JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Growth, Structural, Spectroscopic, Thermal and Non-Linear Optical Studies of L-Arginine Barium Nitrate crystals

R. Selvi[a], S. Anand *[, b], R. Durga R [b], R. S. Sundararajan [c]

[a] Department of Physics, Government College for Women, Kumbakonam, Affiliated to Bharathidasan University, Tiruchirappalli, Tamilnadu, India.

[b] Department of Physics, A.V.C. College, Mayiladuthurai, Affiliated to Bharathidasan University, Tiruchirappalli, Tamilnadu, India.

[c] Department of Physics, Government Arts College, Kumbakonam, Affiliated to Bharathidasan University, Tiruchirappalli, Tamilnadu, India.

[*]Corresponding author E-mail address: **anandphy09@gmail.com**

Tel - +91 9443650530

Abstract

A Non-linear optical crystal, L-Arginine Barium Nitrate (LARBAN) has been synthesized by the low temperature solvent evaporation method. Single X-ray diffraction study reveals the crystal belongs to monoclinic system. Powder X-ray diffraction analysis examines the crystallanity of the grown crystal. The functional groups present in the grown crystal are identified using FT-IR and FT-Raman spectroscopy. The UV-Vis-NIR study gives the wide window of transmission from 246 nm to 1100 nm and the Energy band gap value of the crystal is about 5.04 eV. The mechanical stability of the title compound can be studied by the micro hardness analysis. The TGA and DSC analysis reveals thermal stabilities of the title compound.

Keywords: LARBAN, FT-IR, FT-Raman, TGA-DSC, NLO, Powder XRD.

1. Introduction

Crystals of Non-linear optical (NLO) material has attracted the researchers because of their applications in the fields of Optoelectronics and Photonics. Arginine is a common naturally available amino acid with zwitterionic nature. The side chain of the Arginine is noteworthy more basic than N-terminus [1]. The significance of amino acids for NLO applications is due to the fact that almost all amino acids contain an Asymmetric Carbon and crystallizes in Non-Centro symmetric Space group [2]. Many researches were carried out with Arginine and various organic and inorganic acids in equimolar ratio. L-Arginine and Maleic acid was discussed by T. Baraniraj et al., L-Arginine and HC*l* was analyzed by K. Meera et al., L- Arginium formate (L-Arginine and Formic acid) was characterized by J. Packiam Julius et al., L-Arginine Acetamide and L- Arginium dinitrate were grown by B. Anitha et al., and Preemie. C. Thomas et al.,. This present work is attempted with L –Arginine and Barium Nitrate.

Barium Nitrate [$Ba(NO_3)_2$] crystal was popularly known as Raman crystal and have Non-linear properties. Barium Nitrate is soluble in water. The polar Nitrate ions are attached to polar molecules and goes for the Barium. This is due to the ability of Nitrate ions forming hydrogen bonds with water. The present work deals with growth of L-Arginine Barium Nitrate crystals and are characterized using FT-IR, FT-Raman, UV–Vis–NIR, Powder XRD, Single XRD, Photoluminescence, Vicker's micro hardness and TGA-DSC studies.

2. Experimental Study

Slow Evaporation technique is adopted to grow LARBAN crystals. LARBAN is crystallized from L- Arginine and Barium Nitrate in equimolar ratio. L –Arginine is dissolved in distilled water and the solution is stirred using magnetic stirrer in 4-5 hours. In the same way, Barium Nitrate solution is also prepared. Both the solutions are filtered using Whatmann filter paper and then Barium Nitrate solution is added to L-Arginine solution drop by drop and stirred using magnetic stirrer up to 4 hours to form a homogenized mixture of solution. This solution is covered and small pores are made to enhance the evaporation and kept in a dust free atmosphere without any vibrations in room temperature. After a period of 10-12 days, nucleation is observed. Then, well transparent tiny crystals of LARBAN are harvested after a period of 45 days and the crystals are displayed in Figure 1. The crystal is grown using the following chemical equation.

$$C_6H_{14}N_4O_2 + Ba(NO_3)_2 \longrightarrow C_6H_{14}N_4O_2.Ba^{2+}(NO_3)_2^{-}$$

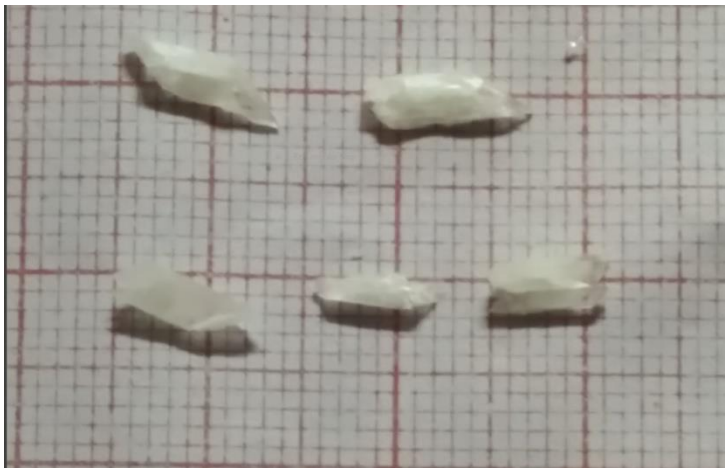

Figure 1: Grown crystals of L-Arginine Barium Nitrate

3. Results and Discussion

3.1 X –Ray Diffraction analysis

3.1.1 Powder X –Ray diffraction analysis

Powder x-ray diffraction studies are carried out to test the crystalline nature of the grown sample. The grown LARBAN crystal is ground into fine powder and analyzed by XPERT PRD X-ray diffractometer with CuKα radiations. The sharp and well defined peaks show the crystalline nature of grown LARBAN crystals. The recorded powder XRD pattern is displayed in Figure 2.

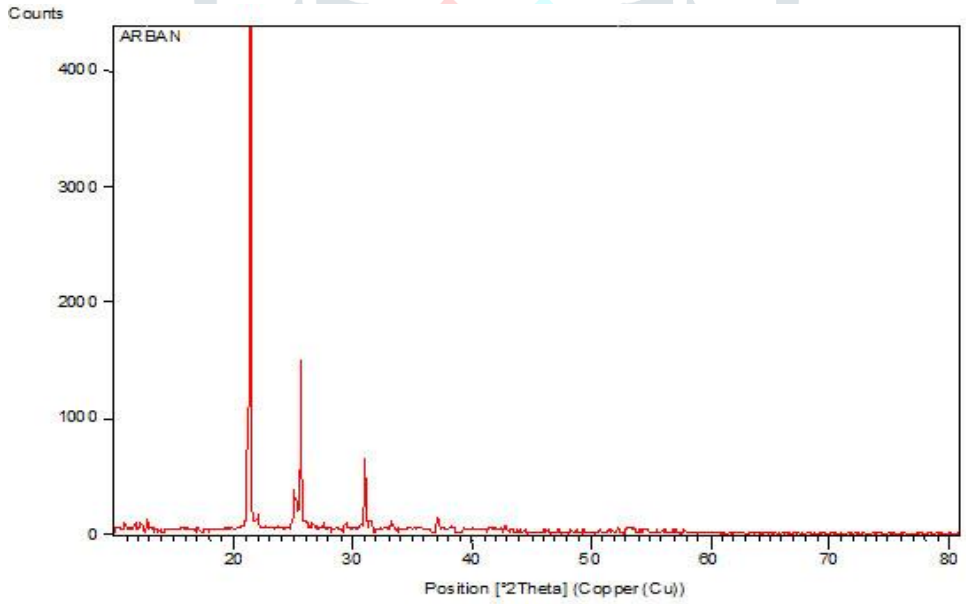

Figure 2: Powder XRD spectrum for L-Arginine Barium Nitrate Crystal

3.1.2 Single Crystal X –Ray diffraction analysis

The grown crystal is diffracted by ENRAF NONIOUS CAD-4 Single X-Ray diffractometer. The Single Crystal XRD results are tabulated in Table.1 and the crystal belongs to monoclinic system.

Crystallographic data	LARBAN crystal
a (Å)	7.40
b (Å)	5.17
C (Å)	10.09
α	90°
β	110.39°
γ	10.09°
Cell Volume (Å)^3	386.02

Table 1: Single XRD parameters of grown crystal

3.2 Vibrational analysis

3.2.1 FT-IR and FT-RAMAN analysis

FT-IR spectrum of LARBAN crystal is recorded using Perkin Elmer Spectrometer using KBr Pellet technique in the range 4000-400 cm^{-1}. The recorded spectra are depicted in Figure 3. The FT-Raman Spectrum is obtained using Imaging Spectrograph STR 500 mm length laser Raman Spectrometer and the recorded spectrum is shown Figure 4. In the recorded spectrum, the high intensity peak present in FT-Raman spectrum at 2922 cm^{-1} and at 2921 cm^{-1} in FT-IR spectrum is due to symmetry stretching of CH_2. The peaks observed at 1428 cm^{-1} and 689 cm^{-1} are assigned to symmetric and asymmetric stretching vibrations of COO^- respectively, the corresponding peak for FT-Raman is observed at 525 cm^{-1}. The above assignments are matched with ref. [3-5]. The peak at 1043 cm^{-1} in FT-IR and at 1046 cm^{-1} in FT-Raman is assigned to symmetric stretching vibrations of NO_3^- ions [6]. The detailed assignments are tabulated in Table 2.

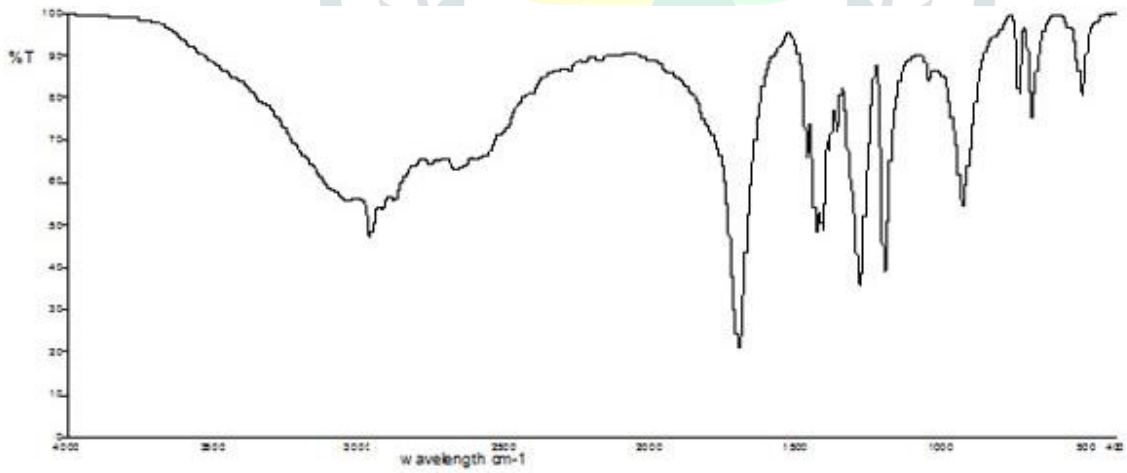

Figure 3: FT-IR spectrum for L-Arginine Barium Nitrate Crystal

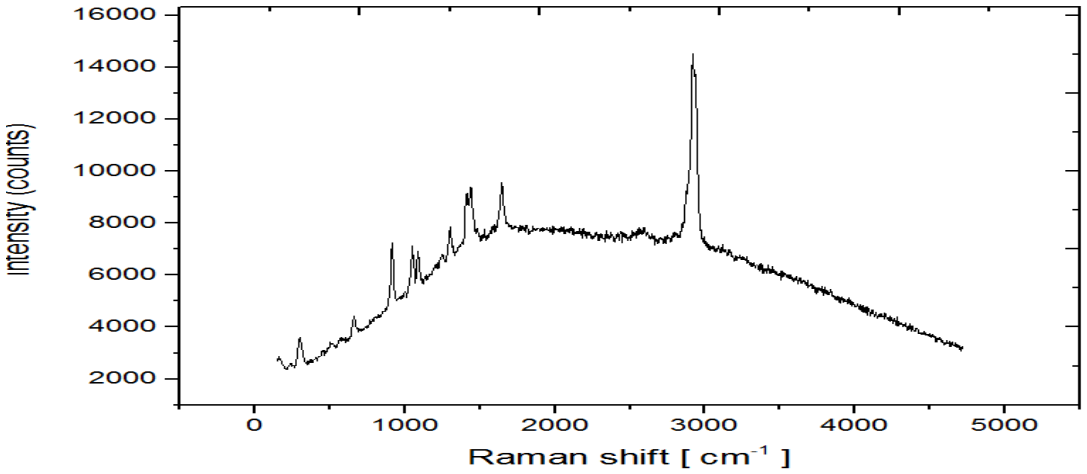

Figure 4: FT-Raman spectrum for L-Arginine Barium Nitrate Crystal

Wave number (cm^{-1})		Assignment
FTIR	**FTRAMAN**	
3037	3039	N – H stretching of amino group
2921, 2880	2922	Symmetric C – H vibrations of CH_2 group
2753, 2669, 2595, 2277	2750, 2666, 2594, 2274	Overtones and combinational band
1694	1650	C = O stretch of carboxylation
1463	1436	CH_2 plane deformation
1428	1413	COO^- symmetric stretching
1358	1301	C – C – H plane deformation
1279	-	CH_2 out- of- plane bending
1043	1046	Symmetric stretching vibrations of Nitrate ions
1194	-	O – H in-plane bending
926	917	CH_2 rocking
689	655	COO^- a symmetric stretching
515	525	N – H rocking

Table 2: FT-IR and FT-Raman assignments of the grown crystal

3.3. Micro Hardness Study

Micro hardness of a crystal is its capacity to withstand indentation. The grown crystals are subjected to indentations of 25g, 50g, 100g. Vicker's hardness number is estimated using the relation, $H_V = 1.8554\ P / d^2\ Kg\ mm^{-2}$, where 'P' is the applied load in Kg and 'd' is the indented impression in mm. A Graph is drawn between the hardness values and the corresponding loads for LARBAN crystals and is depicted in Figure 5. From the plot, it is clear that as the load increases hardness value also increases. Hence the crystal belongs to hard category.

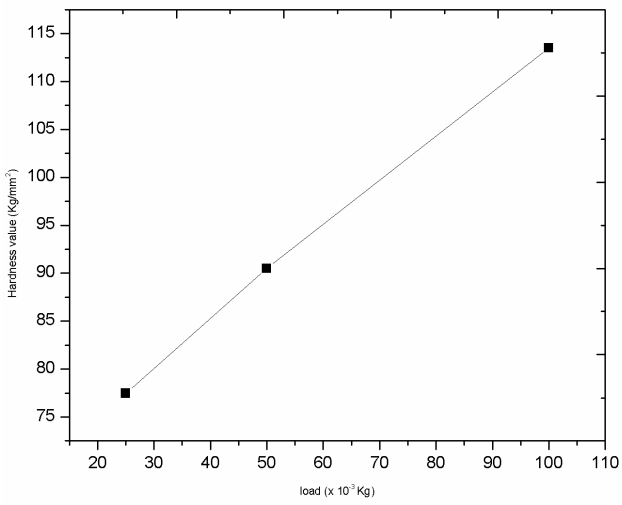

Figure 5: Graph showing relation between load P and H_v

3.4 Optical Properties

3.4.1. UV-Visible-NIR Spectral Study

The UV visible absorbance and transmittance spectra of the grown crystal were recorded using the PERKIN LAMBDA5 spectrophotometer. The spectra are recorded in the entire UV-Vis –NIR range 200-1100 nm and displayed in Figure 6 and 7. The band gap energy is also calculated using the formula $E_g = h c/\lambda$ eV, where h is the Planck's constant, λ is the lower cut-off wavelength in nm and c is the velocity of light in free space (m/second). The value of E_g is found to be 5.04 eV. This higher value of band gap energy shows lesser defects are present in the crystal [7]. From the absorption spectrum, the upper cut-off wavelength is about 246 nm. The cut-off wavelength of the crystal below 300 nm is a significant advantage in the field of NLO crystals. From the transmission spectrum, it is found that the grown crystal has wide transparency window (246 nm-1100 nm) in the UV-Vis-NIR region. This extended wide transparency will lead to higher harmonic generation efficiency [8].

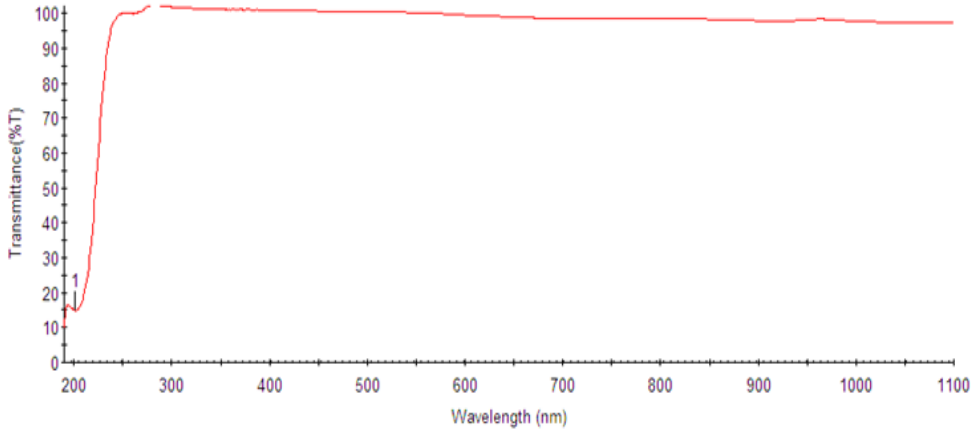

Figure 6: UV-Vis Transmittance spectrum of LARBAN Crystal

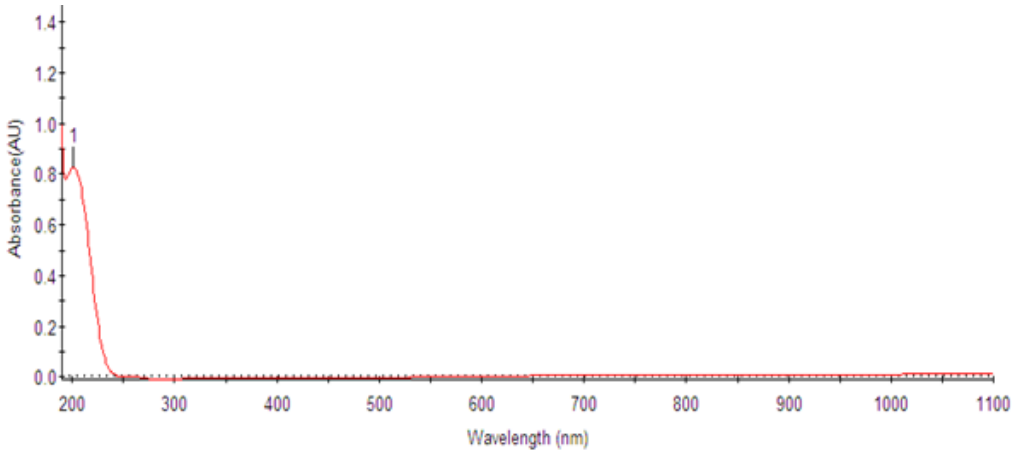

Figure 7: UV-Vis Absorbance spectrum of LARBAN Crystal

3.4.2 Photoluminescence Study

Photoluminescence is a process in which molecules absorb a photon in the lower energy level, exciting to its electron in excited state and then radiates a photon when the electron returns to lower energy state. Photoluminescence emission spectrum is recorded using Varian Cary Eclipse Spectrophotometer in the wavelength range 340 nm – 600 nm at the scan rate of 600 nm/minute and is depicted in Figure. 8. The sample was excited with light source of wavelength of 320 nm, one major and some minor emission peaks are observed. The high intensity peak is observed at 359 nm which corresponds to violet radiation and some minor peaks are also observed at 418, 426, 440, 445, 465 nm. The peak at 480 nm may be due to n-π* transition of Carbonyl group. In the recorded spectrum, the photoluminescence intensity decreases with increase in wavelength. This is due to the rotation of Carbonyl group around C- C bond [9].

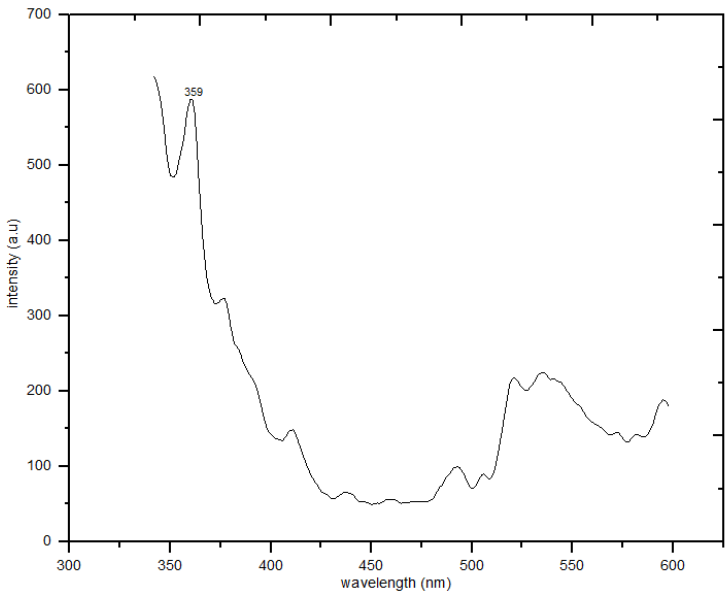

Figure 8: Photoluminescence Spectrum of LARBAN Crystals

3.5. Thermal Properties

The Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves for LARBAN crystals recorded using simultaneous thermo gravimetric analyzer SDTQ600 at a heating rate of 10°C/min in Nitrogen atmosphere are displayed in Figure 9. The DSC results a measure of the difference in ratio of heat absorption by a sample with respect to an inert gas. The TGA curve depicts that there is a

weight loss of about 83.58% in the temperature range 150-240 °C. The TGA curve shows the material is stable up to around 150 °C. At 271 °C, the weight loss is about 90.71% and above 950 °C a residue of 9% is left in the crucible. In the DSC curve, two sharp endothermic peaks are observed at 156 °C and 273 °C. The peak at 156 °C is assigned to liberation of Nitrates present in the compound, and the peak at 273 °C is due to the decomposition of amino acid. An unexpected minor endothermic peak before major decomposition is due to the presence of L-Arginine in the compound.

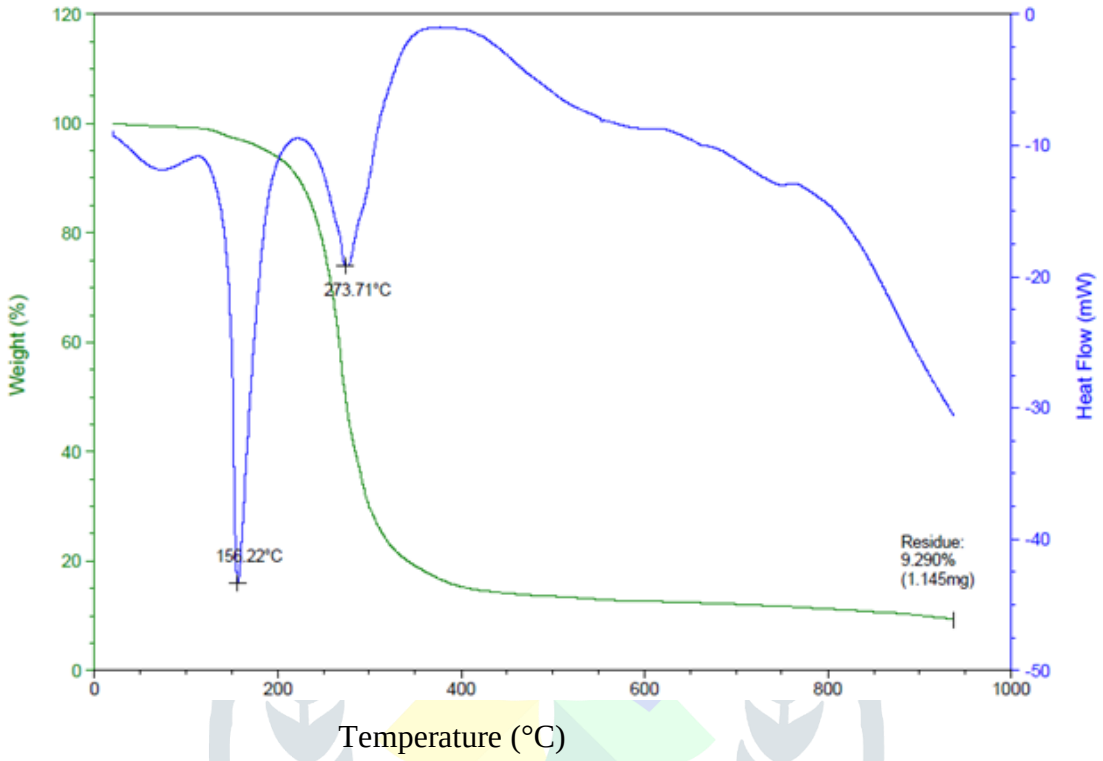

Figure 9: TGA and DSC curves of LARBAN Crystals

4. CONCLUSION

In the present study, L–Arginine Barium Nitrate crystals were grown by slow evaporation method. Unit cell parameters are calculated using Single crystal XRD and the crystal belongs to monoclinic system. Powder X-ray diffraction analysis reveals the crystalline nature of the title compound. The functional group and their interactions are confirmed by FT-IR and FT-Raman spectra. UV–Vis–NIR study shows the wide transparency and the band gap energy of the crystal is found to be 5.04 eV. Photoluminescence spectrum shows that high intensity peak is observed at 480 nm which corresponds to violet radiation. Micro hardness study reveals that the grown crystal belongs to hard material category. A TGA and DSC curve shows the thermal stability and decomposition of the title compound. Thus L–Arginine $Ba(NO_3)_2$ can be exploited as a potential candidate for photonics and NLO applications.

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