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Methyl orange (C.I. acid orange 52) as a new organic semiconductor: Conduction mechanism and dielectrical relaxation

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A B S T R A C T

The structural, electrical and dielectrical properties of the methyl orange (MO) have been investigated by X-ray diffraction and thermal analysis methods. The electrical conduction and dielectrical relaxation mechanisms of the organic compound at various frequencies and temperatures were analyzed by impedance spectroscopy. The direct current (DC) electrical conductivity confirmed that methyl orange is an organic semiconductor with calculated electronic parameters. The alternating current (AC) electrical conductivity of the sample is controlled by the correlated barrier hopping (CBH) conduction mechanism. The values of the activation energy, the density of states and the binding energy for the alternating current mechanism were determined. The real and imaginary (Z' and Z'') parts of the impedance were found to be a frequency dependence. It was found that Cole–Cole plots of the sample confirm the existence of a temperature-dependent non-Debye relaxation mechanism.

1. Introduction

Organic semiconductors have attracted research interest due to their unique electrical and optical properties and have opened many opportunities for electronic and optoelectronic device applications. A considerable amount of work has been devoted to organic materials, allowing a better understanding of their properties as well as the physical processes, which take place in materials and devices. Meanwhile, commercial products making use of organic materials have started to appear in the market, especially in the field of display flat screens [1,2] (car radios, digital cameras, cell phones, computers and televisions). The word “organic semiconductors” include polymers and low-molecular weight organic materials. The optical and electrical properties of such materials have been studied for many years [3,4]. Because of their particular structure, several peculiar physical processes may take place in organic semiconductors while these effects are less or much less significant in inorganic materials. Conversely, several concepts in standard semiconductors lose their meaning in the organic field.

Methyl orange is an intensely colored compound used in dyeing and printing textiles. It is also known as C.I. Acid Orange 52, C.I.13025, helianthine B, Orange III, Gold orange, and Tropaeolin D. Chemists use methyl orange as an indicator in the titration of weak bases with strong acids. It changes from red (at pH 3.1) to orange-yellow (at pH 4.4). Nowadays, dyeing materials are widely used in semiconductor devices due to their stability, having a conjugate structure and being rich in π-electrons [5]. Azo compounds are usually yellow or orange color, since their main absorption band in the visible spectrum is typically in the blue region. Methyl orange (MO) has a drastic change in its color (from orange to red) is easily observed as the pH of its aqueous solution changes in a narrow range of values (namely, from 3.1 to 4.4), and hence, this compound is commonly used as a convenient indicator for the titration of strong acids by weak bases. In fact, the characteristic bright colors of MO make it an important dye for the paint, textile, and photographic industries [6,7].

Thus, it is important to reveal the semiconducting properties of methyl orange as a new semiconductor material for its possibility electronic device applications. In the present work, the structural,

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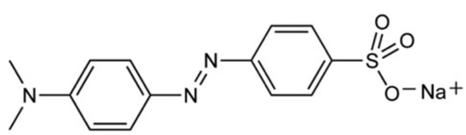
DC and AC conductivities of methyl orange (MO) that formed in pellet shape have been investigated. The structural characterization, the conduction mechanism and the relaxation process of methyl orange have been done using X-ray diffraction, thermal analysis and impedance spectroscopy.

2. Experimental detail

Methyl orange as shown in scheme 1 was purchased from Aldrich Company with high purity. MO powder was formed in the shape of pellet by applying 5 ton by using a hydraulic press. The diameter of the pellets for DC and AC measurements is equal to 13 mm and its thickness equals to 1 mm.

The real (Z') and imaginary (Z'') parts of the impedance Z at different temperatures were directly measured by a computer controlled HIOKI 3532-50 LCR meter. DC electrical conductivity of the sample was measured by a Keithley 6517 A electrometer. A special designed holder was used to study the DC and AC measurements. The present study covered a temperature range from 293 to 523 K. The temperature of the highly shielded home-made furnace controlled via type K thermocouple directly connected to a temperature controller. Powder X-ray diffraction (XRD) analysis of MO was carried out with a Philips model X'pert diffractometer with $CuK\alpha$ radiation operated at 30 kV and 25 mA with CuK_α ($\lambda = 0.15406$ nm) radiation.



Scheme. 1. The molecular structure of methyl orange.

3. Results and discussion

3.1. X-ray diffraction and thermogravimetry analysis

The structural properties of methyl orange powder were investigated by X-ray diffraction (XRD) pattern, as shown in Fig. 1. XRD results indicate that the methyl orange (MO) has a polycrystalline nature. The cell parameters values of MO sample were indexed and refined using crsyfire and checkcell software [8]. X-ray diffraction (XRD) powder pattern of methyl orange indicates that MO sample has a triclinic structure with the unit cell parameters as: $a = 7.0072$ Å, $b = 11.5637$ Å, $c = 16.8413$ Å, $\alpha = 54.34°$, $\beta = 70.33°$ and $\gamma = 85.94°$.

Thermal analysis plays an important role in determining thermal stability of the organic material. The TG curve, as shown in Fig. 2 reveals that the methyl orange decomposes in three steps in the studied temperature range (RT-800 °C). MO is a stable organic semiconductor through a wide range of temperature.

3.2. Electrical properties of the methyl orange

The direct current electrical conductivity dependence of temperature of the methyl orange is shown in Fig. 3. The DC conductivity increases with increasing temperature. The variation of electrical conductivity with temperature was analyzed by the following equation [9,10]:

$$\sigma_{DC} = \sigma_{o1}\exp\left(-\frac{\Delta E_1}{kT}\right) + \sigma_{o2}\exp\left(-\frac{\Delta E_2}{kT}\right) \quad (1)$$

where σ_{o1} and σ_{o2} are the pre-exponential factor for region I and II, respectively, k is the Boltzmann's constant, ΔE_1 and ΔE_2 are the DC conduction activation energy for region I and II, respectively. The values of ΔE_1 and ΔE_2 were calculated from the slopes of the obtained straight lines indicating that there are two conduction mechanisms in the studied range of temperature. The values of DC activation energy and the pre-exponential term were determined using the least-squares fitting of the experimental data via origin software. The values ΔE_1 and σ_{o1} for region (I) were found to be 0.540 eV, and 0.072 $(\Omega\ m)^{-1}$, respectively and the values ΔE_2 and σ_{o2} for region (II) were determined to be 0.837 eV and 663.81 $(\Omega\ m)^{-1}$, respectively. The calculated activation energy values are lower than half of the optical energy gap as in intrinsic semiconductors. The electrical conductivity results indicate that the electrical conduction mechanism is a thermally-activated process and that the DC electrical conductivity increases exponentially over the studied range of temperatures [9,10]. The electrical conductivity of the MO sample increased with increasing

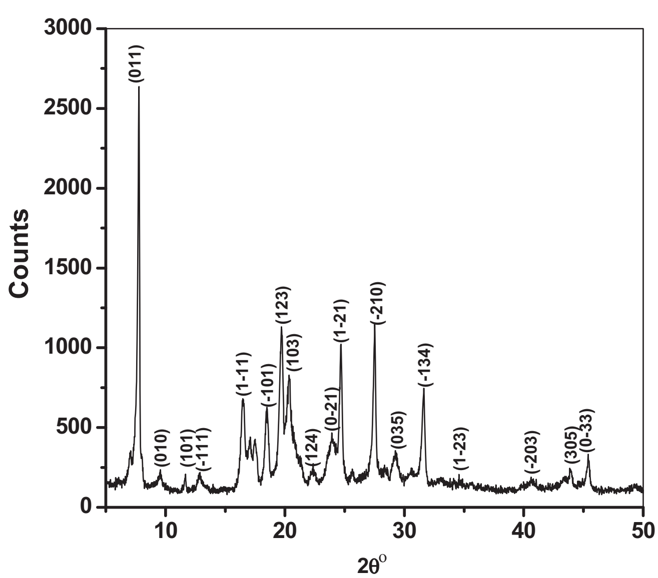


Fig. 1. XRD pattern of methyl orange.

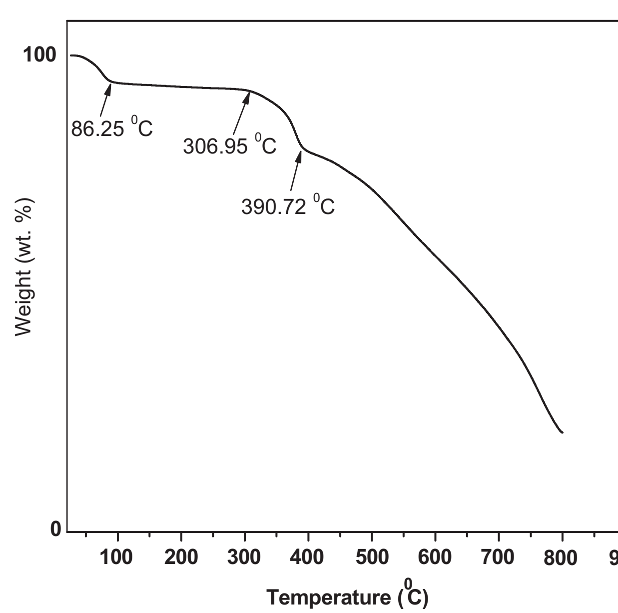


Fig. 2. TGA pattern of methyl orange.