International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 04 Special Issue: 09 | Sep -2017 www.irjet.net p-ISSN: 2395-0072
One Day International Seminar on Materials Science & Technology (ISMST 2017)
4th August 2017
Organized by
Department of Physics, Mother Teresa Women's University, Kodaikanal, Tamilnadu, India

Growth and characterization of Guanidine benzoate (GuBzt) single crystals

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Abstract- *The new organic single crystal Guanidine Benzoate (GuBzt) is grown by slow evaporation method. Optical transparency of the (GuBzt) single crystals measured by UV- Vis spectrum shows the cutoff frequency at 296 nm. Dielectric constant and refractive index of the GuBzt single crystals are also calculated. X- ray diffraction studies showed that GuBzt crystallizes in orthorhombic, Pnma space group.*

Key Words: **GuBzt, UV-Vis, Dielectric, X- ray diffraction Pnma**

1. INTRODUCTION

Guanidine carbonate and benzoic acid have been taken into consideration to grow the organic single crystals. Organic compound of Guanidine carbonate is one among the special product, inspite of its enormous application in the fields of biomedical, cosmetics, detergents, microencapsulation process, optoelectronic and telecommunication etc. Guanidinium ion is relatively simple chemical species, whose structure is related to those of amides and proteins in which there is considerable interest. The guanidinium ion can form a broad family of hydrogen bonded crystals [1]. Guanidine tartarate [2], guanidine acetate [3], guanidine maleate [4] has been chosen, previously for the study as the potential material for nonlinear optics. These crystals belong to noncentrosymmetric space group and also the nonlinear optical (NLO) response was observed. From the NLO response Guanidine based materials exhibits Strong NLO efficiency.

In this strategy, Benzoic acid is taken into account. It is one of the amino acids and it plays a very important role in crystal growth because of its donor carboxyl group and amino acceptor group [5, 6]. The acidic carboxyl group can undergo reactions to form products such as salts, acid halides. Since, all H atoms of the guanidinium cations are involved in N—H···O interactions with the benzoic acid, each carboxylate O atom accepting three H atoms. In each layer, the cation is bonded to three anions to form guanidine benzoate single crystals [7].

The crystal structure of GuBzt single crystals have already been reported [8]. Hence, this article mainly focuses the optical properties of the title compound explained via linear optical study, UV – Vis spectrum which gives the optical transmission and bandgap. In addition, refractive index and dielectric constant of the GuBzt single crystals has also been studied using UV- Vis spectrum and the respective results are discussed.

2. EXPERIMENTAL PROCEDURE

2.1Crystallization method

Guanidine benzoate single crystals are synthesized by slow evaporation method. Commercially available AR grade Guanidinium carbonate (Himedia) and benzoic acid in stoichiometric 1:1 ratio are used to synthesize Guanidine benzoate single crystals. The calculated amount of Guanidinium carbonate is dissolved in deionized water, benzoic acid is then added to the solution slowly by stirring. To remove the contaminations, the stirred solution is filtered using wattmann filter paper and allowed to dry in room temperature for evaporation. The colorless, transparent crystals are of size 10 x 8 x 5 mm^3 obtained after 18 days of the growth as shown in Fig.1.

2.2 Characterization

The powder X-ray diffraction pattern is obtained by SHIMADZU model XRD 6000 instrument with CuKα radiation (λ=1.54060 Å). X- ray diffraction data are collected using an ENRAF NONNIUS- CAD 4 single crystal X- ray diffractometer with MoKα (λ= 0.71073 Å) radiation at room temperature. The UV-Vis-IR transmission spectrum is recorded in the range of 200 - 1200 nm using SHIMAZLER 2410 UV spectrometer. FT-IR spectrum is recorded using BRUKER IFS-66V spectrometer in the range between 4000 and 400Cm^{-1}.

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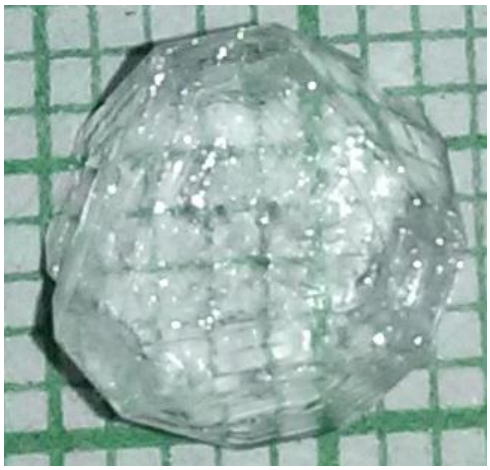

Figure 1: As grown Guanidine Benzoate single crystals

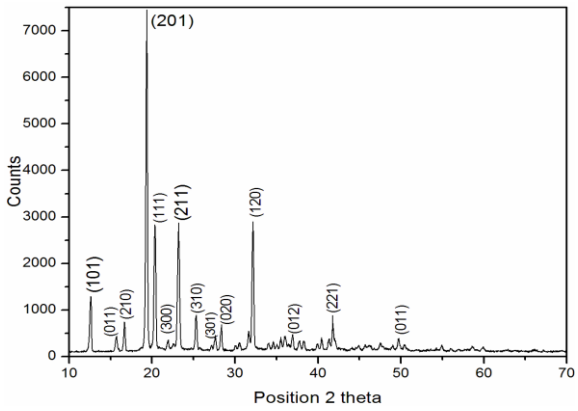

Figure 2: P- XRD pattern of GuBzt single crystals

3. RESULTS AND DISCUSSION

3.1 X- Ray diffraction analysis

Guanidine benzoate single crystals have the good crystalline nature, because of the presence of six potential donor sites for hydrogen – bonding interactions. The GuBzt single crystals belong to the orthorhombic structure and having *Pnma* space group. The cell parameter values are a = 15.7347 Å, b = 8.1216 Å, c = 7.8885 Å,

Volume = 954.1Å^3. These are similar to the reported values [8]. The powder X-ray diffraction pattern of GuBzt single crystals is shown in Fig. 2. The well- defined peaks at specific 2θ values show high crystallinity of the grown crystals. All the reflections of powder XRD patterns of are indexed using the TREOR software package.

3.2 Vibrational Studies

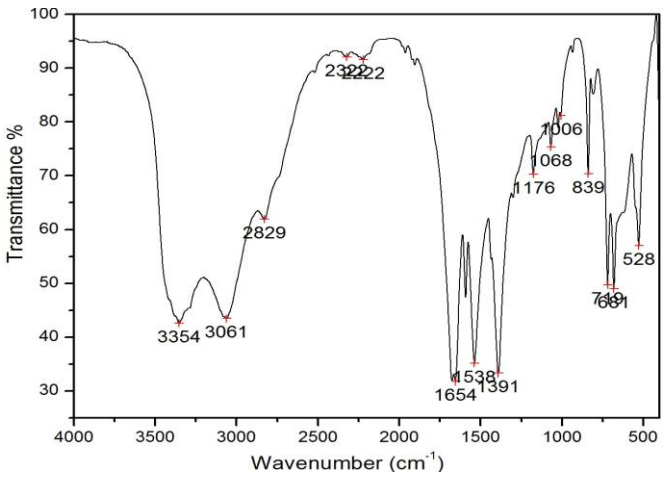

Figure 3: FTIR spectra of GuBzt single crystals

GuBzt single crystals are taken into the ftir analysis to know about the presence of functional groups. GuBzt single crystals samples are broken with a glass mortar and pestle to obtain powdered samples. This is done to obtain uniform particle sizes within the samples. These samples exist as white crystalline forms. The absorption due to various functional groups is shown in Fig. 3. The presence of Guanidine is evident from the FTIR spectrum that the symmetric stretching vibration of N H grouping is present at 3354 cm^{-1}. The peak observed at 3061cm^{-1}is attributed to C N symmetric stretching. The band at 1538 cm^{-1}is associated with C N vibration. The N H wagging frequency is assigned to the peaks at 749 cm^{-1}.The presence of unprotected C O group gives its stretching frequency around 1654 cm^{-1}and C O at 1391 cm^{-1}. This confirms the presence of free carboxylate anion wherein the negative charge is localized on the oxygen atoms in carboxylate anion [3]. The peak at 2829 cm^{-1}for C H stretching and the peak appeared at 1176 cm^{-1}for C H deformation mode confirmed the presence of benzoate. The FTIR spectrum confirms the presence of Guanidine benzoate compound [C $(NH_2)_3$]3C_6H_5COO by the above vibration modes.

3.3 Optical Properties

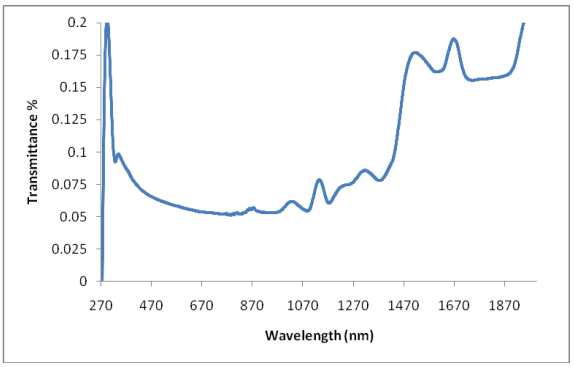

Figure 4: Transmittance spectrum of GuBzt single crystals

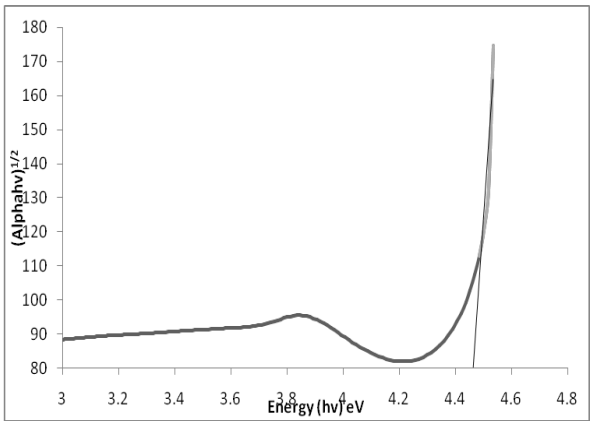

Figure 5: Indirect band gap spectrum of GuBzt single crystals

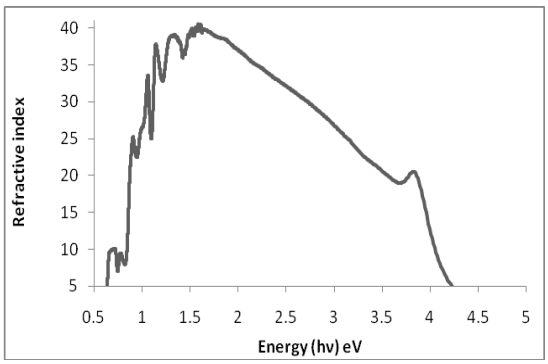

Figure 6: Photon energy Vs Refractive index

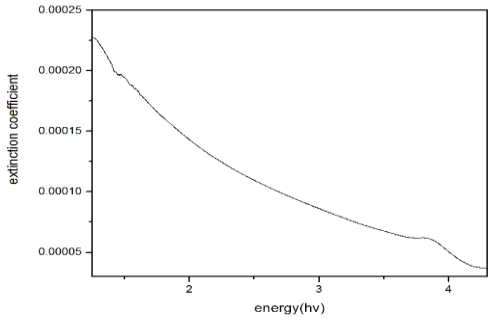

Figure 7: Photon energy with respect to extinction coefficient

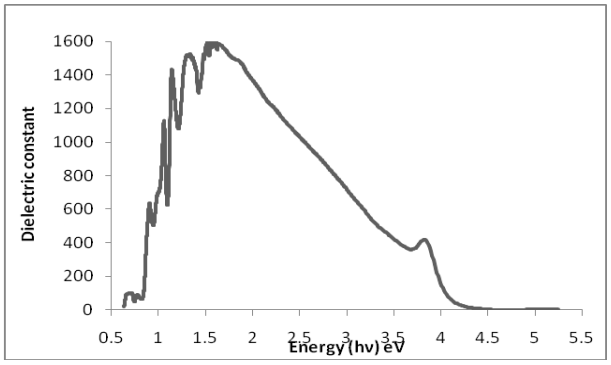

Figure 8: Real part of dielectric constant Vs energy

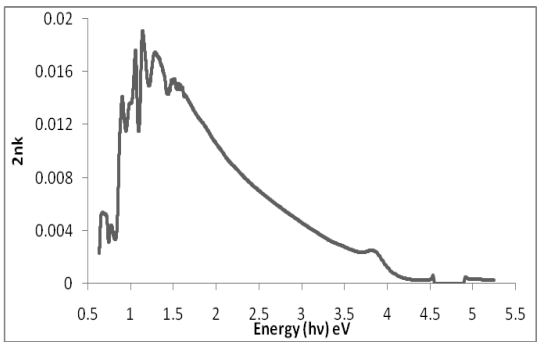

Figure 9: Imaginary part of dielectric constant Vs energy

Linear optical property of the grown single crystals is studied by UV visible spectrophotometer. Optical property gives transparency, band gap and dielectric constant of the title compound. The transmittance spectrum of Guanidine Benzoate is shown in fig.4. The cutoff frequency is observed in the visible region 296 nm. Transmittance observes in the entire visible region. The title compound is transparent in nature and its transmittance graph expressed the nature.

This behavior is applicable in optoelectronic field. GuBzt single crystals have the indirect band gap value of 4.46 eV depicted in Fig.5. Band gap energy of Guanidine hydrogen maleate single crystals is found to be 4.4 eV and the band gap energy of Guanidine aluminium sulphate crystals is found to be 5.44eV [4, 9]. So the GuBzt single crystal value is comparable to the above reported values. Band gap value measured by the relation as shown in equation (1),

$$E = 2.303\frac{log\,{}^{1}/_{T}}{t} \quad \text{---------- (1)}$$

E_g is the Band gap energy, T is the Transmittance, t is the thickness of the crystal.

Refractive index of the GuBzt single crystals is obtained using the following formula (2),

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1+R)^2} - K^2} \quad \text{---------- (2)}$$

Where, n= refractive index, R- reflectance of the as grown GuBzt single crystals. Refractive index Vs energy graph is shown in Fig.6. Refractive index value increases upto 2eV and then decreases up to 4eV.

$$k = \frac{\propto \lambda}{4\pi} \quad \text{---------- (3)}$$

Relation between absorption coefficient and extinction coefficient is described from the formula. Fig.7. shows the photon energy Vs extinction coefficient graph. Extinction coefficient of the title compound is decreases with respect to the increase in photon energy. Decrease in extinction indicates that there is a great transmittance, which is suitable for NLO applications.

The real and imaginary part of the dielectric constant Vs Energy spectrum depicted in Fig. 8 and 9 respectively.Relation between real part and imaginary part of dielectric constant can be written as,

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \quad \text{---------- (4)}$$

Where, $\varepsilon_1 = n^2 - k^2$; $\varepsilon_2 = 2nk$; ε_1 – real dielectric constant, ε_2 – imaginary dielectric constant, n- refractive index, k- extinction coefficient.

The wide band gap nature indicates the dielectric behavior of the title compound [10]. The real part of the dielectric constant increases with the increasing of energy. In real part GuBzt single crystals reaches approximate 1.6 eV and then it decreases with the energy in general. However, the imaginary part of the dielectric constant increases with the increasing of energy in the range of 0.5 to 1.8 eV and decreases with the energy after 1.8 eV in general. The dielectric behavior of the GuBzt single crystals indicates that the possibility of increasing the extinction and the electronic transfers through the material from valence band to the conduction band [11]. It is also obvious that there are three peaks predominate in the dielectric spectrum.

4. CONCLUSION

GuBzt single crystals have been grown by slow evaporation technique. The bright, colorless, transparent crystals are of size 15 x 10 x 8 mm^3 are harvested after 20 days. XRD results of GuBzt single crystals shows that the orthorhombic structure. Powder XRD results reveals that the title compound contains good crystalline nature. From UV visible spectral studies, the cut off wavelength of the GuBzt single crystals is around 296 nm. FTIR spectrum confirms that the functional groups of the title compound.

ACKNOWLEDGEMENT

The authors are thankful to the DST for the financial support to this work. We acknowledge Saif, Cochin for providing Uv - vis characterization.

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