Section: Research Paper

GROWTH AND CHARACTERIZATION STUDIES ON DIPHENYLAMINE ADIPATE CRYSTAL DOPED WITH BARIUM CHLORIDE

A. Rakini*[1], K. Rajarajan[2], R.Maheswari[1]

[1] Research Scholar, [2]Assistant Professor
PG and Research Department of Chemistry, Rajah Serfoji Government College (A) (Affiliated to Bharathidasan University), Thanjavur, 613005, India

ABSTRACT

Pure and Barium chloride doped with Diphenylamine adipate crystal were grown by slow evaporation solution growth method. The various characterization studies were carried out for the crystal synthesized using the proposed approach. The presence of various functional groups in the grown crystal was confirmed by Fourier Transform Infrared (FT-IR) analysis which is the range 600 - 4000^{cm-1}. Ultraviolet and visible (UV-Vis) absorption spectroscopy study shows that the transparency is increased much by the dopant. The thermal properties of the grown crystals were studied by thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) and it was noticed that it is stable up to 235℃. Powder X-ray diffraction of the growing crystal identified the presence of chloride. The SEM studies were also carried out to study the morphology of this synthesized crystal. The band gap energy was calculated to be 4 eV. Thus synthesized crystals exhibits favorable features for non linear optical applications observed from the characterization studies.

1. Introduction

Laser technology, optical communication, and optical storage all benefit greatly from non linear optical frequency conversion materials. Amino acid crystals comprised of organic materials have recently been the focus of research to increase their chemical stability, laser damage threshold, and non linear properties. Various researchers have conducted currently covered on crystals that are both pure and organic as well as doped with metal ions.[1-3], The recently developed organic nonlinear optical single crystals play a significantly more important role in such applications than their inorganic materials because of their highly nonlinear due to highly concentrated electrons, higher molecular dipole moment, ability to modify their structural makeup, inherent synthetic flexibility, low dielectric constant, quick response time, high damage resistance and relative ease of device fabrication. [4-7]. Due to its functional and practical significance in things like high-order nonlinear optical responses, polarity, luminescence, photography, and medication management, semi organic materials have attracted a significant amount of research. [8-11]. The amino acid crystal growth work was done using the slow evaporation solution growth method. The same growth method is used in this study to

produce a high-quality optical crystal with excellent transparency. There are several different types of barium chloride ($BaCl_2$). When the number of coordination is larger than 6, in particular, the Ba^{2+} ion. Barium electron configuration in the alkaline earth metal $6S_2$. A compound is created when barium and an anion, Cl^-. Diphenylamine crystals are created when the electrolyte properties of $BaCl_2$ interact with adipate. The crystals were produced and their characteristics were determined by powder XRD, SEM with EDAX, UV-Vis- NIR, FT-IR, TGA-DTA, and Band Gap Energy. [12-16].

2. Experimental

2.1 Crystal growth

Exactly one molar Adipic acid($C_6H_{10}O_4$)1M solution is prepared by weighing accurately 14.61g of Adipic acid and is dissolved in the 100 ml of double distilled deionised water and Diphenylamine[$(C_6H_5)_2NH$]1M solution is prepared by weighing exactly 16.92g and is dissolved in 100ml of double distilled deionised water. [8-11]. The 1:1 equimolar solutions are heated separately for 5 minutes. They are mixed thoroughly with stirring while in hot condition. The dopant Barium chloride (MF Back;] is added in the ratio of 0.1ml by weighing about 0.20g and is mixed directly into Adipic acid and diphenylamine solution slowly with constant shaking. After having added completely, it is kept aside until it attains the room temperature. After that it is cooled in the ice bath till the precipitate is formed. It is filtered, dried and a portion is taken for preparing the saturated solution. The saturated solution is prepared for growing crystals. It is filtered and kept undisturbed. The fine crystals are harvested. The adipic acid-Diphenylamine crystals are characterized using FT-IR, UV, SEM and Thermal analysis.[14-15].

3. Characterization

Powder XRD analysis was carried out with a Bruker D8 focus to confirm the crystals that have formed. The FT-IR spectra of Diphenylamine adipate crystal doped Barium chloride was acquired in the 4000-600 cm-1 region using an Agilent Technologies Cary 630 FT-IR spectrophotometer utilising the KBr pellet technique. The SHIMADZU- UV 1800 UV -Visible spectrometer was used to carry out the UV-Vis- NIR analysis, which included all of the UV-visible and near infrared spectrum between 200 nm and 800 nm. The thermal properties of the grown crystal were crystal were investigated, and the results demonstrate concurrent TG-DTA studies in the temperature range of 100^{o}C to 1200^{o}C using a model NETZSCH STA 449 F3 JUPITER analyser in an inert atmosphere at the pyrolysis temperature of 20 k/min. SEM spectrum of as grown crystals were analyzed using JEOL MODEL JEOP it 200 at the scanning image range is SED 200 KV to analyze the observation defects. UV data is used to calculate the energy band gap of the harvested crystal.

3.1 Powder X-ray Analysis

Figure 1 displays the PXRD (powder XRD) pattern of the crystal of diphenanylamine adipate. High crystalline quality of the produced crystals is indicated by the presence of strong peaks with high resolution at particular Bragg angles. [13-16] d- values for various h k l were calculated from the crystal structures. The obtained miller indices and d-spacing (hkl) show good agreement with the given values. According to the results of the X-ray powder diffraction study, the crystal is a representative of the triclinic system and has the following lattice parameters [alpha = 90°, beta = 2521.26°, gamma = 90°, volume = 2521.26cc^3; a= 16.97; b=9.600; and c=16.24] are listed in Table 1.

Table 1 Crystal Structure

Crystal system	A	B	C	Alpha	Beta	Gamma	Volume
Monoclinic-b	16.9752	9.5996	16.2446	90.000	2521.26	90.000	2521.26

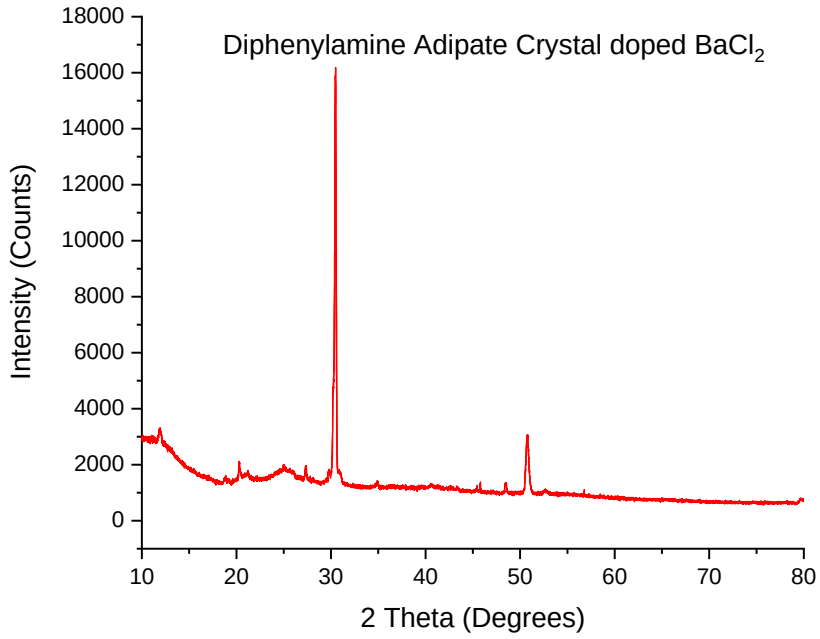


Figure 1 : Diphenylamine adipate crystal doped $BaCl_2$

3.2 UV STUDIES:

Figure shows the absorbance zone around 211nm and 356nm where wide band completely transparent in all the visible range is observed.

Optical properties of the grown crystals were studied using arithmetic UV spectrometer. Optical transmittance & absorption were recorded for the crystals of thickness approximately around 2nm, There is a shift in the cut off wavelength due to additive effect. The peak around 211nm corresponds to $\pi - \pi^*$ conjugation.[17] The depth of the peak varies with the additive present. The increased depth which is favourable for more non-linear effect is observed in this crystal at 356 nm. The dependence of optical absorption co-efficient and the photon energy helps to study the band structure and the type of transmission of electrons. This is very important material possessing nonlinear optical properties. The UV cut- off wavelength for both pure and doped crystals is found 365nm. The wide range of transparency is an added advantage for these crystals to be utilized in the field of optoelectronic devices. .[18]

Table 2 UV-Visible Zone

Λ_{max}(nm)	Transition
211	π-π*
356	n-π*

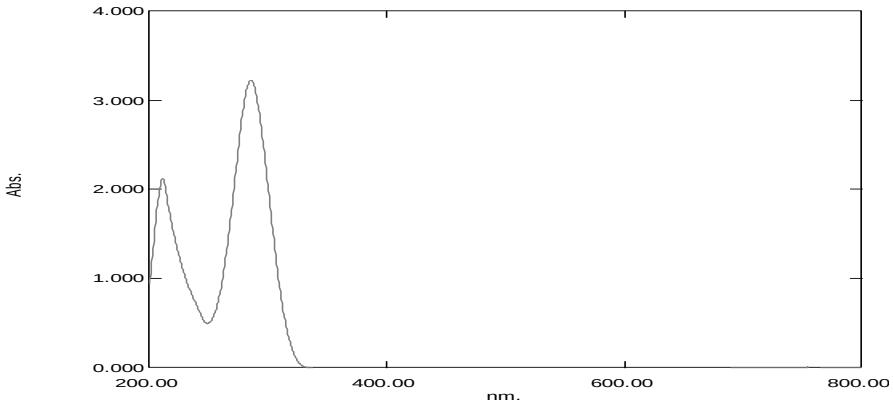


Figure 2 : UV Spectrum of Diphenylamine adipate crystal doped with Barium chloride

3.3 FT-IR STUDIES:

Fourier transform infrared spectroscopy (FT-IR) involves examination of the twisting bending, rotating and vibrational modes of atom in a molecule. Upon interaction with infrared radiation are absorbed at specific wavelengths and the functional groups of a sample can be identified from the spectrum for the grown Diphenylamine adipate crystal doped with $BaCl_2$ crystal is presented in the figure.

The medium C-H Stretching absorption frequency at 2643cm^{-1} and C-N stretching frequency at 1043cm^{-1} confirm the presence of amino group. The appearance of the strong C-Cl stretching absorption frequency at 733cm^{-1} is the indication of the presence of chloride is the compound.

The absorption frequencies at 3014cm^{-1} and 2952cm^{-1} of C-H bending and C-H stretching bonds indicate the presence of medium aromatic compound. The presence of medium C-H bending frequency at 1405cm^{-1} confirms the carboxylic group. [12]

Two absorption frequencies, one NO_2 strong symmetrical stretching appears 1355cm^{1} the another one strong N-O stretching appears at 1460cm^{-1} show the presence of nitro group. The appearance of one more absorption frequency of strong bond C=O 1683cm^{-1} also confirms the presence of keto group. Absence of N-H bent 1550 cm^{1} - 1640 cm^{1} and OH group 3300 cm^{1} - 3500 cm^{1}

From the spectral data it is clearly established that the sample under investigation is Diphenylamine adipate crystal doped with Barium chloride.

Table 3 FT-IR – Diphenylamine adipate crystal doped Barium chloride

S.N0	**WAVE NUMBER**	**MODE**	**COMMENT**
1	3014 Cm^{-1}	C-H Stretching Vibration	Aromatic compounds
2	2952 Cm^{-1}	C-H Stretching	Aromatic ring
3	2643 Cm^{-1}	C-H Stretching	Medium broad highly structured
4	2556 Cm^{-1}	C-H Stretching	Major maximum Aldehyde
5	1916 Cm^{-1}	C-H Stretching Finger print region	Benzene ring substitution
6	1683 Cm^{-1}	C=O bond	Ketone
7	1460 Cm^{-1}	C=C Stretching	Benzene group
8	1405 Cm^{-1}	C-H bend	Aromatic group
9	1355 Cm^{-1}	NO_2 symmetrical Stretching	Nitro group
10	1043 Cm^{-1}	C-N Stretching	Amines
11	733Cm^{-1}	C-Cl Stretching	Mono chlorinated Aromatic

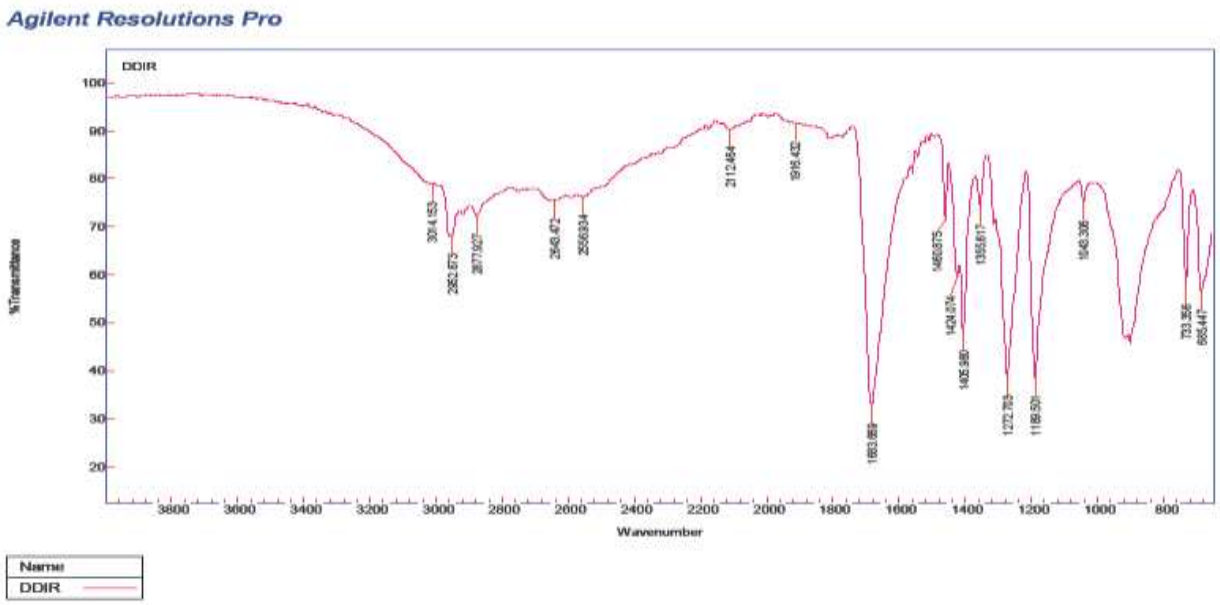


Figure 3 : FT-IR Spectrum of Diphenylamine adipate crystal doped with Barium chloride

3.4 : Thermal analysis

The Thermogravimetric analysis of Diphenylamine adipate crystal is shown in figure, when the compound heated from room temperature 1200°c the compound decompose into two stages. The compound is stable upto 230°C. Afterwards the compound decomposes almost 95%. The first weight loss occurring between 200°C and 250°C. The low temperature DSC (heating and cooling) curves of the compound is depicted in figure. Thermal anomalies are observed at 150°C, 250°C, 520°C in the cooling and heating cycles, respectively. The occurrence at thermal hysteresis during the cooling and heating cycles indicates a first order phase transition. The first order phase transition may be due to the occurrence of thermal changes in the compound. A first order transition is defined as the one in which a discontinuity occurs in the first derivatives of the free energy with respect to temperature and pressure, first order phase transition are associated with thermal hysteresis.[18-20]

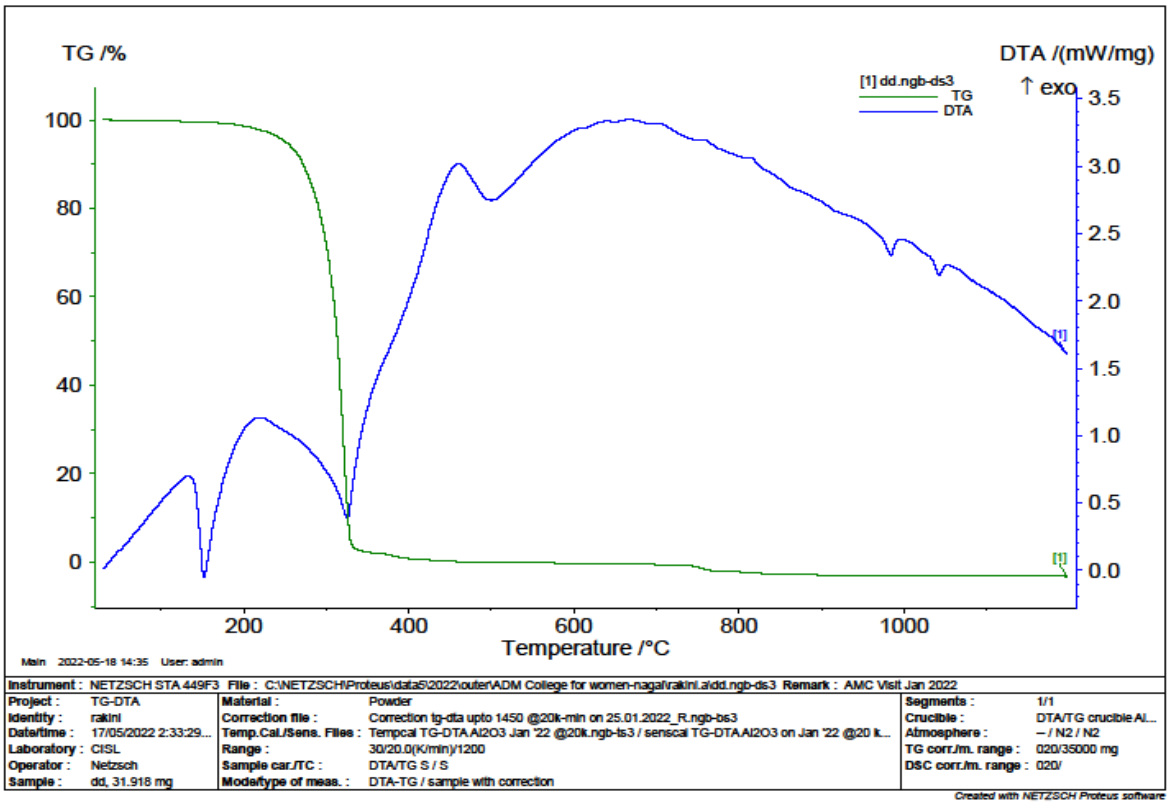


Figure 4: TG-DTA- Diphenylamine adipate crystal doped with Barium chloride

3.5 : SEM analysis of crystal surfaces

JEOL MODEL JEOP IT 200 at the scanning image range is SED 200 KV was used to analyse the SEM spectrum of as-grown crystals to analyse the observation deficiencies. The scanning electron microscope (SEM), which is used to extract information about the size and shape of the particles present in the crystal, was used to analyse the surface morphology of Diphenylamine adipate crystal doped Barium Chloride. The Diphenylamine adipate crystal doped Barium Chloride crystals surface shape is depicted in Fig. 4, and the SEM images were used to make the observations listed below. SEM indicates the grown crystals are of good quality and have a layer -like structure.[20-23]

The surfaces of the crystals are smooth at a scale of 1 µm, 5 µm, 10 µm, 50 µm at a magnification of 200kv.

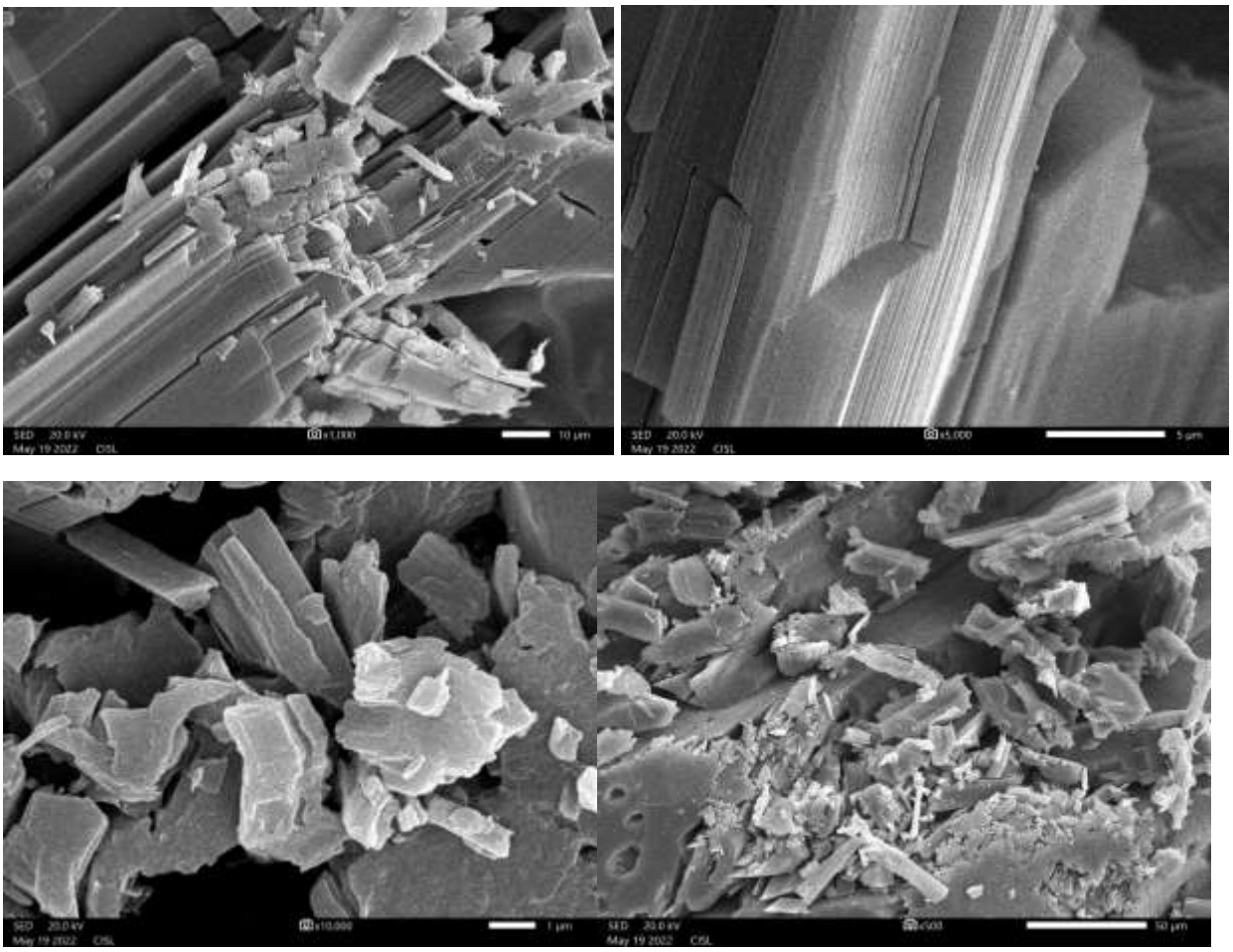
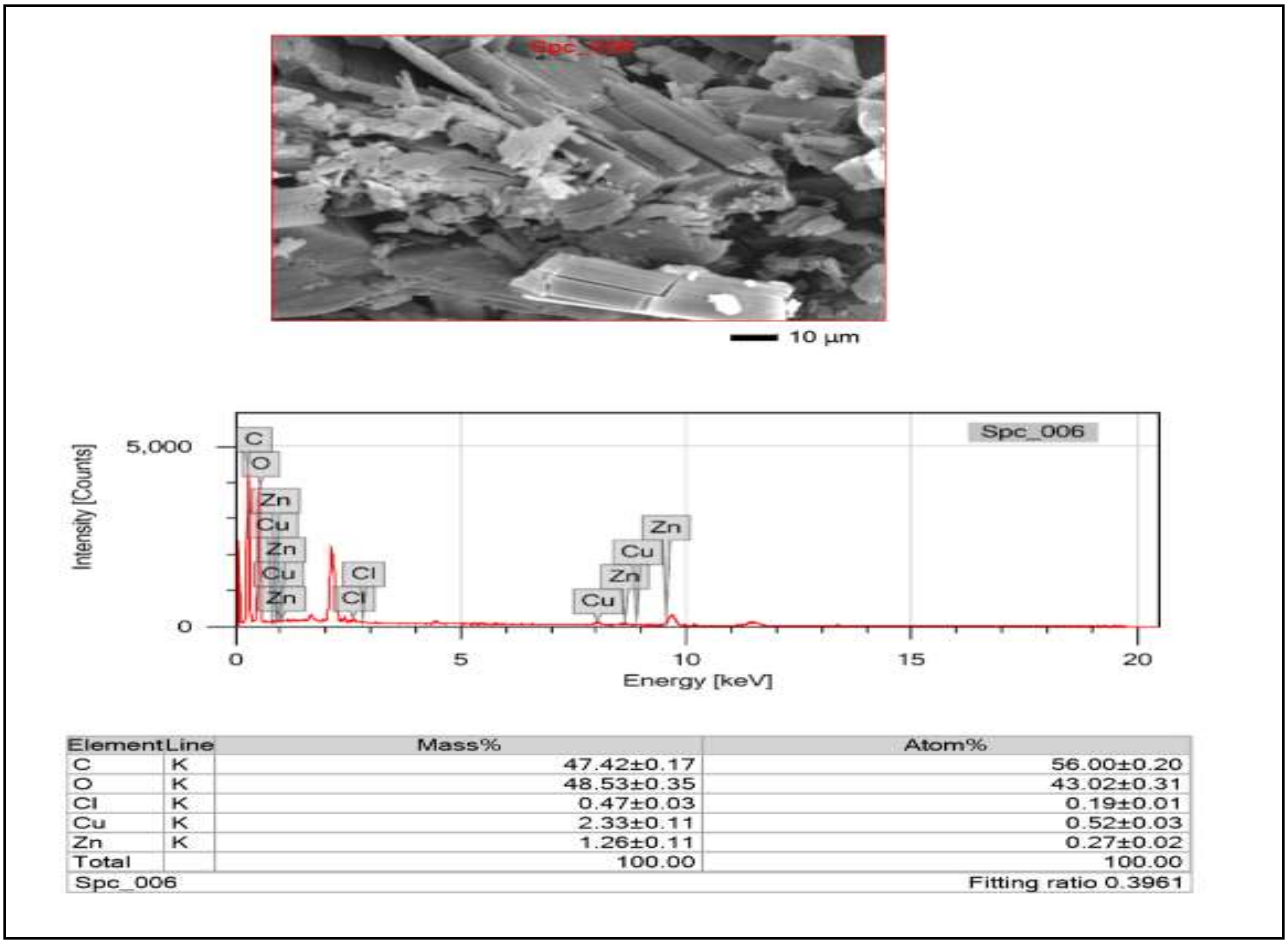


Figure 4 SEM Analysis

SEM With EDAX

Figures 4 and 5 illustrate the variations in the EDAX measurements done at various crystallographic surfaces, and Table 3 displays the values obtained for the presence of the needed atoms and their average weights & atomic percentages. The spectrum indicates the presence of the compounds key constituents, including carbon, oxygen and chlorine and other impurities Cu, Zn are 0.52 and 0.27 respectively.



Element	Line	Mass%	Atom%
C	K	47.42±0.17	56.00±0.20
O	K	48.53±0.35	43.02±0.31
Cl	K	0.47±0.03	0.19±0.01
Cu	K	2.33±0.11	0.52±0.03
Zn	K	1.26±0.11	0.27±0.02
Total		100.00	100.00
Spc_006			Fitting ratio 0.3961

Figure 5 Sem with EDAX

3.6 Band Gap Energy

The sample was prepared by using tweezers and placed on a glass slide. The sample was then covered with a fresh glass slide, each time with taps on both sides to keep it in place. The UV-VIS-NIR study was carried out using a SHIMADZU-UV 1800 UV Visible spectrophotometer, which depicts the original ultraviolet and visible spectrum between 200 and 800 nm. the transmittance, absorbance, and reflectance were all measured. In order to measure transmittance and absorbance, the samples were placed inside the spectrophotometer container, where their surface was vertically exposed by a directional light beam. In order to assess reflectance, the samples were mounted on the refractive index attachment. The rough mixed crystal with a glycine surface's band gap is considered to be 4 eV, showing that the line crossed the X-axis. The band gap Diphenylamine adipate crystal doped Barium chloride are estimated to be 4 eV. [24]

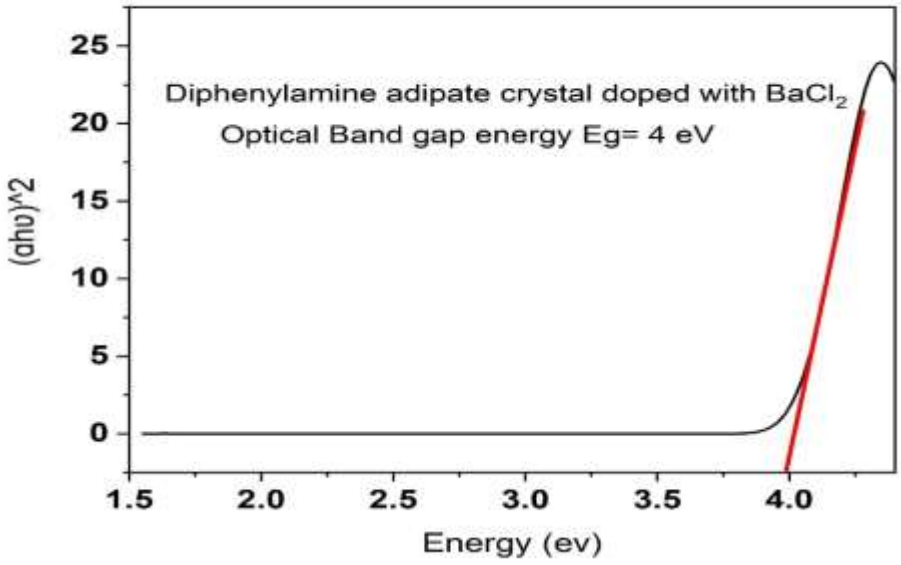


Figure 6 Band gap energy

4. Conclusion

Good optical quality Diphenylamine adipate crystal doped with Barium chloride have been grown by solution growth method at room temperature. The lattice parameters have been found by powder XRD technique. The FTIR spectroscopic examination validates the functional groups in the crystal, the UV-Visible cut-off wave length is 365 nm,With an increase in frequency, the dielectric constant lowers, and extremely low values of the dielectric loss show that the crystal is 100 % pure. The band gap energy is found to be 4 eV, The greatest absorption is suggested by UV-Visible for Barium chloride doped crystals. The surface morphology of Diphenylamine adipate crystal doped barium chloride crystals were analysed by SEM which is used to extract the information about size and shape of the particles present in the crystal. EDAX and chemical analysis confirm the presence of doped specimens. The TGA/DTA supported its application in the electronic industry by studying thermal stability. The thermal studies confirms that the crystal structure is stable upto 230 °C and indicates its suitability for application in lasers field. The Diphenylamine adipate crystal doped with Barium chloride is a feasible option for use in the manufacturing of optoelectronic devices from the conducted experimental characterisation studies. The effect of impurities with different percentage on the growth of these crystals can be study the change in their properties. Further possible derivatives of the crystals may be synthesized and investigated for the improvement on dielectric properties and more.

5. Reference

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