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On the electronic transport properties of some new esters of n-(p-nitrobenzoyl)-d,l-phenylalanine in thin films

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The studied compounds were prepared by decyclization of oxazoline N-acilaminoacid under action of methanol, ethanol propanol and isopropanol. The temperature dependence of the electrical conductivity and Seebeck coefficient of the respective compounds were investigated using thin film samples (d = 0.40 μm – 2.35 μm), deposited from dimethylformamide onto glass substrates. It was found that compounds show typical semiconducting properties. The values of some characteristic parameters of studied compounds (thermal activation energy of electrical conduction, ratio of carrier mobilities, etc) have been determinated. The mechanism of electronic transport in the films is discussed in terms of band gap representations. The values of the optical band gap energy are determined from the absorption spectra.

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Keywords: Thin films, Organic semiconductors, Electronic transport, Absorption spectra

1. Introduction

Semiconducting organic materials find a steadily increasing interest in the last years, owing to their potential applications in the field of solid-state device technology (organic solar cells, sensors, thermistors, photodetectors, etc.)[1-6].

Organic compounds of different classes (monomers, charge transfer complexes, polymers, etc) have been investigated and some important correlations between their molecular structure and semiconducting characteristics have been established [5-10].

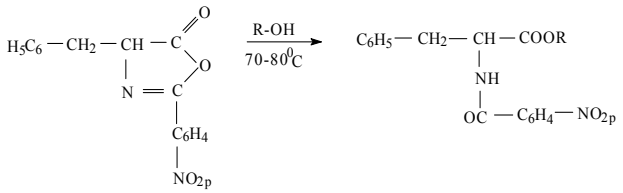
In a series of previous papers [3, 8-13], we studied the electronic transport and optical properties of a large number of organic compounds which showed typical semiconducting characteristics. The measurements have been performed using thin-film samples deposited from solutions.

In this paper we extend these investigations on some recently synthesized esters of N- (p-nitrobenzoyl)-D, L-phenylalanine.

2. Experimental

2.1 Synthesis of compounds

The investigated compounds have been synthesized by decyclization of oxazoline N-acil-aminoacid under action of methanol, ethanol, propanol and isopropanol, respectively, according to the following synthetic route:



where substituent R is indicated in Table 1.

Table 1. The substituient R and melting points of studied compounds.

Compound	Substituient — R	Melting point (K)
EFA. 1	$-CH_3$	428
EFA. 2	$-C_2H_5$	385
EFA. 3	$-(CH_2)_2-CH_3$	388
EFA. 4	$-CH(CH_3)_2$	383

A mixture of oxazoline (0.025 mol.) and corresponding alcohol (50 ml) was heated at 60-90^{0}C for 2-4 hours within a balloon flask with refrigerant. After cooling to room temperature, the distilled water was gradually added.

A glue product is obtained. Then, this is dried under vacuum at 45^{0}C. The collected products were finally purified by recrystallization in water-alcohol mixture.

The preparation method and some physical and chemical of these compounds are presented in detail in [14]. They were obtained as polycrystalline powders and showed chemical stability under normal ambient atmosphere.

Chemical and physical properties of this class of compounds have little studied.

2.2. Study of the electronic transport and optical properties

The temperature dependences of the electrical conductivity and Seebeck coefficient, and also transmission spectra were studied on the thin-film samples deposited onto glass substrates from dimethylformamide solutions of the compounds. Deposition conditions (substrate temperature, solution concentrations, evaporation rates, etc.) have been established in order to obtain samples with compact structure and uniform thickness [3, 8, 11, 12]. During the film growth, the substrates were maintained at approximately 325 K for a slow solvent evaporation [8, 9, 12, 13]. The temperature dependence of the electrical conductivity was measured by using surface-type cells [9, 15, 16]. Thin silver (indium) films (d = 1.0 – 1.5 μm) (thermally evaporated under vacuum) before the deposition of organic compounds) were used as ohmic contact electrodes [12, 15, 16]. All measurements were performed by applying low electric fields (<10^2V/cm), which resulted in the absence of non-ohmic effects [12, 17].

The thickness, d, of organic films determined by an interferometric method [18, 19]) ranged between 0.40 μm and 2.35 μm.

The Seebeck coefficient, S, has been determined by using the method of thermal-sonde electrodes [11, 20]. The temperature difference between electrodes was of 10-12 K. The Seebeck voltage was measured with a Keithley Model 6517 electrometer.

Experimental details and methods of determining the characteristic parameters were described in our previous papers [3, 8, 11, 13].

The reflection and transmission coefficients were recorded (at room temperature) by using a PMQII type spectrophotometer and an ETA-STC spectrometer [21, 22].

The absorption coefficient, α, was calculated according to the expression [3, 13, 23-26]

$$\alpha = \frac{1}{d}\ln\left[\left(1-R_\lambda\right)^2 \Big/ T_\lambda\right] \qquad (1)$$

where d, denotes film thickness and R_λ and T_λ are reflection and transmission coefficient, respectively, at wavelength λ.

IR spectra were recorded on KBr pellets using a Bruker FTIS-66 Fourier Transform Infrared Spectrometer, ^{1}HNMR spectra were obtained by a Varian Gemeni 3000 spectrometer at 75.44 MHz.

3. Experimental results and discussion

The molecular structure of the compounds was confirmed by elemental analysis and spectral methods: infrared spectroscopy (IR) and nuclear magnetic resonance (^{1}H-NMR).

The IR spectra of the compounds show absorption bands in the range 3300-3367 cm^{-1}, which are characteristic for amide group (NH), esteric group (CO) determines the appearance of the strong band at 1707 cm^{-1}. The absorption bands corresponding to amidic group (CO) are in the range 1641 cm^{-1}– 1643 cm^{-1}. The ranges 1519 cm^{-1} – 1529 cm^{-1} and 1350 cm^{-1} – 1352 cm^{-1} characterize the symmetrical and asymmetrical vibrations of the NO_2 group. Aromatic ring determines the appearance of a band placed between 800 cm^{-1} and 825 cm^{-1} [27-29].

Experimentally, it was established that thin-film samples with stable solid-state structure can be obtained, if, after deposition, they are subjected to a heat treatment, consisting of several successive heating/cooling cycles (generally, 2-4 cycles) within a certain temperature range, ΔT, characteristic for, each studied compound [3, 8, 13].

The study of the temperature dependence of the electrical conductivity during this treatment permits to obtain very interesting information on the processes taking place in the respective samples (the removal of some adsorbed and absorbed gases, reduction in concentration of solid-state structural defects and impurities, etc [3,11,13]).

For a great number of inorganic and organic semiconductors in thin films, a detailed analysis of the temperature dependence of the electrical conductivity during heat treatment is presented in a series of our previous papers [3, 10-13].

For heat-treated samples the temperature dependence of the electrical conductivity, σ, becomes reversible. We consider that this fact shows a stabilization of the sample solid-state structure in respective temperature range [3, 8].

For a large number of organic compounds with similar molecular structure [11, 27], we find that temperature dependence of the electrical conductivity, σ, may be expressed as [3, 13, 28-30].

$$\sigma = \sigma_0 \exp\left(-\Delta E \Big/ 2kT\right) \qquad (2)$$

where ΔE denotes thermal activation energy of electrical conduction, σ_0 is a parameter depending on the compound nature, and k is Boltzmann's constant.

Figs. 1 and 2 show the dependence of the d.c. conductivity with reciprocal temperature, 10^3/T, during heat treatment for two studied samples.

As can be seen from Fig. 1, after the heat treatment the $\ln\sigma = f\left(10^3 \Big/ T\right)$ dependence can be approximated by two activation energies within the studied temperature range. For heat treated sample, the respective curve is characterized by two distinct parts: a part with a smaller slope (where probably the extrinsic conduction is predominant) and a part with a larger slope (where it may suppose that the compounds possess an intrinsic conduction) [3, 8, 10, 12]. Similar behavior aspects were noticed for all samples of compounds EFA.1, EFA.2 and EFA.4 under study.

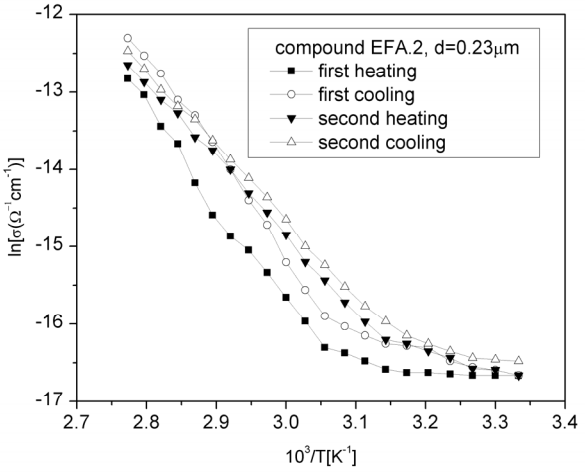


Fig.1. Temperature dependence of the electrical conductivity during heat treatment.

Compound EFA.3 has a specific behavior. Within the lower temperature range (300K-330K), the slopes of the $\ln\sigma = f\left(10^3/T\right)$ curves have smaller values and extrinsic conduction predomines. In the range, ΔT = 300 – 350 K all the impurities are ionized, while at such temperatures the number of the electron hole pairs generated by intrinsic excitation is negligible (carrier concentrations are constant). In the higher temperature range (T>350K), we suppose that the samples of this compound exhibit an intrinsic conduction. The last parts of curves $\ln\sigma = f\left(10^3/T\right)$ are described by Eq. (2). Consequently, the values of the activation energy ΔE, were calculated for intrinsic conduction domain.

The obtained values are presented in Table 2. In this table the values of other characteristic parameters are also listed.

Table 2. Values of characteristic parameters for some studied samples.

Compound	d (μm)	ΔT(K)	$\sigma_c(\Omega^{-1}cm^{-1})$	σ_T ($\Omega^{-1}cm^{-1}$)	T_C(K)	ΔE (eV)
EFA.1	0.17	300-415	5.06×10^{-8}	5.24×10^{-8}	325	1.57
EFA.1	1.16	300-415	3.67×10^{-7}	2.06×10^{-7}	327	1.58
EFA.2	0.23	300-370	6.28×10^{-8}	8.34×10^{-8}	330	1.72
EFA.2	1.06	300-375	5.65×10^{-7}	4.05×10^{-7}	332	1.70
EFA.3	0.11	300-370	8.76×10^{-8}	1.37×10^{-8}	345	1.90
EFA.3	0.95	300-370	3.33×10^{-7}	4.16×10^{-7}	347	1.88
EFA.4	0.22	300-365	4.14×10^{-8}	4.58×10^{-8}	339	1.50
EFA.4	0.86	300-365	1.67×10^{-7}	2.40×10^{-7}	342	1.52

d, film thickness; σ_c, electrical conductivity at room temperature before heat treatment; *ΔT*, temperature range in which the heat treatment of sample was performed; σ_T, electrical conductivity at room temperature after the heat treatment; T_C, characteristic temperature for respective sample; *ΔE*, activation energy of electrical conduction.

The semiconducting properties of investigated compounds are determined by their specific configuration which affords the formation of extended conjugated systems [5, 10, 11, 30-33]. The delocalization of π electrons along the molecular backbone is strongly influenced by the nature and position of substituent R.

For large number of individual classes of organic compounds, the preexponential parameter σ_0, in the Eq.(2), exponentially varies with the activation energy ΔE, according to equation [9, 12, 30, 34, 35]

$$\sigma_0 = \sigma_0^{'} \exp\left(\Delta E / 2kT_0\right) \quad , \qquad (3)$$

where the parameter $\sigma_0^{'}$ and characteristic temperature T_0 ("compensation temperature") do not depend on the temperature.

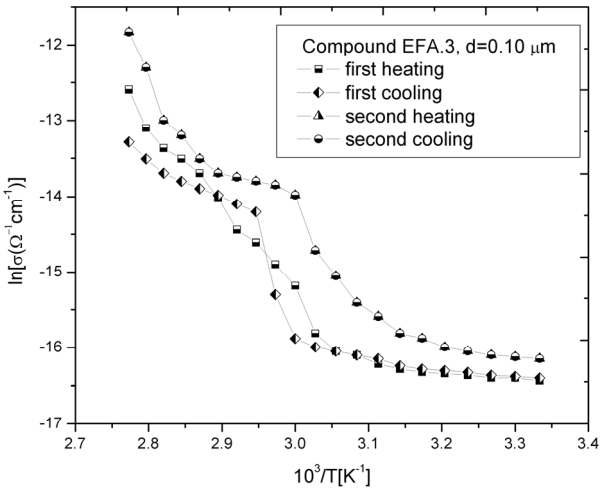


Fig.2. Temperature dependence of the electrical conductivity during heat treatment.

The Eq. (3) shows a linear dependence between $\ln\sigma_0$ and ΔE i.e.[3, 9, 34, 35]

$$\ln\sigma_0 = \beta + \gamma\Delta E \quad , \tag{4}$$

where parameters $\beta = \ln\sigma_0^{'}$ and $\gamma = {}^{1}\!/_{2}\, kT_0$ depend on the individual classes of the organic compounds with similar molecular structure.

Usually, the activation energies are changed by different methods such as chemical vapor adsorption, hydration, formation of complexes, etc. For investigated compounds ΔE is varied by modified the nature of R substituient (Table1).

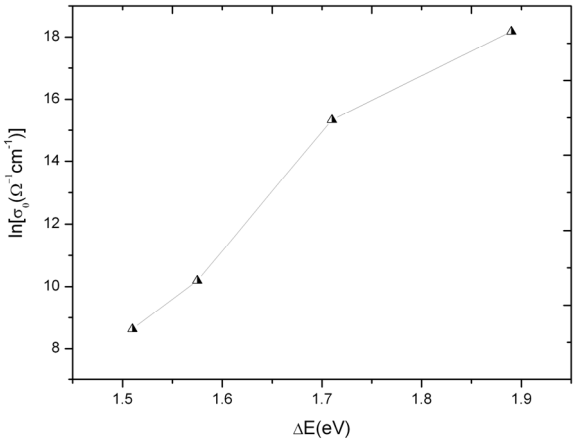


Fig.3. The dependence of lnσ$_0$ on the thermal activation energy, ΔE.

Eq. (3) indicates the "compensation rule" ("compensation effect") and is verified by a very large number of experimental results [3, 9, 34, 35].

Fig.4 shows that Eq.(4) is verified by our experimental data.

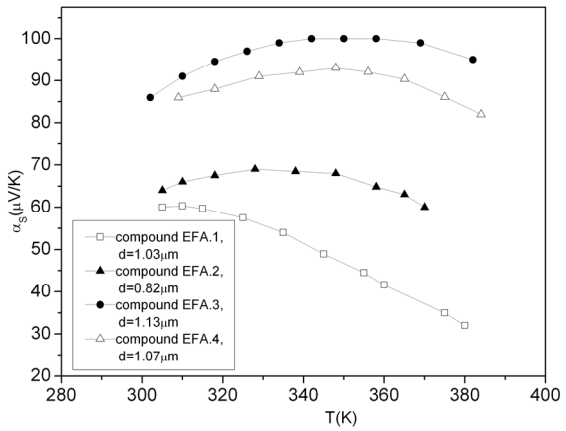


Fig.4. Temperature dependence of the Seebeck coefficient for four heat treated samples.

The parameters β and γ, determined from the linear dependence illustrated in Fig.3, have the following values

$$\beta = 26.67; \gamma = -31.48eV^{-1}$$

The study on the temperature dependence of the Seebeck coefficient offers very useful information about the mechanism of electronic transport in the respective compounds.

For a non-degenerate semiconductor, in domain of intrinsic conduction, the Seebeck coefficient can be expressed by [3, 20, 28, 30]

$$S = -\frac{k}{|e|}\frac{b-1}{b+1}\left[\left(\frac{5}{2} - s\right) + \frac{\Delta E}{2kT}\right] \tag{5}$$

where e is electron change, b denotes the ratio of carrier mobilities ($b = {}^{\mu_e}\!/_{\mu_h}$, μ_e is mobility of electrons and μ_h that of holes), s is scattering parameter depending on the predominant scattering mechanism in studied sample.

By considering that in a small temperature range, $\Delta\left({}^{1}\!/_{T}\right)$, the parameter s can be considered that is independent on the temperature, the Eq.(5) leads to the following expression for b [3, 20, 28, 30]

$$b = \frac{\left({}^{\Delta E}\!/_{2}\right)\Delta\left({}^{1}\!/_{T}\right) - |e|\Delta S}{\left({}^{\Delta E}\!/_{2}\right)\Delta\left({}^{1}\!/_{T}\right) + |e|\Delta S} \quad , \tag{6}$$

where ΔS is the variation of the Seebeck coefficient corresponding to a determined variation $\Delta\left({}^{1}\!/_{T}\right)$ of the reciprocal temperature.

In Fig. 4 are presented temperature dependences of the Seebeck coefficient, S, for four studied samples. The Seebeck coefficient is positive and the $S = f\left(T\right)$ curves are linear in the intrinsic domain.

The values of b (Table 3) are lower than unity.

Table 3. Values of characteristic parameters for some heat-treated samples.

Compound	d (μm)	ΔE(eV)	b
EFA.1	1.03	1.59	0.85
EFA.2	0.82	1.70	0.94
EFA.3	1.13	1.92	0.95
EFA.4	1.0	1.50	0.90

d, film thickness; ΔE, thermal activation energy; b, ratio of carrier mobilities.

Generally, in bulk semiconducting materials, the electron mobility is much greater in comparison with hole mobility and consequently b must exceed unity [28,29].

The obtained values for ratio of carrier mobilities can be also explained in the frame of the Caller model [39, 40], based on the band structure representation.

Structural investigations showed that studied films are polycrystalline. In these conditions the mechanism of electronic transport is based upon the consideration that the crystalline boundaries have an inherent space charge domain due to the interface. Consequently, the potential barriers to the charge carrier transport occur and the carrier mobilities (especially, electron mobility)are reduced as compared to bulk (single-crystal) materials (the boundary scattering is considered in addition to other scattering mechanisms)[36, 37].

Because, in higher temperature range ($T > T_c$), an exponential and reversible change of electrical conductivity with temperature has been observed, we consider that the studied compounds are advantageous in technology of different types of thermistors.

It is known that in intrinsic conduction domain, the temperature dependence of the electrical resistivity can be expressed by [9, 40, 41]

$$\rho_T = \rho_\infty \exp\left(B/T\right),$$

where ρ_T denotes the resistivity at absolute temperature T, ρ_∞ is a parameter depending at semiconductor nature (formally, ρ_∞ represents the electrical resistivity, at temperature $T \to \infty$) and B is temperature sensibility of the semiconductor.

For a homogeneous semiconducting material, β is given by [29, 40, 41]

$$\beta = \Delta E/2k$$

where ΔE is energy band gap, and k is Boltzmann's constant.

The temperature coefficient at the electrical resistivity, α_T, is defined by the following equation [9, 40, 41]

$$\alpha_T = \frac{1}{\rho}\cdot\frac{d\rho}{dT} = -\frac{\beta}{T^2} \quad (8)$$

The parameter α_T is negative because electrical resistivity decreases with increasing temperature of material above a certain temperature. Also, α_T, is dependent on the temperature.

Table 4. Characteristic parameters of some studied films.

Compound	d (μm)	ΔT_1(K)	B(K)	α_T (K^{-1})	T(K)
EFA.1	0.53	325-400	9101	0.070	375
EFA.2	0.75	330-365	9855	0.076	360
EFA.3	0.60	345-370	10898	0.084	360
EFA.4	0.58	340-365	8811	0.068	360

d, film thickness; ΔT_1, temperature range corresponding to intrinsic conduction domain; α_T, temperature coefficient of the electrical resistivity; B, temperature sensibility

For some heat-treated samples the values of parameters β and α_T (at 350 K) are indicated in the Table 4.

It can be observed from this table that the studied organic compounds are advantageous in the technology of thermistors.

By studying transmission and absorption spectra of organic films, very useful information can be obtained about energy bandgap, characteristics of optical transitions, position of the localized impurity levels, etc[42-44].

Figs. 5 and 6 illustrate the typical transmission spectra at normal incidence for five samples in spectral range 400 nm – 1.300 nm.

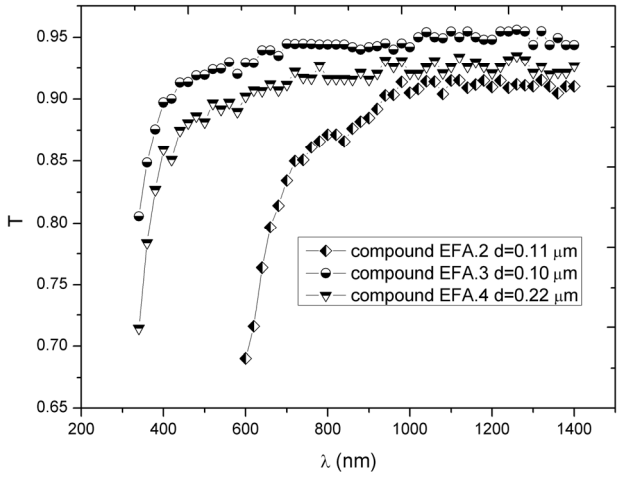


Fig. 5. Transmission spectra for three studied films.

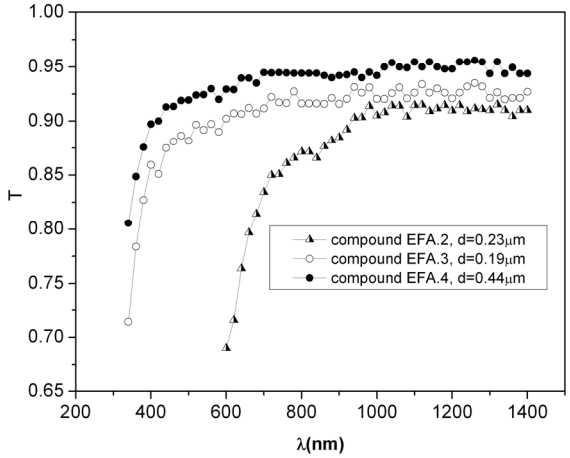


Fig.6. Transmission spectra for three studied films.

It can be observed that for greater wavelengths the studied films have characterized by a higher transparency. Absorption coefficient was calculated from transmission coefficient by taking into account Eq. (1).

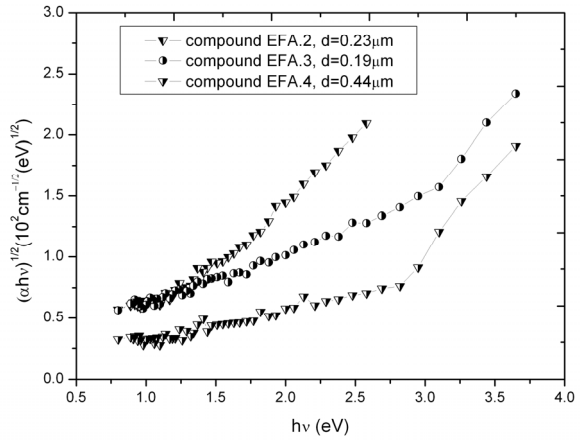


Fig.7. Absorption spectra for indirect transitions

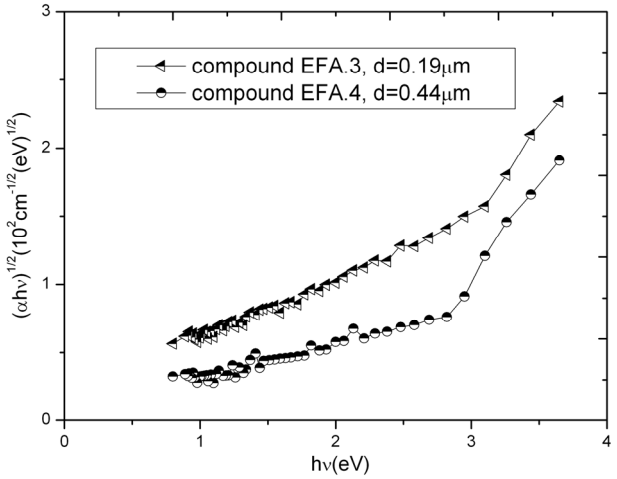


Fig.8. Absorption spectra for indirect transitions.

It is known that for a semiconductor nearly at fundamental absorption edge, the absorption coefficient can be written [9, 21, 37, 42-44] as

$$\alpha h\nu = A\left(h\nu - E_g\right)^{\gamma} \tag{9}$$

where $h\nu$ is incident photon energy, E_g denotes optical energy bandgap, γ is a constant which depends upon, the transition mechanism ($\gamma = 1/2$, for allowed direct transitions, neglecting exciton effects; $\gamma = 3/2$ for forbidden direct transitions; $\gamma = 2$, for indirect transitions, neglecting exciton effects), and A is a characteristic parameter (independent of phonon energy) for respective transitions [43].

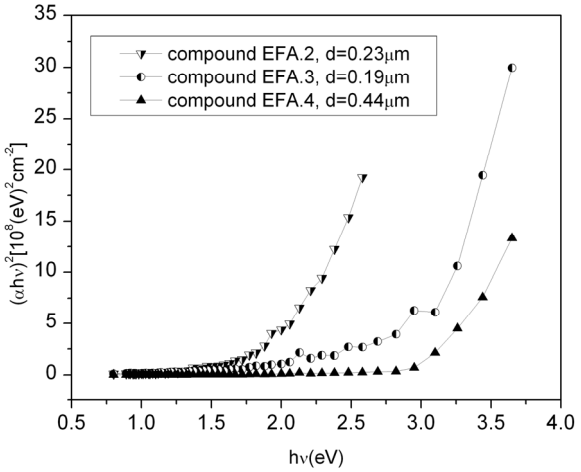


Fig.9 Absorption spectra for direct transitions.

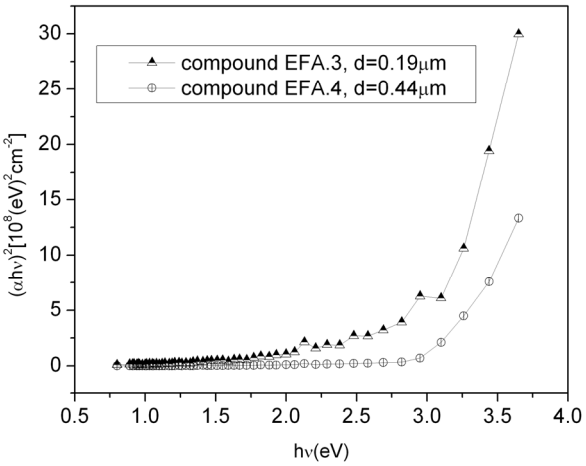


Fig.10. Absorption spectra for direct transitions.

According to Eq. (6), it is possible to fit part of the absorption edge in studied samples to any of the standard dependences of absorption coefficient on the photon

energy $h\nu$, namely, $(\alpha h\nu)^2$ for direct allowed transitions, and $(\alpha h\nu)^{1/2}$ for allowed indirect transitions.

The analysis of our experimental results shows that the $(\alpha h\nu)^{1/2} = f(h\nu)$ dependences are linear for compounds EFA.1, EFA.3 and EFA.4. This fact indicates the indirect nature of fundamental band-to-band transitions.

The values of optical band gap, E_{g0}, have been determined by extrapolating the linear parts of $(\alpha h\nu)^{1/2} = f(h\nu)$ curves to $(\alpha h\nu)^{1/2} = 0$.

For the studied compounds these values ranged between 1.80 eV and 1.95 eV (Table 5).

Table 5. Values of the optical bandgap.

Compound	d (μm)	ΔE (eV)	E_{gd} (eV)	E_{gi} (eV)
EFA.1	0.17	1.58	2.55	1.80
EFA.2	0.23	1.72	1.82	0.85
EFA.2	0.65	1.70	1.85	0.95
EFA.3	0.19	1.90	2.85	1.85
EFA.3	0.54	1.90	2.74	1.95
EFA.4	0.44	1.52	2.82	1.92

d, film thickness; ΔE thermal activation energy of electrical conduction; E_{gd}, optical bandgap (allowed direct transitions); E_{gi}, optical bandgap (indirect transitions neglecting exciton effect)

We consider that for compound EFA.2 optical band-to-band transitions are direct. In this case, the $(\alpha h\nu)^2 = f(h\nu)$ dependences are linear and E_{g0} = 1.82 eV – 1.85 eV. We observe that the values of optical bandgap are in a good agreement with those determined from temperature dependence of the electrical conductivity.

4. Conclusions

The experimental results obtained by studying the temperature dependence of electrical conductivity and absorption spectra can lead to the conclusion that the bandgap representation could explain the electronic transfer mechanisms through the investigated compounds in thin films.

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