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Effect of Cadmium sulphate on the Growth and Characterization of L Valine Crystal

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ABSTRACT

By slow evaporation of a new semi organic nonlinear optical crystal and by synthesizing L-Valine cadmium sulphate good optical quality single crystals were grown. By powder X-ray diffraction studies, the growth conditions of the crystals are studied and the crystalline natures of grown crystals are confirmed. By using powdered XRD, FTIR, UV-Vis-NIR and DSC –TGA, the grown crystals was characterized. The high crystallinity of the grown crystal is shown by the sharp peaks from powdered XRD spectrum. By using FTIR spectroscopic technique the presence of various functional groups were confirmed. The UV-Vis-NIR spectrum is used to indicate that the crystal has very good absorption in the entire visible and near IR region spectrum indicates suitability of the material for NLO applications. By thermo gravimetric analysis, the stability of the thermal and mass loss has been estimated.

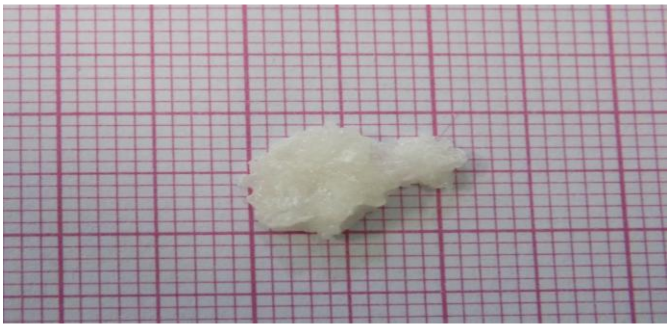
1. Introduction

A number of applications such as second harmonic generation, frequency mixing, electro optic modulation, etc have been proven to be an interesting candidate by nonlinear optical materials. The various possible uses in optical devices due to their large optical nonlinearity, low cut off wavelengths, short response time and time and high laser damage thresholds are attracted by organic NLO materials to understand the microscopic origin of the linear behavior of organic materials. Consider work has been done (11-20). The NLO properties such as large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations have been made widely due to their high nonlinear optical properties, rapid response in electro optic effect and large second or third order hyper polarizibilities compared to inorganic NLO materials (21-23). Thus for SHG applications, there is much impetus to design and understand organic compounds.

Organic crystals have potential applications in nonlinear optics, Nonlinear optics(NLO) plays an important role in the current research because of its importance in providing the key functions of frequency shifting optical modulation, optical switching, optical logic and optical memory for the emerging techniques in the areas of telecommunications, signal processing and optical interconnections. Organic materials have been used particularly due to the nonlinear optical response in this broad class of materials is microscopic in origin, giving an opportunity to use theoretical modeling coupled with synthetic flexibility for designing and producing novel material(24). Due to a very large susceptibility of organic NLO materials, they are used in many cases, several orders of magnitude are higher than that of inorganic crystals such as LiNbO3, KNbO3 and potassium dihydrogen phosphate(KDP). Thus the present investigation deals the growth of L-Valine Cadmium Sulphate an analog of L-Valine single crystal by slow solvent evaporation technique. The grown crystal was subjected to powdered XRD, FTIR, UV-Vis-NIR, DSC-TGA and NLO.

2. Experimental

Using Cadmium sulphate and L-Valine a solution was prepared in the molar ratio of 1:1. 15ml distilled water is used for the preparation of this solution. By slow evaporation method, seed crystals were obtained after one week. These seed crystals were used for the growth of bulk Valine Cadmium sulphate crystals.



3. Characterization

3.1. Powdered X-ray Diffraction

Powder X-ray diffraction studies of L-Valine and LVCS crystal was carried on a Siemens D500 Xray diffractometer with CuKα(k=1.15418A) radiation. The samples were Scanned for 2θ values from 10-50 at a rate of 2 min. The X-ray powder diffraction method used to study the structural property of the single crystals of L-Valine and LVCS. The powder XRD pattern of L-Valine and LVCS crystal is shown in figure1and 2. By least square fit method, the diffraction patterns of LVCS crystal have been indexed. The observed values for different 2θ values of the corresponding reflective planes for the crystal are given.

The results of well defined diffraction peaks at specific 2θ angles testimonies the crystalline nature and purity of the crystal.

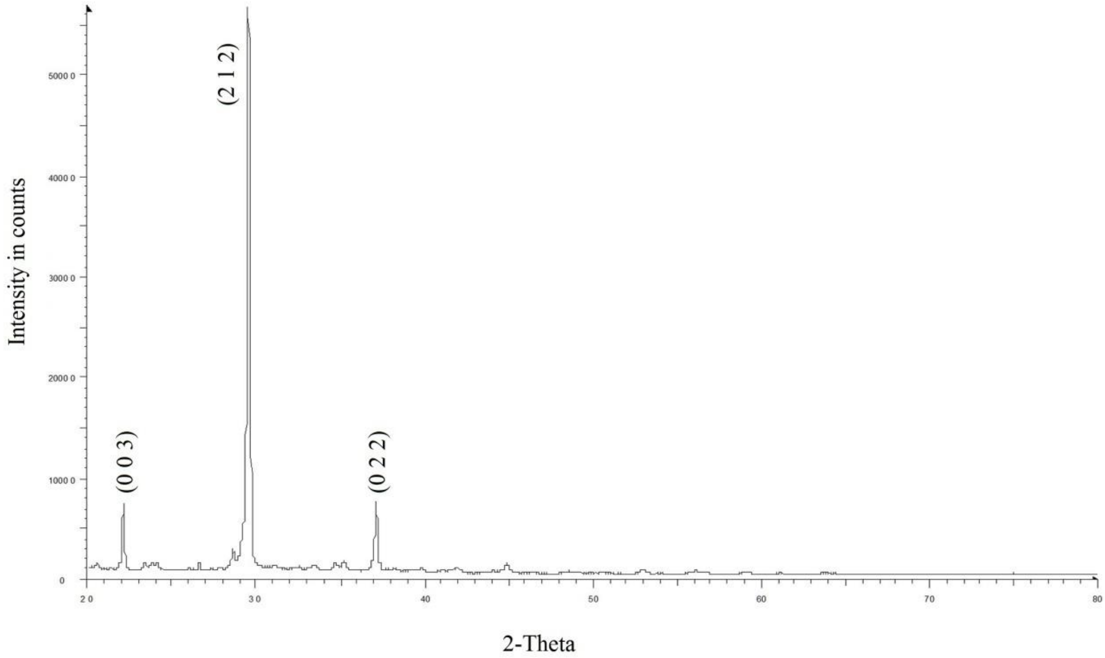


Figure 1 Powder XRD analysis of L-Valine

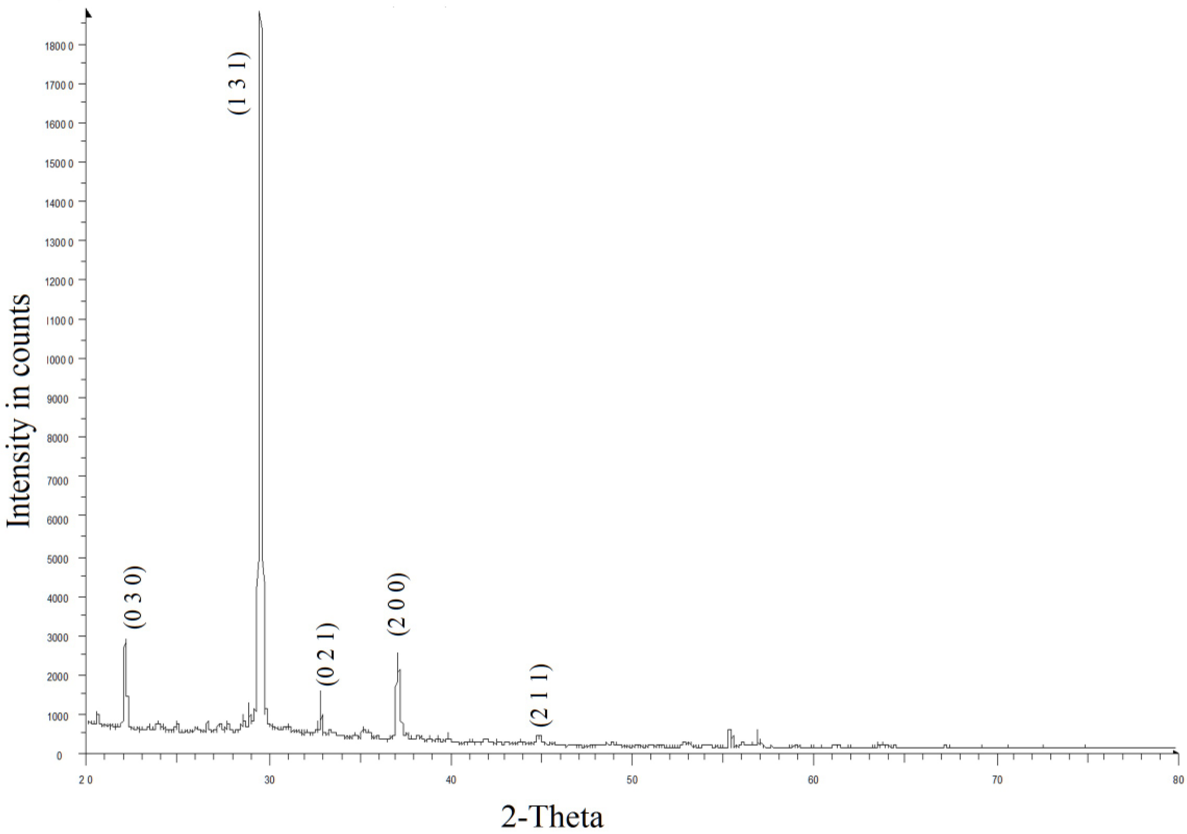


Figure.2. Powder XRD analysis of LVCS

3.2 FTIR spectral studies

From potassium bromide pellets technique the infrared spectra of L-Valine and LVCS were obtained by using Make-Bruker Optic GmbH Model No-TENSOR27 SOFTWARE-OPUS Version 6.5, Spectrophotometer in the range of 4,000-400cm^{-1}. In figure 3 and 4 the infrared spectrum of L-Valine and LVCS are shown, The IR spectra of LVCS mainly arise because of internal vibration of functional groups NH_3,CH,CH_3 and COOH.S-O, The absorptions of LVCS have been compared with those of the parent compound (L-Valine) in Table3. The broad peak at 2,975 cm^{-1} is because of the methylene symmetric stretching and the N-H-O methylene symmetric stretching. The N-H-O valence stretching combination observed at 2.628 cm^{-1}. The sharp peaks at 1586 cm^{-1} and 1395 cm^{-1} are because of COO- asymmetric mode of vibrations. The deformation b and s observed at 1508 cm^{-1} is because of the protonated amino group NH3. The C-C stretching modes are observed at 1270 cm^{-1} and 1137cm^{-1}. The sharp peak at 1033 cm^{-1} is because of C-C-N stretching mode. The C-C=O deformation are observed at 900 cm. The S-O stretching S-O umbrella bending is observed at 1065 cm^{-1} and 663 cm^{-1} respectively. The wave numbers obtained by observing from the recorded spectra were found to be in good agreement with the assignments proposed in some complex amino acids (11-12).

Wave number/cm-1		Assignments
L-Valine	**LVCS**	
2954.77	2975.85	CH2 symmetric stretching
2628.04	2628.28	N–H–O combination
2111.91	2111.15	Nitrile C-N stretching
1586.46	1586.40	COO- asymmetric stretching
1508.04	1508.69	NH3 deformation
1395.76	1395.94	COO- asymmetric stretching
1328.77	1329.03	C–O stretching
1270.16	1270.35	C–C stretching
1189.94	1137.55	C–C stretching
1176.92	1065.55	S-O stretching
1138.90	1033.41	C–C–N stretching
1064.88	947.96	NH3 rocking
1032.65	923.71	C–H deformation
947.69	900.99	C–C–O deformation
775.15	715.97	C–C deformation
752.15	663.89	S-O umbrella bending

Table. 1. Comparison of FTIR Spectra of L-Valine and LVCS

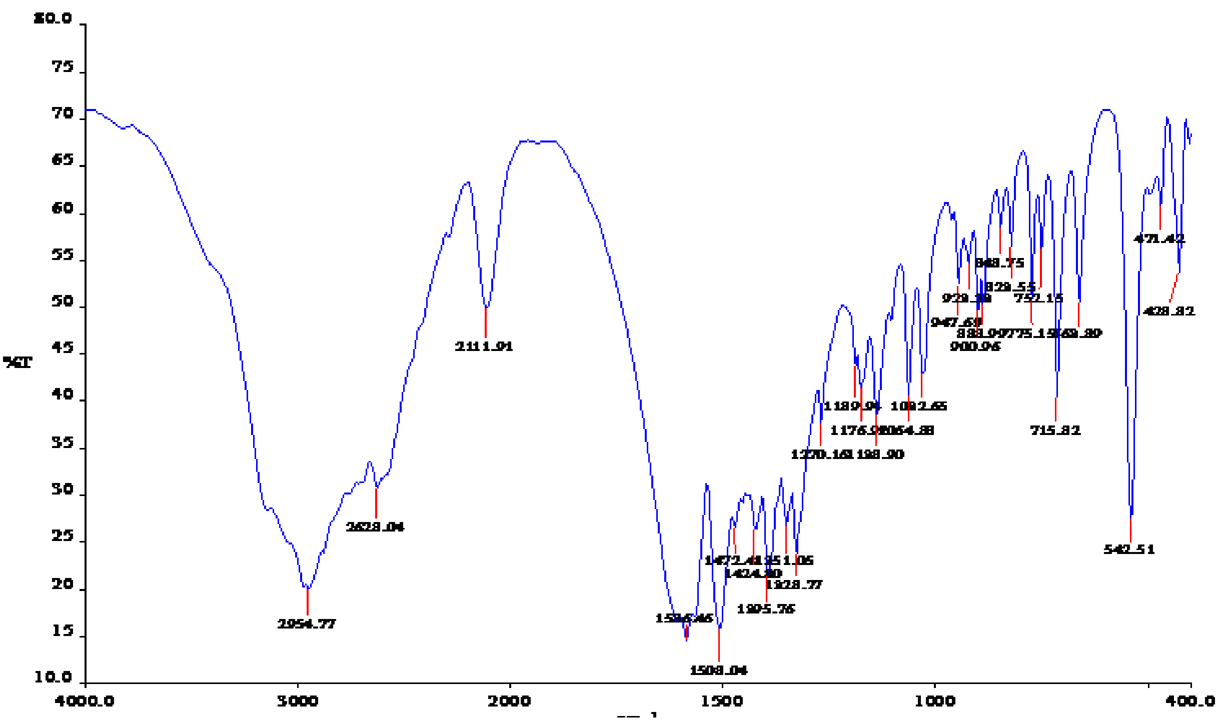


Fig 3 FTIR Spectrum of L-Valine

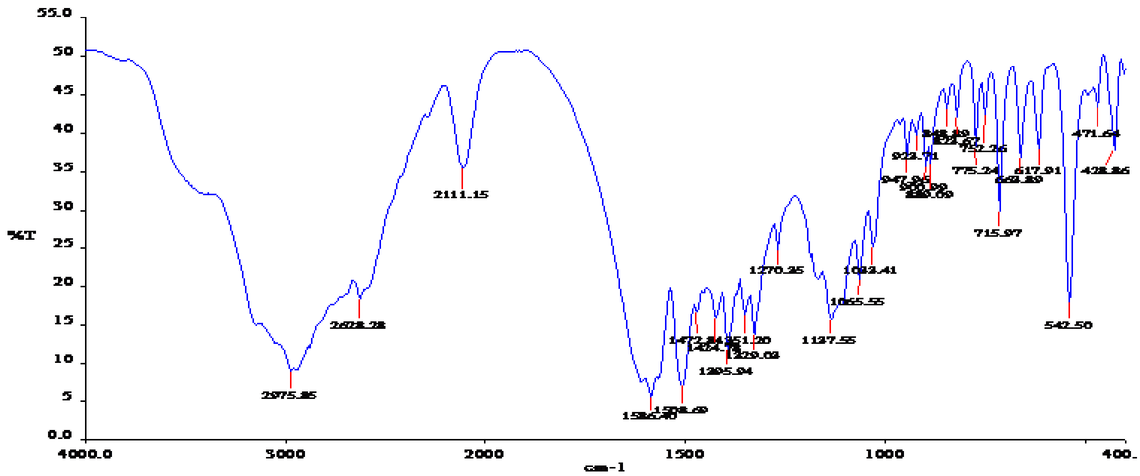


Figure 4 FTIR Spectrum of LVCS

3.3 UV–Vis–NIR spectral analysis

The UV-Vis-NIR spectra were recorded on Jasco V-630 spectrophotometer in the range of 200-1,100 nm with scanning speed of 400 nm min. These UV-Vis-NIR spectra are used to find the optical absorption range of L-Valine and LVCS crystals. (Fig.5,6) when the absorption is monitored from longer to shorter wavelengths, for L-Valine the crystals are optically transparent in the UV-Vis-NIR regions with 80% transmission and for LVCS optical absorption with lower cut-off wavelength below 200nm, which is sufficient for SHG laser radiation of 1.064 nm and the transmittance of the crystal is about 90% in the entire visible and infrared region.(11) Due to the mixture Cadmium sulphate with L-Valine , there is a shift of lower cutoff wavelength in UV region and it is desirable for optoelectronic applications.

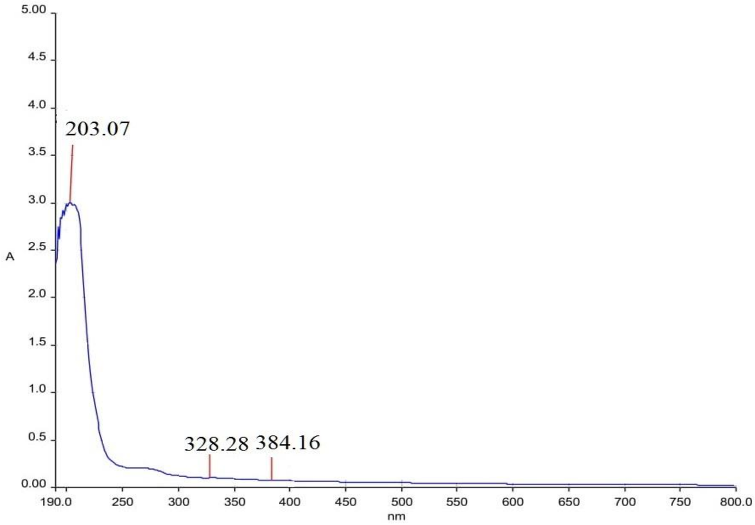


Figure 5 UV-VIS-NIR Spectrum of L-Valine

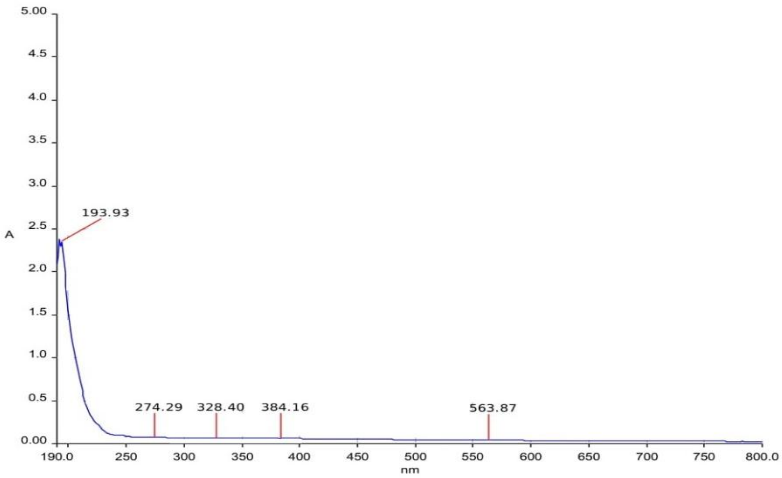


Figure 6 UV-VIS-NIR Spectrum of LVCS

3.4 DSC-TGA studies

The TG and DSC curves of L-Valine and TG and DSC curves of LVCS are shown in the figures 7 and 8 respectively,(Fig.7) It is observed that the material undergoes an irreversible exothermic transition at about 220°C where the decomposition starts. It indicates the material stable up to 226°C. L-Valine is fully decomposed at 300°C. The good degree of crystallinity of the grown crystals are shown by the sharpness of the exothermic peak,. It can be also seen on the TG curve that the mass loss starts at 220°C and ends at about 300°C. The liberation of Volatile substance is responsible for the mass loss. The peak at 287°C indicates a phase change from liquid to vapour state as evidence from the loss of mass on the TG curve. The TG-DSC analysis doesn't show any kind of phase transition of LVCS crystal.

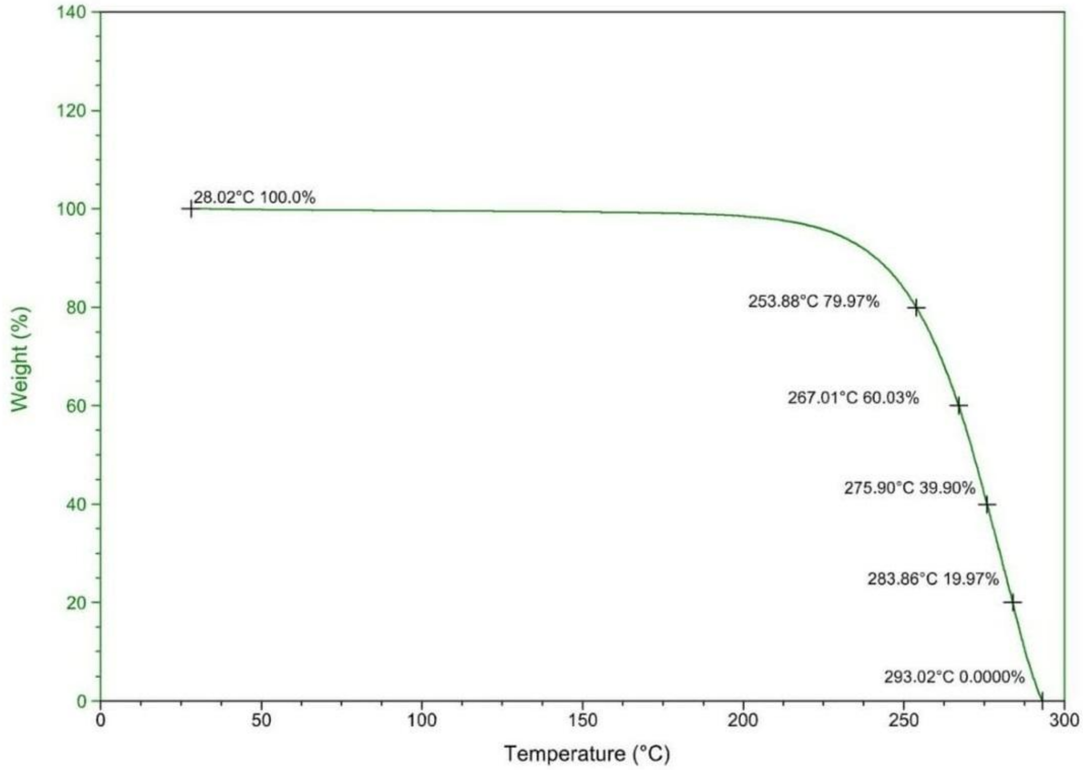


Figure .7. DSC-TGA curves of L-Valine

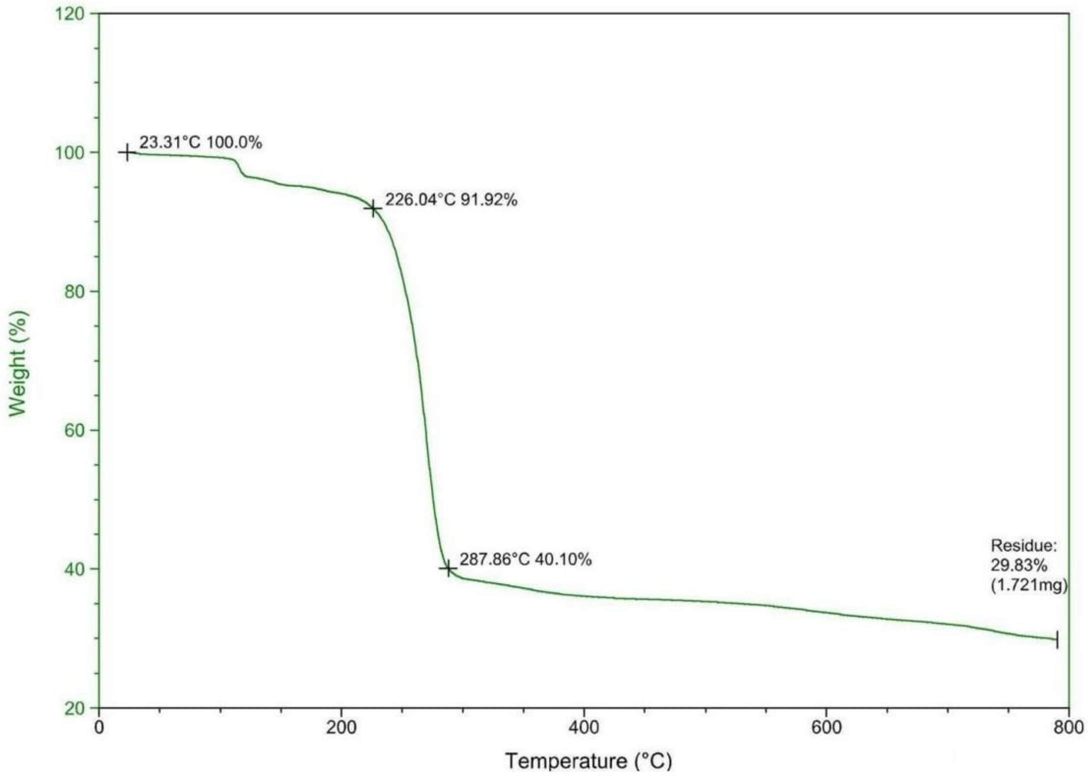


Figure 8 DSC-TGA curves of LVCS

3.5 Second Harmonic Generation

Taking KDP as a reference material the second harmonic generation efficiency of the grown crystal is determined by using Kurtz Perry powder method. Q-switched laser beam of wavelength λ=1.064nm is made to illuminate the microcrystalline powder packed in the glass tube of pulse width 10ns. The photomultiplier detects the emitted radiation from the crystal and same was recorded. Emission of green light (λ=532nm) from the sample confirms that the crystal has NLO potential. It was observed that the efficiency as 198mV and the conversion efficiency of the grown crystal are twice that of KDP crystal.

4. Conclusion

The solution prepared from the raw materials L-Valine, Cadmium sulphate helps the growth of the seed crystals of L-Valine Cadmium Sulphate(LVCS). These crystals are characterized and following results are obtained. The grown crystals are characterized by using powder Xrd diffraction. From the FTIR spectrum it should be confirmed that the structure of the LVCS have both the L-Valine and Cadmium Sulphate molecules. These arrangements are in alternative layers in the crystal and this is evident from the non damage of L-Valine structure. The UV-Vis spectrum establishes the good transmittance window and the lower cut off are found to be as low as 200nm allowing for frequency conversion down to UV-region. The sharpness of the exothermic peak from DSC/TGA themograms shows good degree of crystallinity of the grown crystals and it also indicates its suitability for application is lasers field.

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