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Dielectric Investigation on Single Crystals of Morpholium Cadmium Aceto-perchlorate

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Abstract

Metal-organic crystal of morpholium cadmium aceto-perchlorate (MCAP) is synthesized from morpholine, perchloric acid and cadmium acetate. The crystals are grown by slow evaporation solution growth technique at room temperature. The dielectric measurements for the crystals are carried out in the range 50 Hz to 5 MHz for three different temperatures 40ºC, 80ºC and 120ºC. The dielectric constant, the loss tangent, DC conductivity, AC conductivity and activation energy are calculated. The complex impedance plot of the crystal has been described using a Cole-Cole relaxation. The ionic conduction and relaxation mechanism in the crystal is examined. Fundamental data such as valance electron, Plasmon energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal are determined. Based on dielectric studies, MCAP crystals have been identified to have superior optical quality suggesting the possibility of using the prepared compound for high frequency applications.

Key words: Morpholium cadmium aceto-perchlorate, Slow evaporation, Dielectric constant, Activation energy, Cole-Cole relaxation

1. Introduction

The growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic research and applied research. Among nonlinear optical (NLO) crystals, metal-organic materials occupy an elite position. These crystals are gaining importance in the field of solid state electronics. Morpholine, an organic chemical compound, colourless, oily, volatile in nature is a good nucleophile since the six-member ring exposes the lone electron pair on nitrogen [1]. Morpholine and its derivatives are known to form a

series of molecular complexes such as morpholine, hydrohalides, phenols and phosphoric acid [2-5]. Molecular ionic crystals like perchlorate with morpholine (of ratio 1:1) show NLO physical properties unique to the crystal structure. The structure and characterization of NLO crystal morpholium perchlorate has been reported by Arunkumar and Ramasamy [6]. Transition metal ions when included in crystals are found to have interesting spectroscopic properties making them suitable for laser and optical fiber applications. Metals with d^{10} configuration like zinc, cadmium and mercury readily combine with morpholine resulting in stable compounds with high optical nonlineatiry and good physiochemical behaviour. So an attempt is made to grow single crystal of morpholium cadmium aceto-perchlorate (MCAP). The influence of cadmium on the electrical nature of the crystal is investigated.

2. Experimental Details

The title material morpholium cadmium aceto-perchlorate (MCAP) is synthesized by the chemical reaction of morpholine with perchloric acid, taken in the ratio 1:1 by dissolving in the mixture of (1:1) ethanol and deionized water. Stoichiometrically calculated amounts of the materials are transferred into a beaker and dissolved in ethanol and deionized water which is stirred well with the help of a magnetic stirrer to make a homogeneous solution of the material at room temperature for a proper chemical reaction. Then cadmium acetate is added to the solution. The obtained MCAP solution is allowed to evaporate at room temperature. The well-defined single crystals of MCAP are harvested from mother solution after a growth period of 2 weeks. The grown single crystals of MCAP are shown in Fig 1.

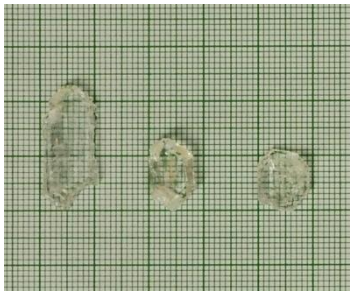

Figure 1 As grown single crystals of MCAP.

3. Dielectric Studies

The study of the dielectric constant of a material gives an outline about the nature of atoms, ions and their bonding in the material [7]. Dielectric properties are related with electric field distribution in solid materials. The electro-optical property of the crystal can be understood by the measurement of dielectric property. From the analysis of the dielectric constant and dielectric loss as a function of frequency and temperature, the different polarization mechanism in solids can be understood.

The dielectric constant is calculated using the formula

$$\varepsilon' = \frac{Ct}{A\varepsilon_0} \quad (1)$$

where C is capacitance, t is thickness of the sample, ε_0 is the permittivity of free space (8.85×10^{-12} F/m) and A is the area of the sample.

A plot between frequency and dielectric constant for three different temperatures 40°C, 80°C and 120°C is shown in Fig 2. It is seen that at low frequencies the value of dielectric constant is high and as the frequency increases the dielectric constant attains a low value. The value of high dielectric constant at low frequency is due to space charge and ionic polarization [8]. The value of dielectric constant increases with increase in space charge polarization due to a large concentration of defects at higher temperatures. The dipolar polarization, which is present in the lower frequency region, is very important for applications in capacitive and insulating properties of crystals. It is understood that the contribution of all types of polarization will be more at lower frequencies. The low value of dielectric constant at higher frequencies are due to factors such as voids, grain boundaries, purity and other defects too, which are present in the sample. The electronic and ionic polarizations always exist at higher frequencies. The considerable low value of dielectric constants observed for the grown crystals is important for extending the material applications towards photonic, electro-optic and NLO devices.

Dielectric or tangent loss (tan δ) is the wastage of energy. For a material to be a potential candidate for NLO applications, the dissipation factor (tan δ) must be kept as low as possible. Dielectric loss is mainly of four kinds: (1) distortional, (2) dipolar, (3) interfacial and (4) conduction loss. Among these, two important losses are distortional and interfacial losses. Distortional loss is the effect of electronic and ionic polarization and interfacial loss originates from the polarized interface induced by the fillers.

A graph plotted between frequency and dielectric loss/dissipation factor (ε'') in Fig 3 shows that at low frequencies the value of dielectric loss is high and as the frequency increases the dielectric loss attains a low value. The low value of dielectric loss at high frequencies shows that the sample has enhanced optical quality with minimum defects. This parameter is of vital importance for NLO applications [9].

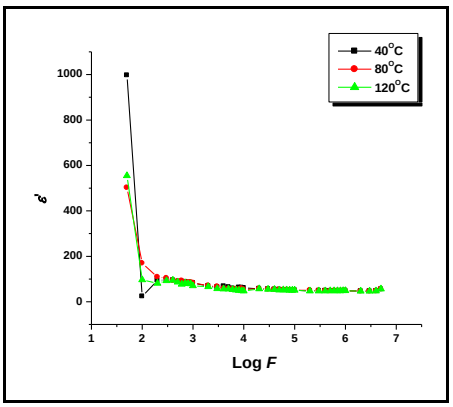

Figure 2 Variation of dielectric constant with frequency.

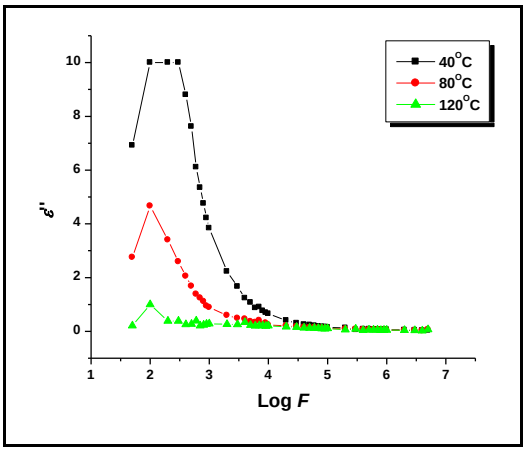

Figure 3 Variation of dielectric loss with frequency.

3.1 Determination of Penn Gap Energy

A simple isotropic model for the electronic spectra of (sp^3)-bonded crystals has been proposed by Penn. Using this model, Penn calculated the diagonal part of the microscopic dielectric tensor in Hartee approximation [10]. Using this model, the energy bands of Si and Ge have been found. A theoretical calculation shows that the high frequency dielectric constant explicitly dependant on the valence electron, Plasmon energy, an average energy gap referred to as the Penn gap and the Fermi energy. The molecular weight of the grown crystal MCAP is M = 187.58 g and the total number of valence electron is Z = 68. The density of the grown crystal is found to be ρ = 1.611 mg/m^3 and the dielectric constant at 5 MHz is ε_∞ = 54. The Penn gap is determined by fitting the dielectric constant with the Plasmon energy. The valence electron plasma energy ($\hbar\omega_P$) is calculated using the relation,

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \tag{2}$$

The Plasma energy in terms of Penn gap and the Fermi energy given by

$$E_P = \frac{\hbar\omega_P}{(\varepsilon_\infty - 1)^{1/2}} \tag{3}$$

$$E_F = 0.2948(\hbar\omega_P)^{4/3} \tag{4}$$

Then electronic polarizability α is

$$\alpha = \left[\frac{(\hbar\omega_P)^2 S_0}{(\hbar\omega_P)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3 \tag{5}$$

where, S_0 is a constant given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \tag{6}$$

The value of α obtained from equation (5) closely matches with that value obtained using Claussius-Mossotti relation:

$$\alpha = \frac{3}{4}\frac{M}{\pi N_a \rho}\left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right] \quad (7)$$

The results obtained are compiled in Table 1.

Table 1 Dielectric parameters of grown crstals

Parameters	Value
Plasma energy ($\hbar\omega_P$)	22.0061 eV
Penn gap (E_P)	3.02 eV
Fermi energy (E_F)	18.1777 eV
Electronic polarizability (Penn analysis) α_P	4.4467×10^{-23} cm^3
Electronic polarizability (Claussius-Mossotti relation) α_{CM}	4.3707×10^{-23} cm^3

4. DC and AC Conductivities

The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region and the energy needed to form the defect is much larger than the energy needed for its drift. Useful information regarding the mobility and generation as well as the movement of lattice defects in hydrogen bonded crystals can be obtained by studying the electrical conductivity of these crystals. The conductivity process is visualized as a series of consecutive and independent hops of ions over the barriers along the direction of an electric field. In many nonmetallic ionic conductors, DC or AC electrical conductivity is the result of diffusion of ions through the conductors. The value of conductivity strongly depends on frequency.

4.1 DC Conductivity

The DC conductivity can be calculated using the formula

$$\sigma_{dc} = \frac{t}{AR_b} \quad (8)$$

where t and A represents the thickness and area of the sample, respectively. Fig 4 shows the temperature dependence of DC conductivity of the material. The DC conductivity increases with rise in temperature, which implies that negative temperature coefficient of resistance (NCTR) behavior is exhibited by the material. This behavior can be explained by thermally activated transport processes, governed by an empirical Arrhenius relation [11,12]:

$$\sigma = \sigma_0 \exp\left(\frac{E_a}{kT}\right) \quad (9)$$

where k = Boltzmann constant (1.38066×10^{-23} J/K = 8.617385×10^{-5} eV/K), σ_0 = pre-exponential factor and E_a = activation energy. The plot of σ_{dc} versus $1000/T$ is shown in Fig 4. The activation energy (E_a) of the electrical process is calculated from the slope using the relation E_a = – slope × 1000 × k. The values of activation energy are tabulated in Table 2. From the table it is evident that the low value of activation energy establishes that the crystal contains less number of defects. Defect free crystals are generally used for device fabrication [13].

Table 2 Activation energy for different frequencies

F (Hz)	E_a (eV)
5000	$1.72348E^{-06}$
10000	$1.72348E^{-06}$
50000	$2.58522E^{-06}$
100000	$1.72348E^{-06}$
500000	$5.17043E^{-06}$
1000000	$5.17043E^{-06}$
5000000	$7.75565E^{-06}$

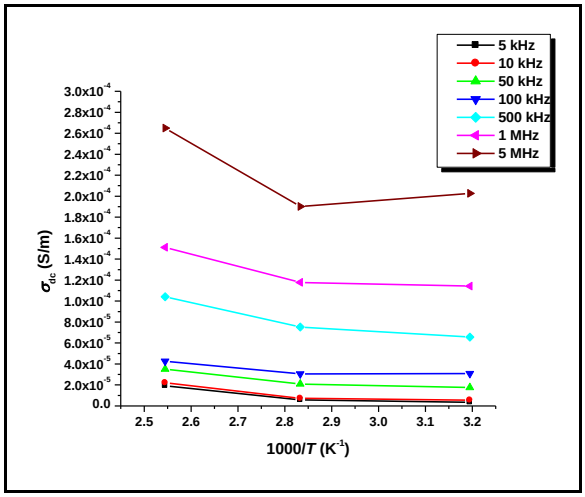

Figure 4 Variation of DC conductivity with temperature.

4.2 AC Conductivity

Study of AC electrical conductivity is normally carried out to get better understanding of the frequency dependence of electrical transport properties of the material. Using dielectric data the AC electrical conductivity (σ_{ac}) of the material is calculated with an empirical formula:

$$\sigma_{ac} = \omega\varepsilon_0\varepsilon' \tan\delta \qquad (10)$$

where ω is the angular frequency (=$2\pi f$), ε_0 is the permittivity of free space (8.85×10^{-12} F/m), ε' is the relative dielectric constant and tan δ is the loss tangent or dielectric loss. Fig 5 shows the angular frequency–temperature dependence of AC conductivity for MCAP. It is observed that the AC conductivity has low values at lower frequencies and it increases with increase in frequency. It obeys the empirical law $\sigma(\omega)$ α ω^n, where ω is the angular frequency and the value of n is frequency exponent. At low frequencies the AC conductivity can be assigned to the trapping of some carriers at defect sites in the crystal. The increase in AC conductivity could be due to the reduction in the space charge polarization and disordering of cations between neighboring sites [14].

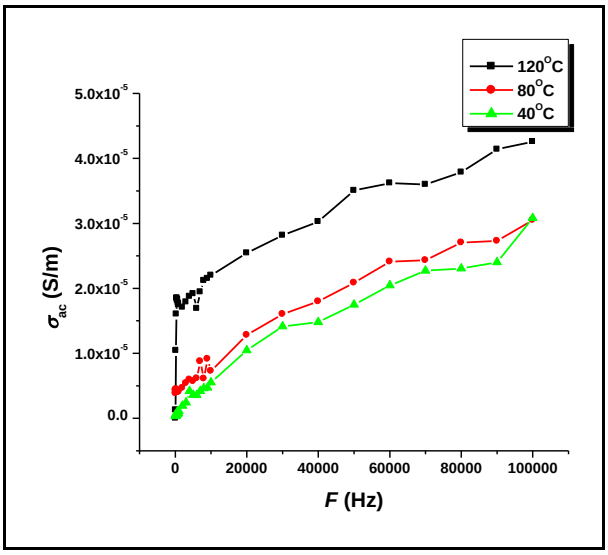

Figure 5 AC conductivity as a function of frequency at various temperatures.

5. Complex Impedance Analysis

Impedance spectroscopy is a powerful method for electrical characterization of various ion conducting solids. The vital property of impedance spectroscopy is its exclusive capability to distinguish the different steps in an ion conducting process including the detailed information about the surface and bulk properties. Using the values of capacitance (C_p) and conductance (G) the real and imaginary parts of the complex impedance is evaluated using the following standard relations [15,16]:

$$Z^* = Z' + jZ'' = \frac{1}{(G + j\omega C_p)}$$

$$Z' = \frac{G}{\left(G^2 + \omega^2 C_p^2\right)} \quad . \qquad (11)$$

$$Z'' = \frac{\omega G_p}{\left(G^2 + \omega^2 C_p^2\right)}$$

Figs 6-8 shows the variation of Z' and Z'' with frequency at different temperatures. The value of Z' decreases with the rise in both frequency and temperature. Therefore, the conducting property of the material increases with rise of temperature and frequency. The value of Z'' first increases with frequency and attains a maximum value (Z''_{max}) at a particular frequency known as relaxation frequency (f_r). The value of Z'' then decreases with rise of temperature which implies the presence of relaxation in the material. The relaxation process occurs due to the presence of immobile charges at lower temperatures, and due to defects and vacancies at higher temperatures [17].

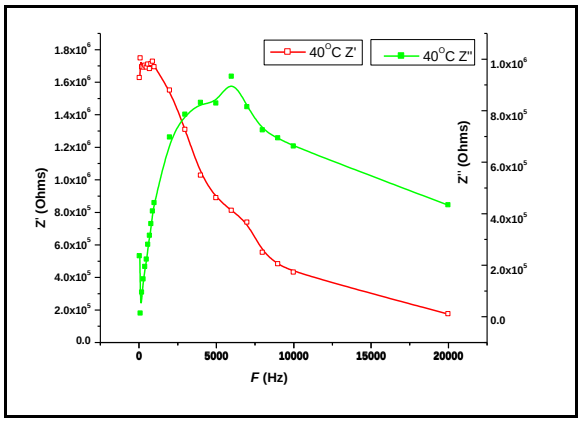

Figure 6 Variation of real and imaginary part of impedance with frequency at temperature 40ºC.

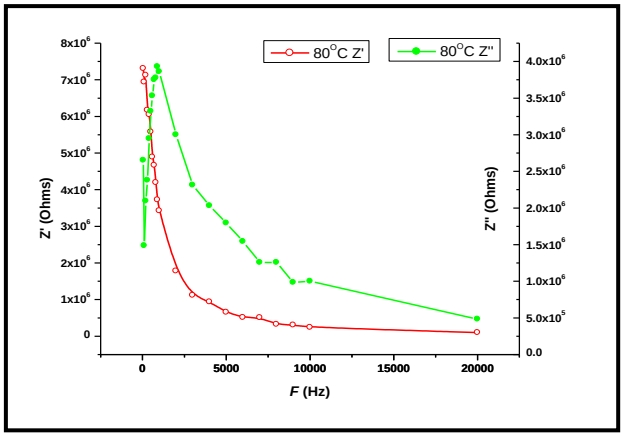

Figure 7 Variation of real and imaginary part of impedance with frequency at temperature 80ºC.

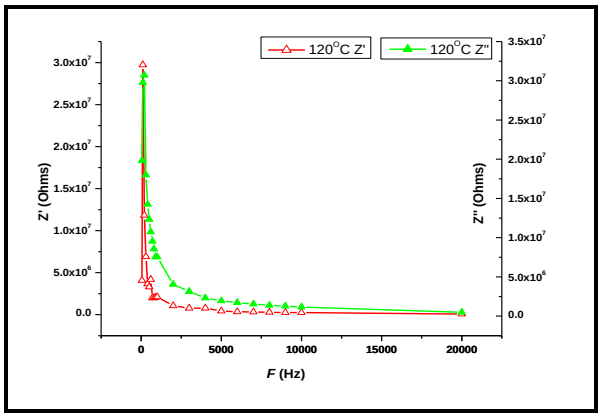

Figure 8 Variation of real and imaginary part of impedance with frequency at temperature 120ºC.

5.1 Cole-Cole Plot

Complex impedance plots at different temperatures in the range 40°C to 120°C of the sample are shown in Figs 9-11. At 120°C a steep rising of Z′ almost parallel to Z″ is observed. At temperatures 40°C and 80°C the curve bends toward real axis, that is, Z axis and takes the shape of a semicircle. The high frequency arcs at 40°C and 80°C pass through the origin. At all temperatures centre of the semicircle arc below the real axis, that is, depressed semicircles are observed. The center of the impedance semicircles lies below the real axis, which indicates that the impedance response is a Cole-Cole type relaxation [18,19].

Total impedance of a polycrystalline has contribution of grain, grain boundaries and sample/electrode interface. It is noticed that there are no separate semi-circular arcs for grains and grain boundaries probably implying that the total impedance of the crystal is only due to the bulk. Hence the single crystal of MCAP has no prominent defects. The resistance and capacitance values obtained from the impedance plot are given in Table 3.

Table 3 Determination of R (CR) values from Cole-Cole plot

Temperature (°C)	Bulk (g)		
	R_g (ohms)	F_g (hertz)	C_g (farad)
40	1.72×10^{6}	5000	1.830×10^{-11}
80	7.33×10^{6}	900	2.33×10^{-11}
120	2.699×10^{5}	200	2.675×10^{-11}

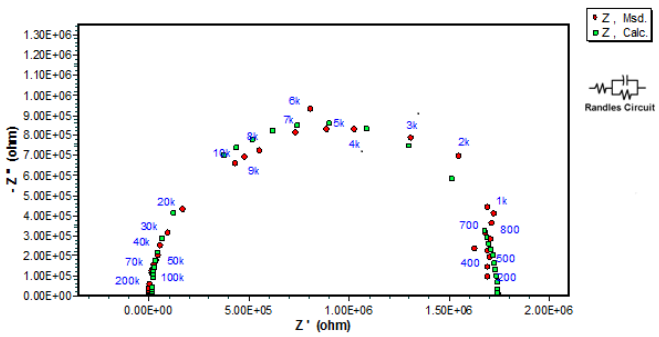

Figure 9 Complex impedance plot at temperature 40°C.

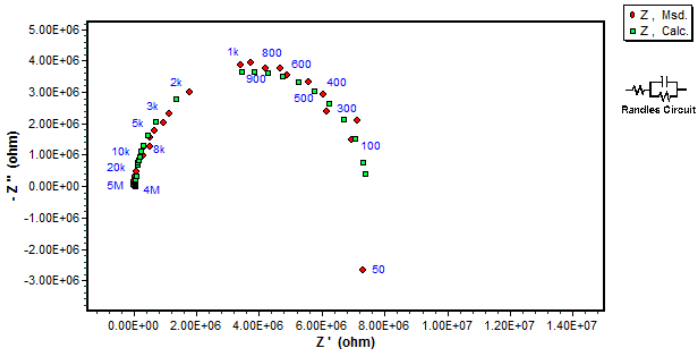

Figure 10 Complex impedance plot at temperature 80°C.

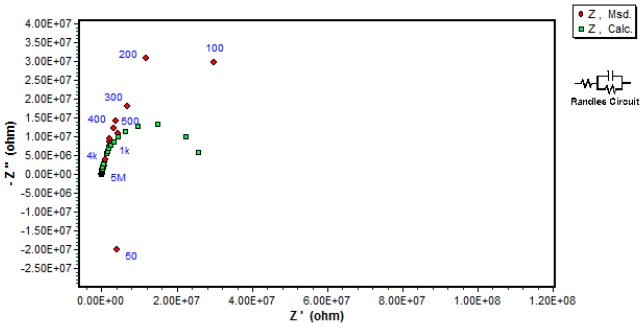

Figure 11 Complex impedance plot at temperature 120°C.

6. Conclusion

Metal-organic crystals are attracting attention because of their promising applications. A combination of cadmium (metal ion) along with morpholinium perchlorate (organic ligand) is successfully grown as single crystal of MCAP. In order to estimate the electrical nature of the grown crystal, dielectric constant and dielectric loss with frequency is recorded for different temperatures. Dielectric studies reveal that the crystal shows good optical quality. The absence of sharp peaks in dielectric profile reveals that the grown material does not undergo any decomposition in the accounted temperature range. The low loss tangent at high frequency is generally expected in the samples with good optical quality. The fundamental data such as valence electron, Plasmon energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal are calculated. In impedance spectroscopy, the Cole-Cole plot of the crystal is plotted for temperatures 40^{o}C, 80^{o}C and120^{o}C. The complex impedance plot consists of semi-circular arcs for all three temperatures. On increasing temperature the intercept of the semicircles (at the Z' axis) shifts towards lower side of Z', indicating the reduction of the bulk resistance (R_g). The DC and AC conductivities show decreasing impedance with frequency and temperature suggesting that the

conductivity increases which is a suitable behaviour. Therefore MCAP crystal could be an interesting candidate for high speed optoelectronic applications as interlayer dielectric and for high speed telecommunications as optical wave guide.

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