THE EFFECT OF TEMPERATURE AND FREQUENCY ON THE DIELECTRIC PROPERTIES OF 4-METHOXYTRIPHENYLMETHYLCHLORIDE

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In the present work, temperature and frequency dependent properties of 4-Methoxytriphenylmethylchloride have been studied. The temperature is found to be directly proportional to the capacitance. The variation in dielectric constant (ε) and tangent loss (tan δ) occurs due to the existence of both the internal field in the material and the external ac field. In the tan δ, the appearance of peaks indicates the presence of the relaxing dipoles. Electrical resistivity is inversely proportional to the temperature and it seems to follow the power law $A\omega^s$. The direct current (dc) conductivity is directly proportion to the temperature and it shows the high mobility with the increase of temperature. It may be due to free ions, free charges and polarons at high temperature.

1. Introduction

The physicists are fascinated to know about the microscopic processes like dielectric relaxation. The temperature and frequency based dielectric constant, dielectric loss are studied because these parameters are more sensitive and convenient for the study of an organic compound structure [1]. In the previous years, the dielectric properties of a numerous organic compounds have been investigated [2-7], but orientation of the molecules and the phenomena related to relaxation mechanism is not understood fully by the researchers. The relaxation behavior of 4-Methoxytriphenylmethylchloride is mostly structure morphology dependent. Tanaka et al. [8] have investigated the dielectric relaxation mechanism in organic compounds and polarization phenomenon is observed in the low frequency range. It may be due to the coexistence of all type of polarization like dipolar, ionic, interfacial and electronic. Dielectric material exhibits numerous type of polarization in different frequency range. Dispersion in the dielectric material is observed by the variation of the dielectric constant value and it is mostly related with the dielectric loss peaks. Frequency and temperature dependent dielectric properties are commonly used to reveal a lot of information regarding the physical and chemical properties of an organic material. Dielectric measurement is used to investigate the effect of frequency on the interaction of the molecules with in the structure of the organic material and it is also used to study the relaxation mechanism which is useful for the comprehension of phase transformation. The material with low dielectric constant less than 3.0 are mostly used as a interlayer dielectric and these are commonly used at large scale in the formation of integrated circuits. The two main required things for the best perform material are the thermally stable and low dielectric constant value. The stability of the material should be greater than 450˚C and dielectric constant value should be less than 3.0. In the past decades, remarkable efforts have been done to prepare a material which possesses such properties. Tremendous efforts have done to make new low dielectric films and materials. In order to assure

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the desired electrical properties and device reliability, low dielectric materials are appearing fruitful because of their mechanical, thermal and chemical properties. In the light of observation both the inorganic and organic materials are not up to the mark. Inorganic materials show the high value of dielectric while the organic one has low thermal stability. In this paper, we have studied the dielectric and electrical properties of an organic compound which has less value than 3.0 value of dielectric constant but its stability is still less than the demanding value of 450°C.

2. Experimental

The organic compound 4-Methoxytriphenylmethylchloride ($CH_3OC_6H_4C(C_6H_5)_2Cl$) having 97% purity of Sigma Aldrich was obtained. The X-ray diffraction (XRD) measurements were performed with the help of Bruker D8 modern diffracto-meter with Cu K_α (λ= 1.540598 Å) radiations in the 2θ range from 10° to 80° with a step of 0.025°. In order to measure the electrical properties, the material was grinded again with the help of mortar and pestle; the powder was pressed in to pellets (13 mm diameter and 3 mm thickness) under the pressure of (~60 KN) by using the Paul-Otto Weber Hydraulic press. Infrared reflectivity was measured by using the Fourier transform infrared (FTIR) spectrometer (Vertex 80v) at room temperature. The measurements in the range 400–7500 cm^{-1} were performed using KBR-DLa TGS beam splitter-detector combination, respectively with spectral resolution of 2 cm^{-1}. The UV-visible absorption spectra have been obtained using Perkin Elmer Lambda 950 UV/visible/NIR spectro-photometer in the range of wavelength 200–1000 nm. The dielectric measurements were taken with the help of Agilent 4287A with a frequency range of 1 MHz to 3 GHz. The dc resistivity was taken with the help of Quad Tech 7600 LCR Analyzer at different temperature by using two probe techniques.

3. Results and discussions

Fig.1 shows the XRD graphs for the 4-Methoxytriphenylmethylchloride at room temperature. The sharp peaks in the 2θ range from 10° to 50° indicates the crystalline nature of the present organic compound. XRD pattern indicates that the organic material is triclinic having unit cell parameters a = 7.565Å, α = 89.15º, b= 7.75Å, β = 78.42º, c = 16.865Å and γ = 86.66. From the XRD pattern, it can be observed that the material is crystalline having triclinic structure along with some amorphous traces as indicated by the lower angle peaks. The inter plane space is 3.43Å [9, 10]. Debye Scherrer formula can be used to calculate the crystallite size i.e

$$D = \frac{0.9\,\lambda}{\beta\,cos\theta} \qquad (1)$$

Where β the FWHM of strong intensive peak, λ is the wavelength of the X-ray, θ is the Bragg angle and D is the crystallite size. The average of the crystallite size is 30 nm.

This crystalline behavior indicates the presence of a typical structure of the 4-Methoxytriphenylmethylchloride that has been further confirmed by FTIR analysis. Fig. 2 demonstrate the infrared reflectivity of the 4-Methoxytriphenylmethylchloride in the frequency range 400–1600 cm^{-1} at room temperature.
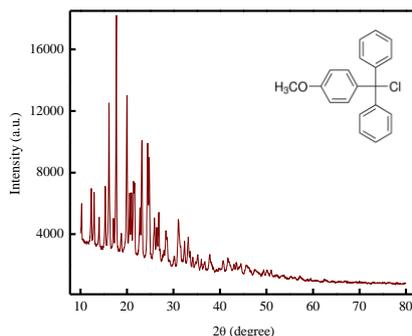
Fig. 1 X-Ray diffraction (XRD) of 4-Methoxytriphenylmethylchloride,
Inset is the structural formula of 4-Methoxytriphenylmethylchloride

The spectrum exhibits some sharp peaks that may be described to various modes of vibrations and confirms the existence of crystalline structure of the organic compound as already observed in XRD pattern. Moreover, the spectrum resembles that of a typical semiconductor. The major peaks that may corresponds to a group of vibrations are 596, 696, 761, 828, 996, 1158, 1235, and 1510 cm^{-1} as shown in Fig. 2. According to mode assignment, in the structure of 4-Methoxytriphenylmethylchloride, four types of vibrations may be observed. First, the Alkyl chloride vibrations (C-Cl) which are mostly seen in the range of 540-680 cm^{-1}and we have observed it clearly at 596 cm^{-1}(see Fig. 2). Second, aromatic bending vibrations are mostly observed in the range 690-900 cm^{-1} and we have observed a strong peak at 690 cm^{-1}. Another type is C-O vibrations are observed in 900-1300 cm^{-1} and we have observed the main peak in 1158 cm^{-1}. Finally, the bending vibration (1375-1450 cm^{-1}) of alkanes is observed at 1510 cm^{-1} [11,12].
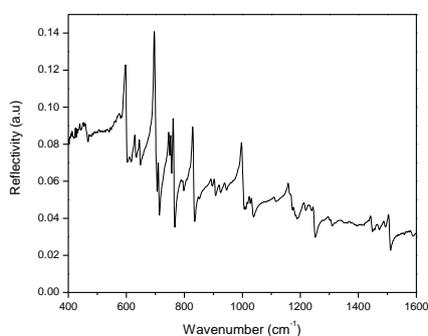

Fig. 2:Infrared reflectivity spectrum of 4-Methoxytriphenylmethylchloride.

The optical band gap of 4-Methoxytriphenylmethylchloride can be evaluated from the absorption spectrum using the Tauc relation

$$(\alpha h\nu) = C(h\nu - Eg)^{n} \tag{2}$$

where C is a constant,$\alpha$is molar extinction coefficient, Eg is the energy band gap and n depends on the type of transition. For n = 2, Eg in equation (2) is indirect band gap transition. The energy band gap was estimated from the linear intercept portion of the $(\alpha h\nu)^2$ versus hν plot as it is depicted in Fig.3. Two band gap values have been found 2.4 eV and 3.7 eV as indicated by the extrapolation of red line to the liner portion of graph (see Fig.3).The obtained band gap values indicating the semiconducting nature, as higher value for instance diamond has a band gap of 6 eV [13,14]. It can be concluded that the material exhibits semiconductor behavior as already observed in IR reflectivity spectrum.
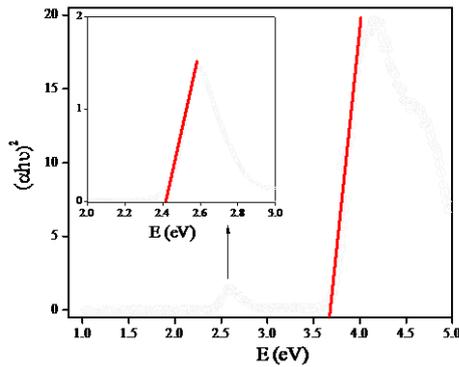
Fig. 3 The plot showing the relation ($\alpha h\nu)^2$ vs hν. The inset shows the lower band gap.

Fig. 4 demonstrate the dielectric constant (ε) exhibiting the small dispersion in dielectric constant. The materials with low dielectric constant less than 3.0 are under intense consideration because they can be used in interlayer dielectrics. These can also be used in integrated circuits for multilevel metallization. High thermal stability greater than >450 ˚C and low dielectric values are the two most important requirements for interlayer dielectrics. The material is stable up till 250˚C but it has a low value of dielectric constant i.e.1.98 to 2.45. The dielectric constant value is inversely proportional to the frequency. The slow decrease in dielectric constant value is related to the space charge polarization increases the dielectric constant and compensate for the decrease which is due to orientation polarization. The high value of the permittivity at low frequency is attributed to the Maxwell Wagner interfacial polarization mechanism.
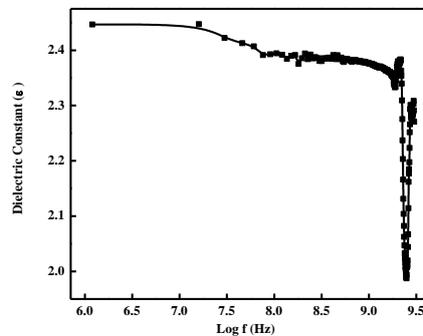

Fig. 4 Variation of dielectric constant with log f (Hz).

Fig. 5 shows the effect of frequency on the dielectric loss (tan δ). It is clear from the figure that the material has a small value of tan δ.The tangential loss peaks are observed at high frequency which may be attributed to the decrease in polarization. The loss at lower frequencies could be associated with the polarization of trapped charge carriers, when the dipoles are able to respond readily with changes in electric field. As the material has low value of dielectric loss so it has a high value of quality factor (Q $= \frac{1}{tan\delta}$.).The maximum value of the dielectric loss at a particular frequency indicate that quality factor of the material is low at a particular frequency log f = 9.3Hz and it indicates the presence of relaxing dipoles in the material [15, 16].
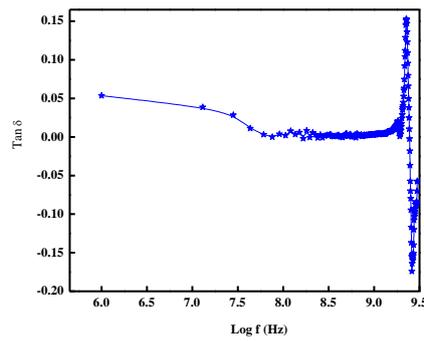
Fig. 5 Variation of Tan δ with log f (Hz).

The variation of ac resistance with frequency is shown in Fig.6. The high value of resistance at low frequency reflects that the grain boundary plays an important role in conduction. At a frequency of log f = 9.3Hz the increase in tan δ is due to the increase in conductivity and less polarization effect take place in the material [17].

Table 1. The main parameters related to 4-Methoxytriphenylmethylchloride like energy band gap, dielectric constant, dielectric loss, capacitance and resistivity are listed below.

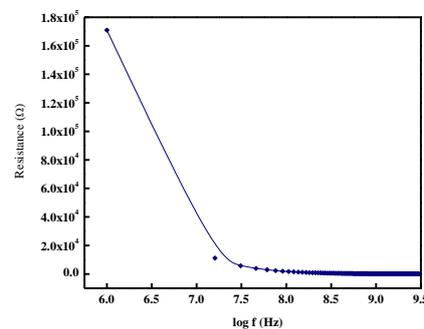| Energy Band Gap Eg(eV)	Dielectric Constant	Dielectric Loss	Capacitance (PF)	Resistivity (ohm cm)
2.4, 3.7	1.98-2.45	0.15	0.78-1.07	10^8 - 10^9

Fig. 6: Variation of resistance (Ω) with log f (Hz).

The capacitance is inversely proportional to the frequency as depicted in Figs.7, 8 and 9 respectively. In fact at the high frequency the alternating voltage half period becomes shorter and the space charge polarization cannot settle itself as a result the capacitance begins to decrease. Actually , the required time for ionic or electronic polarization to set in is comparatively small with respect to the change of voltage sign between two half period of the alternating voltage. The value of the capacitance is also increasing with the rise of temperature but as a like a resistance it increases up to a certain temperature then it tends to decrease. It means that the material changes its state from crystalline to amorphous phase. The capacitance is measured by LCR meter in a low frequency range of 1 Hz to 3GHz.
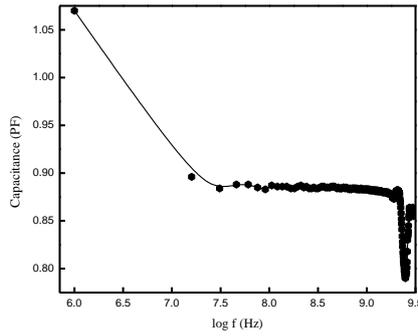
Fig.7 Variation of capacitance with log f (Hz).

The change of capacitance with frequency can be given by the relation [18].

$$C = C_g + [s\tau/(\omega^2\tau^2 + 1)] \tag{3}$$

Where C_g, τ, s and ω represents the geometrical capacitance, dipole relaxation time, conductance and angular frequency respectively. In the light of given relation capacitance shows maximum value at $\omega = 0$ and minimum at $\omega = \infty$ [18].
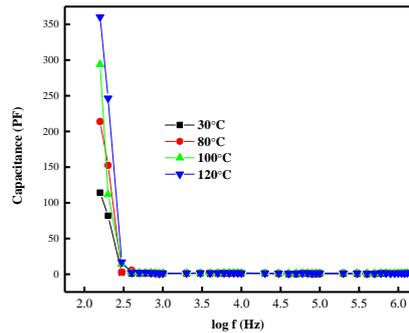

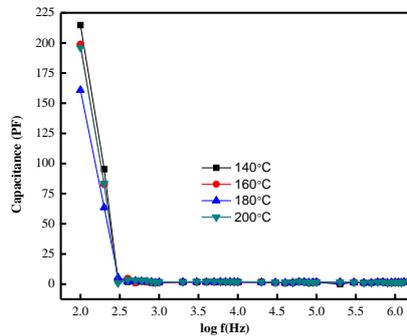*Fig. 8 Variation of capacitance (PF) vs log f (Hz) at various temperatures, 30˚C, 80˚C, 100˚C and 120˚C*

Fig. 9 Variation of capacitance (PF) vs log f(Hz) at various temperatures
140˚C, 160˚C, 180˚C and 200˚C.

The variation of ac resistivity with frequency is shown in Fig.10. At low frequency the resistivity is high its mean, the grain boundary plays a vital role but as the frequency becomes high, the resistivity becomes low; so the grains play an effective role at the high frequency and resistivity is inversely proportional to the frequency. Resistivity is inversely proportional to both

parameters like temperature and frequency; this behavior shows that the material is semiconductor in nature [19-23].
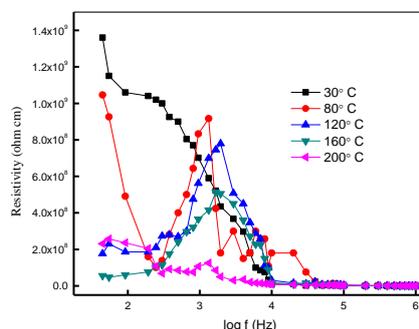

Fig. 10 Variation of resistivity vs frequency as a function of temperature.

4. Conclusions

It is clear from the XRD analysis that the structure of 4-Methoxytriphenylmethyl chloride is triclinic. The energy band gap value and temperature dependent resistivity indicate that the material is semiconductor. We have found that dielectric constant is inversely proportional to the frequency, It may be due to orientation polarization. The dielectric study shows that the material has a low value of dielectric constant so it can be used for microwave absorption. The tangent loss peak appearing at a particular frequency suggests the existence of the relaxing dipoles in the material. It is concluded from the results of IR reflectivity spectrum, energy band gap value and temperature dependent resistivity that the material is semiconducting in nature and thus can be used for various technological applications.

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