Structure, Electrical Conductivity and Dielectric properties of bulk, 2-amino-(4,5-diphenylfuran-3-carbonitrile)

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Abstract: X-ray diffraction patters showed that the powder of 2-amino-(4, 5-diphenylfuran-3-carbonitrile) has polycrystalline nature with triclinic structure. Miller's indices, (hkl), values for each diffraction peak in XRD spectrum were calculated. The Electrical conductivity, dielectric constant ε' and dielectric loss ε" have been calculate for bulk in the frequency range from 40 Hz to 5MHz and at the temperature (298-473) K. The obtained results have been discussed in terms of the correlated barrier hopping (CBH) model, which is well adapted to 2-amino-(4,5-diphenylfuran-3-carbonitrile) semiconductor material. The dc conductivity, σ_{dc}, is described by the variable range hopping (VRH). The values of dielectric constant,ε', and dialectic loss,ε" decreased with increasing the frequency due to the interface states capacitance and the decrease in conductance with increasing both the frequency and temperature.

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1. Introduction

Organic semiconductors are of steadily growing interest as active components in electronics and optoelectronics. Due to their flexibility, low cost and ease of production they represent a valid alternative to conventional inorganic semiconductor technology [1]. The increasing environmental consciousness throughout the world has triggered a search for new products and processes that are compatible with the environment. The furo[2,3-d] pyramiding ring system, because of a formal isoelectronic relationship with purine, is speacilly of biological interest [2,3], it has numerous pharmacological and agrochemical applications viz.herbicides[4],antimalarials [5], antihypertensive [6] and potential radiation protection agents[7]. The understanding of charge transport mechanism in the composite materials is very important both from fundamental and technological point of view. Dielectric measurements are important means for studying the dynamic properties (capacitance, conductance, permittivity and loss factor) of dielectrics, this work deals with the electrical conductivity and dielectric properties of 2-amino-(4,5-diphenylfuran-3-carbonitrile) . This is done for two reasons: firstly, to determine the possible conduction and dielectric relaxation mechanisms. Secondly, very little articles are found to deal with the dc and ac electrical conductivities of 2-amino-(4,5-diphenylfuran-3-carbonitrile) .

2. Experimental procedures

2.1. Materials

The starting materials for the syntheses were purchased from Aldrich and used as received.

2.2. Synthesis

A mixture of the solution benzoin (0.01 mol) **(1)** and malnouitrile CH_2 $(CN)_2$(0.01 mol) **(2)** in ethanol (10 ml) we added basic alumina (20 g) and montomorillonite (15 g) with constant stirring.

The mixture was air dried at room temperature, placed in an alumina bath and subjected to MWI for 1.3 min/ 4 min respectively [8] as shown in scheme (1).

2.3. Measurements

The structural characteristics of 2-amino-(4,5-diphenylfuran-3-carbonitrile) was investigated

by X-ray diffraction patterns (XRD). Using a Philip X-ray diffractometer (model X- pert) with utilized monochromatic CuK_α radiation and operated at 50 kV and 40 mA. The diffraction patterns were recorded automatically with a scanning speed of 2deg/min.

2-amino-(4,5-diphenylfuran-3-carbonitrile) were firstly compressed under a pressure of ~ 2×10^8 N/m^2 in the form of a pellet and sandwiched between two evaporated gold, Au, electrodes which provide ohmic contacts to the sample..

A programmable automatic RLC bridge, model Hioki 3532 Hitester, was used to measure the frequency F ,impedance Z, the capacitance C, and the loss tangent (tanδ) directly. The range of frequencies was 42 Hz-5MHz. The temperature of the sample was measured by a thermocouple over a temperature range 298-423 K. The total conductivity was calculated from the following equation: $\sigma_t(\omega) = d/ZA_o$, where d is the thickness of the sample and A_o is the cross-section area. The dielectric constant, ε_1, was calculated from the equation: $\varepsilon_1 = dC/A_o \varepsilon_o$, where ε_o is the permittivity of free space.

3. Results and discussion

X-ray powder diffraction (XRD) of 2-amino-(4,5-diphenylfuran-3-carbonitrile) was taken for the first time in a 2θ range from 5 to 40°, and its spectrum is presented in Fig. 2. As shown in this figure, the pattern has many diffraction peaks with different intensities indicating that the powder of 2-amino-(4,5-diphenylfuran-3-carbonitrile) has a polycrystalline nature. The unit cell parameters of 2-amino-(4,5-diphenylfuran-3-carbonitrile) were determined for the first time by using the CRYSFIRE computer program [9].

The data analysis of the structure is highly matched with a triclinic structure with lattice constant a=11.63,b=18.933,c=22.226, α=96.72, β =55.14, γ = 132.66 and space group *P1*. The value of Miller indices, (hkl), and lattice spacing, d_{hkl}, corresponding to each diffraction line was indexed using CHECKCELL program [10]. Table 1 gives the values of Miller indices (hkl) for each diffraction peak, 2θ and the interplaner spacing (d_{hkl}) before and after refinement.

The variation of $\sigma_{ac}(\omega)$ as a function of frequency (42-5MHz) at different temperature range (298-423) K is shown in Fig. 3 for 2-amino-(4,5-diphenylfuran-3-carbonitrile) bulk sample. It is seen that $\sigma_{ac}(\omega)$ remains almost constant at low frequency and after a certain characteristic crossover frequency, ω_o, it increase with power law fashion. Similar behaviour has been observed in many organic materials in bulk and thin film forms [11–14].

The electrical conductivity, $\sigma_{ac}(\omega)$, of many materials including glasses, organic, polymer and crystal materials over wide range of frequency and temperature are given using the relation [15]

$$\sigma_{ac}(\omega)=\sigma_{tot}(\omega)-\sigma_{dc}(\omega) \quad (1)$$

where $\sigma_{tot}(\omega)$ is the total electrical conductivity at a particular angular frequency ω at a certain temperature. In this equation, the dc conductivity is taken to represent the ac conductivity in the limit $\omega \rightarrow 0$.

The values obtained from extrapolation of the experimental data of $\sigma_{tot}(\omega)$ at low frequencies up to zero frequency are assumed to be equivalent to the dc conductivity for 2-amino-(4,5-diphenylfuran-3-carbonitrile) at each temperature is shown in Fig. 4.

In general, in the case of semiconductors, the dc conductivity varies exponentially with temperature and is given by the Arrhenius equation:

$$\sigma_{dc} =\sigma_o \exp(\Delta E / k_{eB}T) \quad (2)$$

where ΔE is the dc electrical activation energy, T is the absolute temperature, k_B is Boltzmann's constant and σ_o is the pre exponential factor including the charge carrier mobility and density of states. The value of ΔE was found to be 0.20 eV.

The experimental data could be analyzed using Mott's variable range hopping conduction process and the following expression for the dc conductivity was used [16]:

$$\sigma(T)\sqrt{T} = \sigma_{oo} \exp(-B\,T^{-1/4}) \quad (3)$$

where σ_{oo} and B are constants and B is given by

$$B^4 = T_o = \frac{18.1\alpha^3}{k_B N(E_F)} \quad (4)$$

The hopping distance and hopping energy are given by [19]:

$$R = \left(\frac{9L_{loc}}{8\pi kTN(E_F)}\right)^{1/4}, \quad (5)$$

$$W = \left(\frac{3}{4\pi R^3 N(E_F)}\right), \quad (6)$$

where T_o is the characteristic temperature and $\alpha = 1/L_{loc}=10^{-7}$cm

The corresponding T_o has been evaluated from the linear slope of ln ($\sigma_{dc}\,T^{1/2}$) versus $T^{-1/4}$ as depicted in Fig. 5.

The value of parameter T_o was found to be 3.725×10^8 K. In addition, the density of localized states at Fermi level, $N_{(EF)}$, has been calculated taking a constant value of α^{-1} (10^{-7} cm) and found to be 5.63×10^{17} eV^{-1} cm^{-3}. The values of R and W are calculated and found to be 5.2×10^{-6} cm and 299 meV respectively. The value of W and αR according to [16] should have a value greater than kBT and unity respectively.

The $\sigma_{ac(\omega)}$ is commonly characterized by an approximate power law over a wide range in frequency represented by Jonscher's law [17]:

$$\sigma_{ac}(\omega)=A\,\omega^s \quad (6)$$

where A is constant, ω is the angular frequency, $\omega = 2\pi f$, and s is the frequency exponent.

The frequency exponent, s, can be calculated from the slope of the straight lines in Fig.6 for high ranges of frequencies. The calculated values of s decrease from 0.98 at 303 K to 0.67 at 413 K.

This behavior was associated with a hopping mechanism in terms of correlated barrier hopping (CBH) model for ac loss, first developed by Pike [18] for single-electron hopping, and has been extended by Elliot [19] for simultaneous two electrons hopping. According to the correlated barrier hopping (CBH) model, values of s decrease with increasing temperatures. In this model, carrier motion occurs by means of hopping over the Coulomb barrier separating two defect centers. A Coulomb correlation between the charged defect centers results in the relaxation variable W of the Coulomb barrier and the intersite separation

The $\sigma_{ac}(\omega, T)$ conductivity in the CBH model to a first approximation is given as [20]:

$$\sigma_{ac}(\omega) = \frac{\pi(N_{(EF)})^2\varepsilon}{24}\left(\frac{8e^2}{\varepsilon W_m}\right)^6 \frac{\omega^s}{\tau_o^{1-s}} \quad (7)$$

where ε is the dielectric constant, W_m is the maximum barrier height over which the electrons hop E_{opt} (optical band gap), e is the electronic charge and τ_o is the effective relaxation time. According to reference [20], τ_o is expected to have a value of the order of an inverse phonon frequency ($=10^{-13}$ s).

The frequency exponent s for this model is given by

$$s = 1 - \frac{6k_BT}{[W_m + k_BT\ln(w\tau_o)]} \quad (8)$$

A first approximation of this equation gives the simple expression for the frequency exponent s:

$$s - 1 = \frac{6k_BT}{W_m}, \quad (9)$$

The binding energy W_m is related to the maximum barrier height at infinite interstatic separation, which is called the polaron binding energy.

Fig. 7 show the ac conductivity ln $\sigma_{ac}(\omega)$ as a function of the reciprocal temperature 1000/T in the investigated temperature range at different frequencies From the figure, σ_{ac} (ω) increases linearly with increasing temperature. This may indicate that the ac conductivity is a thermally activated process it can be analyzed according to the well-known Arrhenius equation:

$$\sigma_{ac}(\omega) = \sigma^* \exp(-\Delta E_{ac}/kT) \quad (10)$$

where σ^* is constant and ΔE_{ac} is the activation energy for conduction.

The obtained values of the ac activation energy for different frequencies are decreased from 0.24eV to 0.15 eV.

Dielectric dispersion implies the variation of real and imaginary parts at fixed temperatures.

The complex dielectric function for the investigated organic dye is expressed as [21]:

$$\varepsilon^*(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (11)$$

where $\varepsilon_1(\omega)$and $\varepsilon_2(\omega$ are the dielectric constant and the dielectric loss respectively. The dielectric constant is associated with the polarization of the material under the influence of sub-switching ac field [22]. The dielectric constant $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ were calculated in the range of frequency 42Hz-5MHz and temperature range (298-423)k. Figs. (8and 9) show the variation of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ with frequency at different temperatures, respectively. As seen in Figs. (8 and 9) $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ decrease with increasing frequency. The decrease of $\varepsilon_1(\omega)$ with frequency can be explained as follows; at low frequencies the dielectric constant $\varepsilon_1(\omega)$ for polar materials is due to the contribution of multi-component of polarizability, deformational polarization (electronic and ionic polarization) and relaxation polarization (orientational and interfacial polarization) [23].

When the frequency is increased, the dipoles will no longer be able to rotate sufficiently rapidly, so that their oscillations begin to lag behind those of the field. As the frequency is further increased, the dipole will be completely unable to follow the field and the orientation polarization stopped, so $\varepsilon'(\omega)$ decreases at higher frequencies approaching a constant value due to the interfacial or space charge polarization only [24, 25].

Conclusion

Structural investigation using X-ray confirmed that the powder of 2-amino-(4,5-diphenylfuran-3-carbonitrile) has a triclinic structure with lattice constant a=11.63, b=18.933, c=22.226, α=96.72, β =55.14, γ =132.66 and space group *P1*. Electrical conductivity and dielectric properties of bulk, 2-amino-(4,5-diphenylfuran-3-carbonitrile) was measured as a function of frequency range 42Hz-5M kHz and temperature range 298-423k in a compressed pellet, with evaporated ohmic Au electrodes. The dc conductivity was explained according to the VRH mechanism. The ac conductivity σ_{ac} (ω) was found to vary as ω^s in the frequency at high range of frequency the frequency exponent, s, was less than unity and decreases with the increase in temperature indicating a dominant correlated barrier hopping (CBH) mechanism.

The calculated ac activation energy was found to decrease with increasing frequency. This may be indicated that the ac conductivity is a thermally activated process. The dielectric constant, $\varepsilon_1(\omega)$ was found to decrease by increasing frequency .The dielectric loss, $\varepsilon_2(\omega)$, was also found to be decreased by increasing frequency .

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Table.1 X-ray for powder of 2-amino-(4,5-diphenylfuran-3-carbonitrile) **.**

No	$2\theta_{measured}$	$2\theta_{calculated}$	$d_{measured}$	$d_{calculated}$	I/I_o	(hkl)
1	6.735	6.727	13.113	13.13	15.73	(001)
2	7.078	7.095	12.477	12.488	100	(010)
3	10.596	10.591	8.342	8.302	41.16	$(0\,\bar{1}\,1)$
4	10.872	10.843	8.131	8.153	6.27	(002)
5	11.071	11.087	7.985	7.947	15.41	(101)
6	13.994	14.006	6.323	6.318	16.19	(100)
7	14.220	14.218	6.223	6.224	63.88	(020)
8	15.292	15.301	5.789	5.786	4.97	$(1\,\bar{3}\,1)$
9	15.449	15.418	5.731	5.742	6.81	$(0\,\bar{1}\,2)$
10	15.801	15.81	5.604	5.599	1.56	(113)
11	17.016	17.002	5.203	5.211	7.78	(111)
12	17.868	17.89	4.959	4.954	1.88	(114)
13	19.996	20.003	4.437	4.435	33.28	$(2\,\bar{4}\,0)$
14	20.251	20.247	4.381	4.382	2.97	$(1\,\bar{4}\,0)$
15	20.581	20.581	4.312	4.312	1.24	$(2\,\bar{1}\,5)$
16	21.025	21.022	4.222	4.223	1.75	$(1\,\bar{2}\,4)$
17	21.406	21.397	4.147	4.149	3.12	(030)
18	21.645	21.636	4.102	4.104	3.23	$(\bar{1}\,23)$
19	22.009	22.027	4.035	4.032	4.14	(124)
20	22.276	22.28	3.987	3.987	17.10	(202)
21	22.434	22.436	3.959	3.991	11.75	(205)
22	22.868	22.875	3.885	3.884	6.73	$(\bar{1}\,02)$
23	24.134	24.135	3.685	3.681	9.34	$(3\,\bar{4}\,4)$
24	24.361	24.362	3.651	3.651	11.75	$(3\,\bar{3}\,2)$
25	25.945	25.931	3.431	3.433	16.55	$(\bar{2}\,32)$
26	26.262	26.264	3.391	3.393	3.82	(213)
27	26.698	26.698	3.336	3.338	1.85	$(3\,\bar{3}\,1)$
28	26.996	27.042	3.300	3.291	3.02	$(3\,\bar{5}\,4)$
29	27.701	27.714	3.218	3.216	1.82	(216)
30	28.003	28.003	3.184	3.184	5.10	(212)
31	29.926	29.927	2.983	2.983	2.98	(117)
32	30.528	30.528	2.925	2.924	8.21	$(\bar{2}\,53)$
33	31.321	31.320	2.853	2.854	9.41	$(1\,\bar{2}\,6)$
34	31.525	31.535	2.835	2.832	3.60	$(0\,\bar{4}\,1)$
35	38.7525	38.751	2.321	2.322	1.67	$(\bar{2}\,55)$
36	39.1759	39.176	2.297	2.296	1.69	(301)
37	40.596	40.596	2.220	2.221	1.27	(048)

Fig. 1: Scheme 1. Synthesis of -amino-(4,5-diphenylfuran-3-carbonitrile).

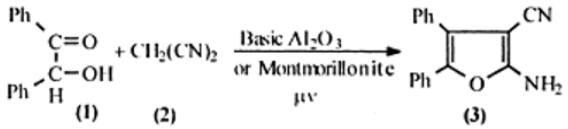

Fig. 2: XRD of 2-amino-(4,5-diphenylfuran-3-carbonitrile) in the powder form.

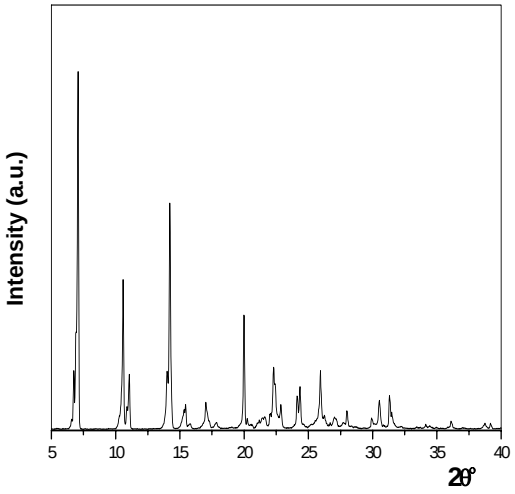

Fig. 3: **Fig. 3:** Frequency dependence of AC conductivity $\sigma_{ac}(\omega)$of 2-amino-(4,5-diphenylfuran-3-carbonitrile) at various temperatures

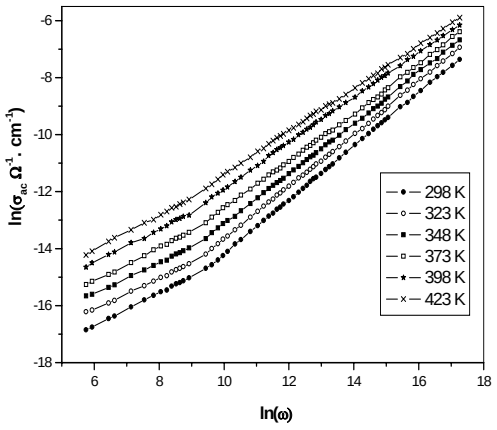

Fig. 4: Temperature dependence of DC conductivity of 2-amino-(4,5-diphenylfuran-3-carbonitrile).

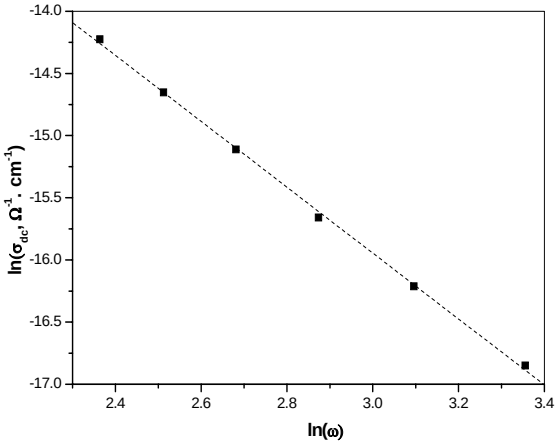

Fig. 5: Plots of $\ln(\sigma_{dc}T^{1/2})$ versus $T^{-1/4}$ for 2-amino-(4,5-diphenylfuran-3-carbonitrile).

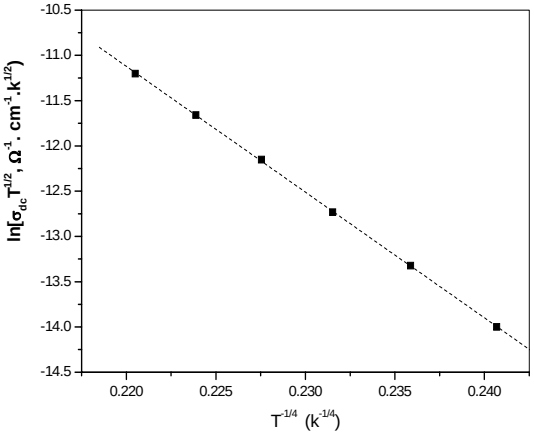

Fig. 6: Temperature dependence of the frequency exponent s for 2-amino-(4,5-diphenylfuran-3-carbonitrile).

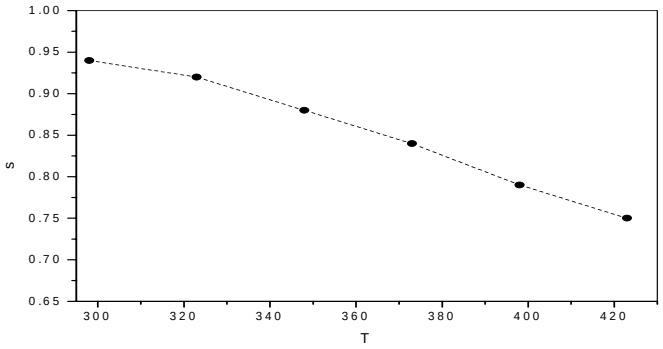

Fig. 7: Variation of AC conductivity, $\sigma_{ac}(\omega)$, with temperature at different frequencies for 2-amino-(4,5-diphenylfuran-3-carbonitrile). (4,5-diphenylfuran-3-carbonitrile).

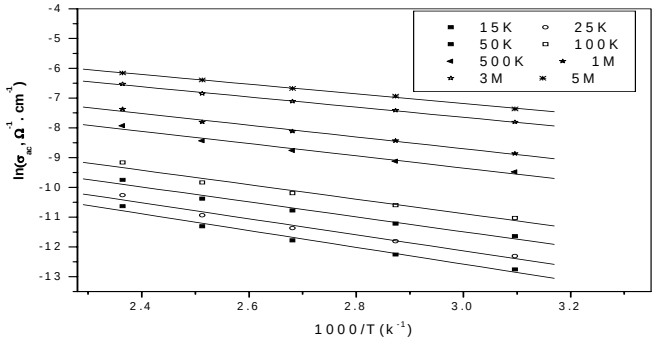

Fig. 8: Variation of the dielectric constant ε'(ω) with frequencies at different temperature at for 2-amino-(4,5-diphenylfuran-3-carbonitrile).

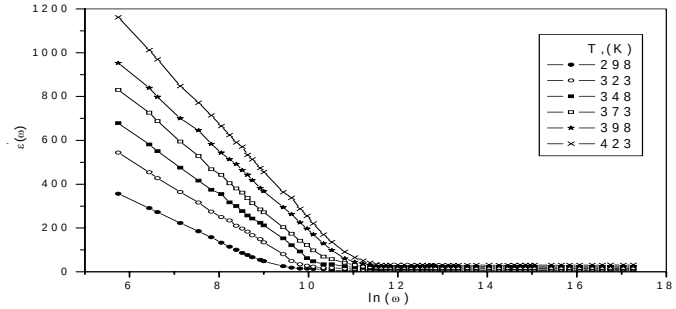

Fig. 9: Variation of the dielectric loss ε"(ω) with frequencies at different temperature for 2-amino-(4,5-diphenylfuran-3-carbonitrile).