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Dielectric properties and relaxation mechanism of organic *trans*-stilbene and *p*-terphenyl molecular crystals using impedance spectroscopy

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HIGHLIGHTS

- Dielectric properties of *trans*-stilbene and *p*-terphenyl are studied from 1 Hz–1 MHz.
- Dielectric constant and loss spectra show quality and homogeneity of the crystals.
- Electronic and molecular relaxation mechanisms were observed in *trans*-stilbene.
- Secondary relaxation mechanisms were not presented in the *p*-terphenyl crystals.

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ABSTRACT

Dielectric properties of *trans*-stilbene and *p*-terphenyl have been studied in the frequency range (1 Hz–1 MHz) at room temperature (300 K). The results of dielectric constant and loss spectra have revealed high quality and high homogeneity of the single crystalline phase of the crystals grown with negligible impurity and defect concentrations. The electrical modulus clearly shows a low frequency maximum indicating that the electronic relaxation processes were presented in the both crystals. The molecular relaxation mechanisms were also observed in the *trans*-stilbene crystals and no other secondary relaxation mechanisms were presented in the *p*-terphenyl crystals.

1. Introduction

Organic materials offer flexibility in molecular design and crystalline structures and they can replace many electronic systems. Organic molecular crystals are widely used in the field of molecular electronics [1,2] and for their applications in optics and electronics have been attracting increasing interest [3]. Although development of growth techniques has resulted in significant improvement in the purity of such crystals [4], studies on intrinsic defects in organic molecular crystals [5] are still limited. Studying the optical and electrical behavior would offer a lot of insight into the defects in these type of crystals [6]. The theoretical and experimental approaches based on dielectrics are helpful for the understanding of dielectric polarization, dielectric energy loss and relaxation of charge carriers in molecular crystals. The study of dielectric properties of single crystals serves as an important source of information on the electrical properties of ions, atoms and molecules, and their behavior in the polycrystalline state. The dielectric properties of organic molecules strongly depend on the structure of the samples [7]. Defects in single crystal materials affect the change in the order of magnitude of polarization. Dielectric behavior is essential to analyze the crystal defects, and this is obtained at best using impedance measurements and analysis.

The general behavior of electric polarizability of different dielectric materials [8], basic polarization mechanism and its influence on crystal defects has been reported [9]. Cummins and Dunmur [10] have reported electrical permittivity studies on molecular crystal measured at different orientation axes. The results show that the crystalline polarizability along different symmetry axes is higher than that of the liquid state [11]. *p*-Terphenyl is chemically stable and more suitable for the study of excitonic as well as electrical properties [12]. Bak [13] has observed a dielectric loss peak due to the relaxation of the charge carriers between traps in more defect crystals. The dielectric loss curves were observed in both the crystalline and polycrystalline samples but such a loss does not exist in comparatively more monocrystalline structures [7]. In order to investigate the fundamental properties of organic scintillators, it is necessary to obtain high quality single crystals. Residual disorder, traps, dopants, or grain boundaries can mask

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the intrinsic charge transport mechanism [14]. The electronic polarization and dielectric loss factor as functions of frequency can be used as a tool to check the quality of the single crystals, because these properties are very sensitive to microstructure (viz, defects, grain boundary, etc) of the crystals.

In the present work, the dielectric properties of *trans*-stilbene and *p*-terphenyl single crystals are studied for their quality and to understand their electrical behavior. However, literatures on the study of impedance spectroscopy for organic scintillators are very few [9–13]. Hence, we have carried out impedance measurement on the selective self-seeded vertical Bridgman Technique (SSVBT) grown single crystals [15–18] in the frequency range from 1 Hz–1 MHz at 300 K. The electrical relaxation data have been analyzed using the modulus spectroscopy to investigate whether these single crystals exhibit Debye or non-Debye type relaxation.

2. Experiment

The SSVBT grown *trans*-stilbene and *p*-terphenyl crystals were cut and polished in the dimensions of 5.58 × 4.31 × 1.4 mm^3, and 2.13 mm thick and 8.17 mm diameter respectively. The samples were uniformly coated with silver paste for homogeneous contact between sample and electrodes, and samples were sandwich between platinum electrodes. These samples were used for the impedance analysis with impedance analyzer (Solartron impedance/gain phase analyzer 1260) in the frequency range of 1 Hz–1 MHz, in air atmosphere at 300 K. A simple RC equivalent circuit was obtained by analyzing the experimental data by using non-linear least square fitting routine [19]. The contribution of electrode polarization phenomenon [20,21] is negligible on $Z^*(\omega)$ of *p*-terphenyl samples and which is not observed for *trans*-stilbene samples. The real (Z') and imaginary (Z'') parts of the complex impedance (Z^*) were measured from $|Z|$ associated with phase angle as a function of frequency by using impedance analyzer. The conductivity (σ), the real (ε') and imaginary (ε'') parts of the complex dielectric constant (ε^*) as well as real (M') and imaginary (M'') part of the complex modulus M^* were extracted from the raw data of $|Z|$, phase angle and from the sample dimensions.

3. Results and discussion

3.1. Impedance formalism

Fig. 1 shows the complex impedance plot of *trans*-stilbene and *p*-terphenyl single crystals. The complex impedance measured at 300 K in the frequency range from 1 Hz to 1 MHz exhibited a single semicircle in nature for all these organic single crystals.

The complex impedance Z^* measurement can be expressed as a function of resistance R and capacitance C using the following equations

$$Z^*(\omega) = Z''(\omega) - jZ''(\omega) \quad (1)$$

where

$$Z'(\omega) = \frac{R}{(1+\omega^2R^2C^2)} \quad (2)$$

and

$$Z''(\omega) = \frac{\omega R^2 C}{(1+\omega^2R^2C^2)} \quad (3)$$

are, respectively, the real and imaginary parts respectively of the impedance given by the equations and ω is the angular frequency [22]. When plotted in complex plane, Eq. (1) gives the form of a semicircle. It is observed that single relaxation in these samples evidences the uni-polarization and of high degree of chemical and

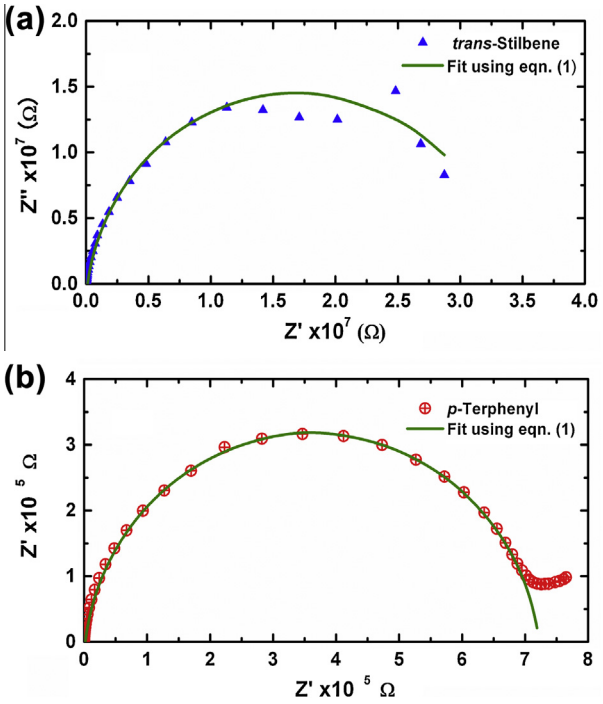

Fig. 1. Complex impedance plot of (a) *trans*-stilbene and (b) *p*-terphenyl.

Table 1
The bulk conductivity, resistivity and the conductivity relaxation frequency for the *trans*-stilbene and *p*-terphenyl single crystals.

Single crystals	Resistivity ($\rho = RA/l$) (Ω cm)	Conductivity ($\sigma = l/RA$) (S cm^{-1})	Angular frequency (Hz)
trans-Stilbene	9.9849×10^7	1.0015×10^{-8}	5
p-Terphenyl	1.786×10^4	5.5991×10^{-5}	150

electrical homogeneity present in these high quality organic single crystals. Similar observation was made by Niitsu et al. [23] in lithium niobate single crystal wafer. The equivalence of R and C parallel network obtained by this fitting procedure, this means that only bulk contribution is detected. In Table 1 shows the bulk values of the resistivity, conductivity and relaxation frequency for the trans-stilbene and *p*-terphenyl single crystals. It is observed that the conductivity for the trans-stilbene sample shows very low conductivity than the *p*-terphenyl crystals. The relaxation frequency was observed at very low frequency region. The resistivity values ($\rho = RA/l$) obtained from the resistance values are 9.9849×10^7 and 1.786×10^4 Ω cm for *trans*-stilbene and *p*-terphenyl crystals, respectively. The obtained angular frequency values are 5 and 150 Hz for *trans*-stilbene and *p*-terphenyl single crystals respectively.

3.2. Permittivity formalism

The measured impedance data were used to calculate the real (ε') and imaginary (ε'') parts of the complex dielectric permittivity from the relation

$$\varepsilon^*(\omega) = \frac{1}{j\omega C_0 Z^*(\omega)} \quad (4)$$

where $\omega = 2\pi f_r$ is the angular frequency, C_0 is the vacuum capacitance of the measuring cell and electrodes with an air gap without the sample given by $C_0 = \varepsilon_0 A/d$, where A is the area of the sample, d