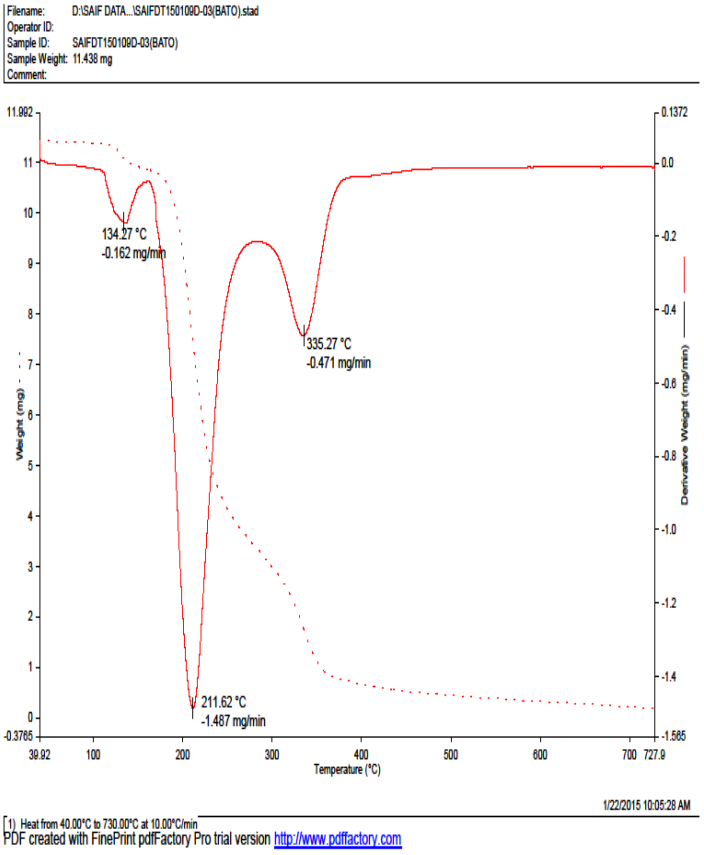

Fig.11.TG-DTA Curve of the grown crystal

3.5.2. DSC ANALYSIS

DSC analysis was performed using Mettler Toledo DSC 822e instrument in the temperature range – 50^0 C to 300 ^{0}C at a heating rate of 10 ^{0}C per minute in nitrogen atmosphere. The obtained DSC spectrum is shown in fig.12 .Fine powdered specimen of the grown crystal of mass 5.043 mg was used for the analysis. No phase change was recorded in the material before 92.52^{0}C .Two small endothermic peaks seen at 92.52^0 C and 111.9^0 C may be due to stepwise removal of water from the sample and due to crystallization. The sharp endothermic peak at 172.13^0 C indicates the melting point of the crystal. This also confirms the good crystalline nature of the crystal. Another broad endothermic peak at 225.95^0 C can account for the beginning of decomposition.[11-12].

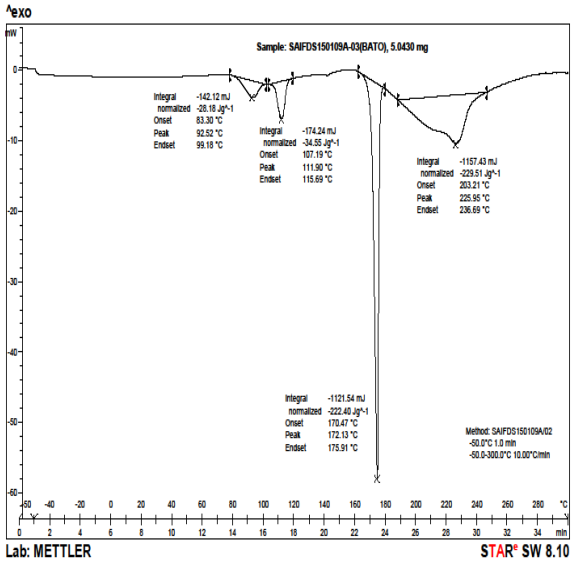

Fig.12.Recorded DSC Graph

4. CONCLUSION

Single crystals of BATO were grown successfully by slow evaporation solution growth method. The dielectric behavior of the crystal suggested its suitability in device fabrication in the field of optoelectronics and other related fields. Thermal analysis revealed the thermal stability of the material so that it can be used in different applications .Moreover its SHG efficiency was found to be 0.59 times that of KDP crystal.

ACKNOWLEDGEMENT

The authors express their sincere gratitude to SAIF-STIC, Cochin and S.T. Hindu College, Nagercoil for TG-DTA , DSC analysis and dielectric studies respectively.

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