



Scholars Research Library

Archives of Applied Science Research, 2010, 2 (4): 119-127

(<http://scholarsresearchlibrary.com/archive.html>)



ISSN 0975-508X

CODEN (USA) AASRC9

Dielectric characteristion of Benzoyl Glycine crystals

S. Suresh^{*1}, A. Ramanand¹, P. Mani² and K. Anand³

¹Department of Physics, Loyola College, Chennai, India

²Department of Physics, Hindustan University, Padur, India

³Department of Physics, Sri Manakula Vinayagar Engineering College, Pondicherry, India

ABSTRACT

The variation of dielectric constant (ϵ' and ϵ''), the dielectric loss ($\tan \delta$), and the conductivity (σ_{ac}) of benzoyl glycine at different temperatures (35°C - 135°C) in the frequency range (50 Hz–5 MHz) of the applied alternating current field is analyzed. The dependence of $\tan \delta$, ϵ'' and σ_{ac} on temperature and frequency of the applied field (50 Hz–5 MHz) is established. The empirical equations obtained fit very well with the experimental data. These equations are suggestive of functional relationship between the dielectric parameters ϵ' , $\tan \delta$ and σ_{ac} and the temperature and frequency of the applied field.

Key words: Solution growth, X-ray diffraction, dielectric constant.

INTRODUCTION

New molecular organic compounds with one or more aromatic system in conjugated positions leading to highly efficient optical non-linearity have been actively studied for the past two decades [1]. The organic non linear optical materials play an important role in second harmonic generation, frequency mixing, electro-optic modulation, optical parametric oscillation and optical bi-stability [2]. Recently, an extremely large number of organic compounds with non-localized π -electron systems and a large dipole moment have been synthesized to realize the nonlinear susceptibility compared to the inorganic optical materials [3]. The first observation of SHG in an organic material was reported in benzopyrene by Rentzepis and Pao [4]. Two years later Orlov [5] reported SHG from hippuric acid. Hippuric acid also called N—Benzoyl glycine, is a colorless NLO crystal with chemical formula $\text{C}_6\text{H}_5\text{CONHCH}_2\text{-COOH}$ [6–7]. It crystallizes in orthorhombic structure with space group $\text{P}2_12_12_1$ and lattice parameters $a=8.874\text{\AA}$, $b=10.577\text{\AA}$ and $c=9.117\text{\AA}$ [8]. Growth of Benzoyl chloride by double diffusion method in silica gel was reported earlier. [9, 10]. To enable a material to be potentially useful for NLO applications, the material should be in bulk single crystal form. Hence bulk single crystals of benzoyl glycine

were grown by slow evaporation solution growth technique using N, N-dimethyl formamide as a solvent. The grown crystals were characterized by single crystal XRD analysis, dielectric and conductivity studies. The results are discussed in detail.

MATERIALS AND MTHODS

The starting material was synthesized according to equation [1] by stoichiometric incorporation of Glycine and Benzoyl chloride which were taken in the appropriate 1:1 ratio .To this 10 % calculated amount of NaOH was added and a saturated solution was prepared. The purity of the synthesized salt was further recrystallized using N, N-dimethyl formamide as the solvent. Single crystals of Benzoyl glycine were grown by slow and controlled evaporation of the solvent using a constant temperature bath. The supersaturated solution was kept in a constant temperature bath at 30°C. Crystals obtained by spontaneous nucleation were used as seed crystals. The lattice parameters of the seed crystals were confirmed by single crystal x-ray analysis. These values match well with the reported values. [11].The grown crystal shown in Fig.1.

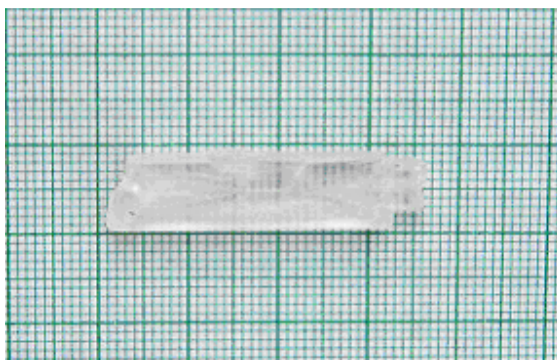
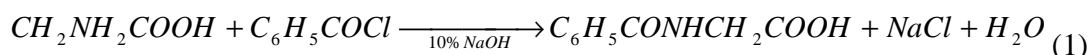


Fig. 1. BG grown crystal

The Dielectric Constant

The dielectric constant is calculated using the formula

$$\epsilon' = Ct / \epsilon_0 A \quad (2)$$

Where C is the capacitance (F), t the thickness (m), A the area (m^2), ϵ_0 and the absolute permittivity in the free space having a value of $8.854 \times 10^{-12} \text{ Fm}^{-1}$. The imaginary dielectric constant (ϵ'') of the material is calculated using the relation

$$\epsilon'' = \epsilon' \tan \delta \quad (3)$$

Where $\tan \delta$ is the dielectric loss measured directly from the impedance analyzer. The alternating current (ac) conductivity σ_{ac} is calculated using the relation

$$\sigma_{ac} = 2\pi f \epsilon_0 \epsilon' \tan \delta \quad (4)$$

Where f is the frequency of the applied ac field (Hz). The activation energy of the crystal is calculated from an Arrhenius plot of $\ln \sigma$ using the relation [12]

$$\sigma = \sigma_0 \exp [-E_a/kT] \quad (5)$$

Where σ is the conductivity at temperature T , E_a the activation Energy for the electrical process and k the Boltzmann's constant.

RESULTS AND DISCUSSION

Dependence of Dielectric constant and Dielectric loss on frequency

The dependence of the dielectric constant (ϵ'), imaginary dielectric constant (ϵ''), and dielectric loss ($\tan \delta$) on frequency of the applied ac field was studied in the temperature range of 35⁰C–135⁰C and frequency range of 50 Hz–5 MHz. The data so obtained are recorded in Tables 1 and 2. The variation of the dielectric constant with frequency of the applied ac field is shown in Fig. 2. The behavior of the material could be described with respect to frequency intervals, first in the lower frequency range 50Hz–1 kHz and second in the higher frequency range 1 kHz–5 MHz. In the lower frequency range (50–1 kHz), the following points may be noted:

(i) At room temperature (35⁰C), the value of ϵ' is very small, of the order of 487.59, showing hardly any dependence on frequency. At 85⁰ C, the dielectric constant rises to a value of 578.66 at 50 Hz. It however, decreases as the frequency increases to 1 kHz, after which it shows a little dependence on frequency. At 135⁰C, ϵ' is raised to 611.56 at 50 Hz which starts decreasing with frequency. Particularly after 1 kHz it attains saturation.

(ii) In the higher frequency range (1 kHz–5 MHz), the value of the dielectric constant almost attains saturation at all the measured temperatures. From the above discussion it is clear that the dielectric constant of the material is strongly dependent on both temperature and frequency, provided the frequency of the applied ac field is in the lower frequency range of 50Hz-1 KHz. The dielectric constant decreases with frequency and achieves a maximum value of 611.56 at 50Hz, the rate of decrease being maximum at 85⁰ C which is the transition temperature.

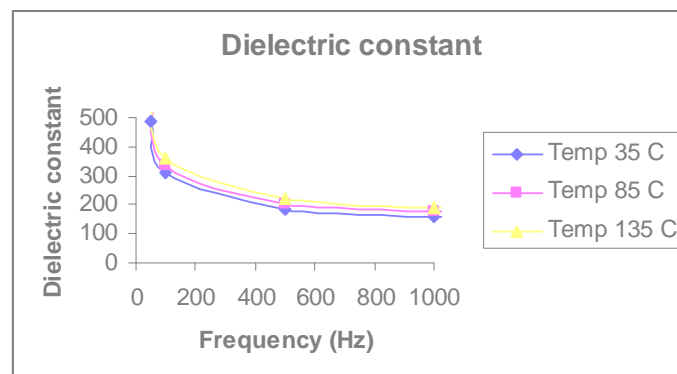


Figure 2. Variation of dielectric constant with frequency of the applied ac field

Table 1: Data on experimental and empirically calculated dielectric constant values (ϵ' and ϵ'') of benzoyl glycine crystal at various temperatures and frequencies

f (Hz)	35°C	85°C	135°C
50	484.3	575.62	610.50
100	310.62	334.80	358.48
500	186.30	202.25	220.94
1000	158.43	174.90	186.92
5000	110.32	127.86	142.85
10000	102.30	117.01	123.08
50000	92.29	107.03	114.60
100000	89.64	101.02	111.12
500000	86.05	94.11	104.01
1000000	82.02	89.20	95.02
5000000	77.80	84.31	91.12

Table 2: Data on experimental (Ex) and empirically calculated (Th) dielectric loss ($\tan \delta$) and imaginary dielectric constant values (ϵ' and ϵ'') benzoyl glycine crystal at various temperatures and frequencies*Temperature=35⁰ C*

f (Hz)	$\tan \delta$ (Ex)	ϵ'	ϵ''	$\tan \delta$ (Th)
50	4.838	484.3	2343.04	4.83
100	3.398	310.62	1055.48	3.40
500	2.566	186.30	478.04	2.57
1000	1.580	158.43	250.31	1.58
5000	1.226	110.32	135.25	1.23
10000	0.878	102.30	89.81	0.88
50000	0.512	92.29	47.25	0.51
100000	0.265	89.64	23.75	0.27
500000	0.172	86.05	14.80	0.17
1000000	0.092	82.02	7.54	0.09
5000000	0.051	77.80	3.96	0.05

Temperature=85⁰ C

f (Hz)	$\tan \delta$ (Ex)	ϵ'	E''	$\tan \delta$ (Th)
50	5.621	575.62	3235.56	5.62
100	3.692	334.80	1236.08	3.70
500	2.541	202.25	513.91	2.54
1000	1.657	174.90	289.80	1.66
5000	1.234	127.86	157.77	1.23
10000	0.881	117.01	103.08	0.88
50000	0.581	107.03	62.18	0.58
100000	0.304	101.02	30.71	0.30
500000	0.182	94.11	17.12	0.18
1000000	0.103	89.20	9.18	0.10
5000000	0.052	84.31	4.38	0.05

Temperature=135⁰ C

f (Hz)	tan δ (Ex)	ε'	E''	tan δ(Th)
50	6.492	610.50	3963.36	6.49
100	4.132	358.48	1481.23	4.13
500	2.622	220.94	579.30	2.62
1000	2.123	186.92	396.83	2.12
5000	1.532	142.85	218.84	1.53
10000	0.893	123.08	109.91	0.89
50000	0.596	114.60	68.30	0.59
100000	0.337	111.12	3.744	0.34
500000	0.192	104.01	19.96	0.19
1000000	0.113	95.02	10.73	0.11
5000000	0.067	91.12	6.10	0.06

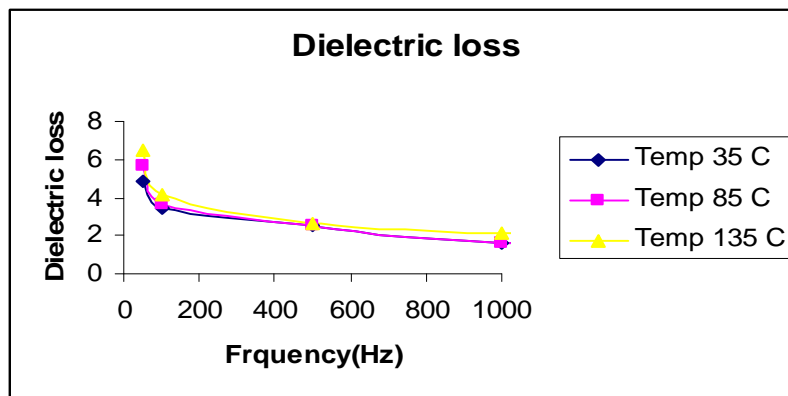


Figure.3. Dependence of dielectric loss on frequency (50 Hz- 5 MHz) of the applied field at different temperatures (35⁰ C – 135⁰ C)

Fig 3 shows the dependence of the dielectric loss on frequency in the range 50Hz-5MHz. It is interesting to find that the dielectric loss decreases with frequency at all temperatures ranging from 35⁰C-135⁰C. The maximum value of dielectric loss is 6.485 at a frequency of 50 Hz.

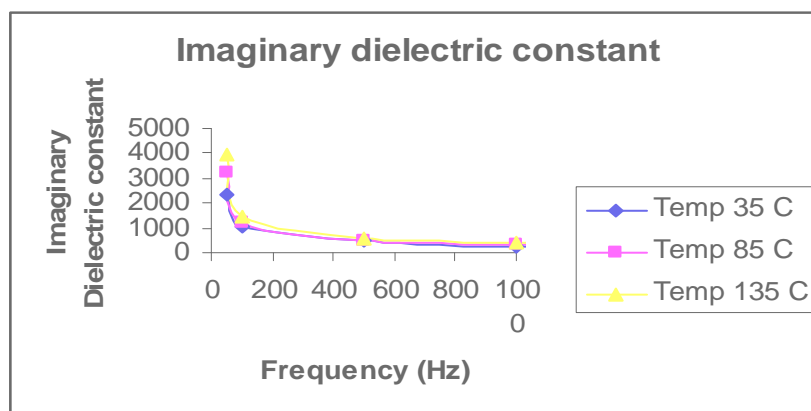


Figure.4. Variation of imaginary dielectric constant ε'' with frequency at different temperatures (35⁰C- 135⁰C)

Fig 4 shows the variation of imaginary dielectric constant (ϵ'') with frequency at different temperatures ranging from 35⁰C-135⁰C. The value of ϵ decreases in the frequency range 50Hz-5MHz. This behavior is true at all the temperatures ranging from 35⁰ C -135⁰ C.

D.C.Conductivity

The study of electrical conductivity in crystalline solid helps to understand the nature of defects, carrier conduction, Fermi level, activation energy. Conductivity and diffusion in ionic crystalline solids are mainly due to the presence of point defects in the lattice. If the conductivity is due to different types of mobile charges then the electrical conductivity σ is given by

$$\sigma = \sum_k n_k q_k e \mu_k \quad (8)$$

Where summation is taken over all the charged species k, n indicates the number of mobile charges of the type k having net charge $q_k e$ and μ_k represents electrical mobility. For a charged particle, μ and D are related through Nernst Einstein equation as

$$\frac{\mu}{D} = \frac{qe}{K_B T} \quad (9)$$

$$\frac{\sigma}{D} = \frac{n(qe)^2}{K_B T} \quad (10)$$

$$\sigma = \frac{e^2}{6K_B T} \sum_k n_k q_k^2 Z_k S_k^2 \quad (11)$$

Where z denotes jump frequency and s represents one jump distance.

Defect free transparent crystals of appreciable size were selected and used for electrical conductivity measurements. The extended portions of the crystals were removed completely and the opposite faces were well polished and coated with good quality graphite to obtain ohmic contact. The D.C. conductivity measurements were carried out along the c-axis using the conventional two probe technique at various temperatures ranging from 40 °C - 140 °C. The dimensions of the crystal were measured using traveling microscope.

The conductivity (σ) of the crystal was calculated using the relation

$$\sigma = \frac{t}{RA} \quad (12)$$

Where, R is the measured resistance, d is the thickness of the sample crystal and A is the area of the face of the crystal in contact with the electrode. Plots between $\ln \sigma_T$ and $1000/T$ were found to be very nearly linear. So the conductivity values can be fitted to the equation

$$\sigma_T = \sigma_0 \exp(-E/kT) \quad (13)$$

Where, E is the activation energy, k the Boltzmann constant, T the absolute temperature and σ_0 a parameter depending on the material. The value of activation energy E for pure Benzoyl Glycine crystal was calculated as 0.1068 eV. The electrical conductivity increases with increase in temperature. The defect concentration also increases exponentially with temperature and consequently the electrical conduction also increases.

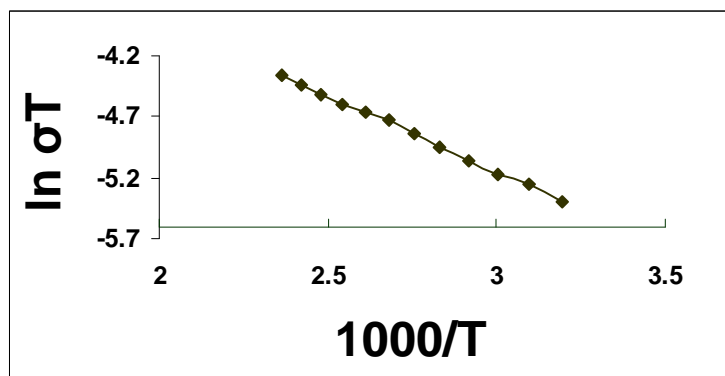


Figure. 5. Variation of $\ln \sigma_T$ with $1000/T$ for Benzoyl Glycine crystal

A.C. Conductivity

A.C. conductivity is one of the studies done on solids in order to characterize the bulk resistance of the crystalline sample. The measurement of electrical conductivity using blocking electrode is a powerful method for determining both ionic and electronic conductivity of the materials. By proper choice of electrodes, either ionic or electronic transport is suppressed in a mixed conductor and the contribution to the conductivity by the non suppressed transport can be determined. The current through an ionic conducting material in a constant DC field decreases with time, because in dc measurement a space charge region is often setup as a result of a partial blocking of the ionic current by the electrodes. Therefore, the electrical characteristics of ionic conducting materials are studied by ac technique to avoid the necessity of developing the non blocking ion conducting electrodes for dc measurements.

The electrical conductivity measurements are carried out with the same setup as that for dielectric measurement. The opposite faces of the specimen are coated with a thin layer of silver paint. This ensures good contact with the electrodes. The sample is placed over a copper base and a copper rod with spring arrangement is placed at the top of the specimen. The bottom plate and the upper copper rod serve as the electrodes. Ceramic beads covering the copper wire prevent it from touching the stainless steel tube to maintain thermal and electrical insulation. This setup is kept inside a muffle furnace. The temperature of the crystal is varied by changing the furnace current with the help of variable autotransformer, energized by a stabilized A.C. power supply. Measurements are taken after a period of one hour at each setting of the furnace current to ensure that a constant temperature is reached. An iron constant thermocouple is placed very close to the crystal to measure the temperature with an accuracy of $\pm 0.1^\circ\text{C}$.

The ac conductivity $\sigma(\omega)$ of the material is given by:

$$\sigma(\omega) = \omega \epsilon_0 \epsilon \tan \delta \quad (14)$$

where $\omega = 2\pi f$ and f is the frequency of the applied alternating field, ϵ_0 the dielectric constant of free space, ϵ' the real part of dielectric constant, $\tan \delta$ is the loss factor. The ac conductivity of the sample in the present study showed the frequency dependence, σ_{ac} increases with increase in frequency. It has been reported that dispersion in the conductivity is the direct evidence for the hopping of charge carriers around the lattice imperfection. The dispersion in conductivity will occur when the carriers are not free to move through the sample. Fig.6 shows variation of $\log \sigma_{ac}$ vs. frequency at different temperatures.

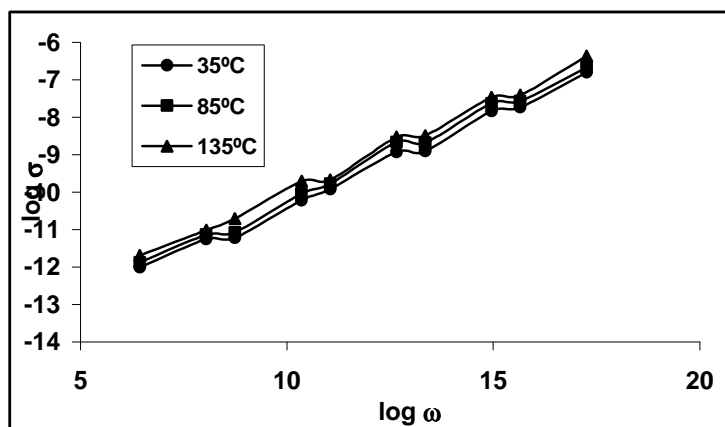


Figure.6.variation of $\log \sigma_{ac}$ vs. frequency with different temperature

CONCLUSION

The dielectric constants (ϵ' and ϵ''), dielectric loss ($\tan \delta$) and conductivity (σ_{ac}) of benzoyl glycine crystals are strongly dependent on temperature and frequency of the applied ac field, the variation depends on the ranges of temperature and frequency. The dielectric constant ϵ' is dependent on both the temperature as well as frequency, provided the frequency of the applied field is in lower frequency range of 50 Hz to 1 KHz, the dielectric constant decreases with increasing frequency. In the higher frequency range 1KHz-5MHz, this dependence almost ceases to exist. The rate of variation of imaginary dielectric constant (ϵ'') with temperature is strongly dependent on temperature and frequency of the applied field. The conductivity remains almost the same in the temperature range of 35°C-135°C corresponding to a frequency of 5MHz. The conductivity increases with temperature till 135°C.

REFERENCES

- [1] Corento, A.; Jerphagon, J.; and Perigand A.; *J. Chem. Phys.*, (1977), 66, 3806.
- [2] Rentzepis, P.M.; and Pao, Y.H. *Appl. Phys. Lett.* (1964), 6, 156.
- [3] Orlov, R. Yu.; *Soviet. Phys.* (1966) 11, 410.
- [4] Ringertz, H.; *Acta Cryst.* (1971), B 27, 285.
- [5] Nagaraja, H.S.; Upadhyaya, V.; Mohan Rao, P.; Sreeramana Aithal, P.; and Bhat, A.P.; *J. Cryst. Growth.* (1998) 193, 674.
- [6] Vijayan, N.; Ramesh Babu, R.; Gopalakrishnan, R.; Ramasamy, P.; Ichimura, and Palanichamy, M.; *J. Cryst. Growth.* (2005), 273, 564.

- [7] Selvaraju, K.; Valluvan,R.; and Kumararaman,S.; *Mat. Lett.* (2006) ,60, 1549.
- [8] Narayan Bhat,M.; and Dharmaprakash,S.M.; *J. Cryst. Growth* ,(2002),243, 1549.
- [9] Ramachandran ,E.; and Natarajan,S.; *Cryst. Res. Technol.* (2002),37, 1274.
- [10] Ramachandran,E.; and Natarajan,S.; *Cryst. Res. Technol.* (2005),40, 765.
- [11] Ringertz,H.. *Acta Cryst.* (1971),B27, 285-291.
- [12] Verwey,E.J.W.and Heilman, *J.Chem.Phys.* (1947),15 ,174.