

The structure and optical properties of organic semiconductor bulk heterojunction blend (NiPcTs/Alq₃) thin films

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Abstract

The effect of heat treatment on the optical properties of the bulk heterojunction blend nickel (II) phthalocyanine tetrasulfonic acid tetrasodium salt and Tris (8-hydroxyquinolinato) Aluminum (NiPcTs/Alq₃) thin films which prepared by spin coating was described in this study. The films coated on a glass substrate with speed of 1500 rpm for 1.5 min and treated with different annealing temperature (373, 423 and 473) K. The samples characterized using UV-Vis, X ray diffraction and Fourier transform Infrared (FTIR) spectra, XRD patterns indicated the presence of amorphous and polycrystalline blend (NiPcTs/Alq₃). The results of UV visible shows that the band gap increase with increasing the annealing temperature up to 373 K and decreases with increase the annealing temperature to (423, 473)K respectively.

Key words

Organic semiconductors, bulk heterojunction blend NiPcTs /Alq₃ (B.HJ. blend), optical properties, XRD.

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الخصائص التركيبية والبصرية لاغشية الخليط المتباين الهجين (NiPcTs)/Alq₃ الرقيقة

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الخلاصة

في هذه الدراسة تم بيان تأثير المعاملة الحرارية على الخصائص التركيبية البصرية لاغشية المتغاير الهجين (NiPcTs/Alq₃)، والمحضرة بطريقة الطلاء البرمي على قواعد زجاجية بسرعة دوران (1500) دورة خلال 1.5 دقيقة، اجريت المعاملة الحرارية باختلاف درجات الحرارة (373, 423, 473)K. درست خصائص العينات باستخدام قياسات الاشعة السينية و UV-Vis وطيف فورية للاشعة تحت الحمراء FTIR. طيف الاشعة السينية يشير الى خليط من العشوائية والمتعدد التبلور لاغشية المتغاير الهجين. نتائج UV-Vis توضح ان فجوة الطاقة تزداد بزيادة درجة الحرارة الى 373K ثم تتناقص مع زيادة درجة الحرارة الى (423,473)K على التوالي.

Introduction

Organic semiconductors are a portion of materials that gathering between the mechanical and chemical advantages of organic compounds like plastics with the electronic characteristics of semiconducting materials, and that the amendment by chemical synthesis it has the ability to absorb light, conduct electricity, and

emit light is united with a material structure for example, to assign electronic properties such as the desired emission wavelength, to allow for mechanically strong or to becomes it soluble, or, lightweight, and flexible thin film. There are two types of organic semiconductors: low molecular weight materials and polymers [1].

The bulk heterojunctions blend is the two components are intimately

mixed in one layer [2]. As show the Fig.1.

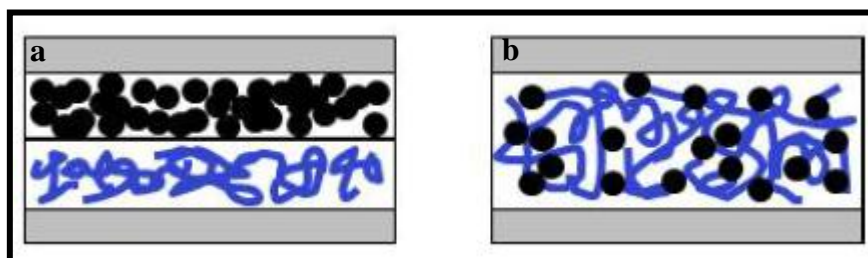


Fig.1: Schematics of examples of (a) bilayer and (b) BHJ blend [3].

The introduction of bi-layer architecture significantly improved the device performance [4, 5].

Today, the most commonly used architecture is the so-called bulk-heterojunction blend (BHJ blend) the first BHJs was presented by the groups of Friend [2] (polymer-polymer solar cells) and Heeger [6], and it has been shown to be superior to earlier architectures. Compared to the bi-layer architecture, the BHJ provides a larger interfacial area between the donor and the acceptor material, which is beneficial for the formation of the charge-transfer state (CTstate) as well as charge separation.

Many BHJ blends are not compatible with elevated production and operation temperatures. Phase separation and crystallization occur once the blend is heated above its glass transition temperature. In many cases, this leads to a detrimental decrease in device performance. The blend transition temperatures can strongly differ from those of the neat components [7-9].

Nickel (II) phthalocyanine tetrasulfonic acid, tetrasodium salt (NiPcTs) is a conjugated molecule. The molecular structure of NiPcTs/Alq₃ which used as quick materials in this work. Attached to the angles of benzene rings in molecular structure of NiPcTs polar NaO₃S and make this compound water soluble as shown in Fig.2a.

Tris(8-hydroxyquinolinato) Aluminum (Alq₃) is the key electroluminescent material presently working in organic light emitting diodes(LED) based on "small molecules" with stable and efficiency photoluminescence (PL) of 25-30% [10].

Alq₃ is well localized on the quinolate {quinoline (organic compound) any of a class of aromatic heterocyclic compounds containing a benzene ring fused with a pyridine ring} connections but donor-acceptor characteristics are due to electron movement between a phenoxide donor side-located HOMO and apyridyl acceptor side-located LOMO of the quinolate ligands.

Alq₃ possesses comparatively high mobility of electrons and low mobility of holes. This difference in mobility is attributed to the distribution of the electronic on a neutral molecule of Alq₃. Due to ionic bonding of aluminum-oxygen, a cloud of excessive electronic density forms of the oxygen as shown in Fig.2b [11]. The study structure and optical properties

Experimental

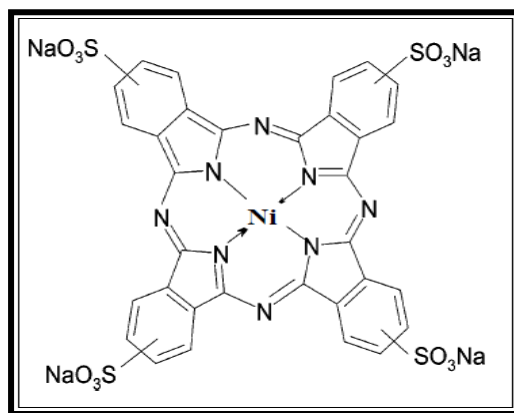
In this work Nickel (II) Phthalocyanine Tetrasulfonic Acid Tetrasodium Salt (NiPcTs) & Tris(8-hydroxyquinolinato) Aluminum (Alq₃) were purchased from Sigma- Aldrich and used without further purification. The molecular formula of NiPcTs is

$C_{32}H_{12}N_8Na_4NiO_{12}S_4$ and has 979.4g/mol molecular weight as shown in Fig.2a, and Tris(8-hydroxyquinolino) Aluminum is the chemical compound of molecular formula $C_{27}H_{18}AlN_3O_3$ and has molecular weight of 459.43 g/mol shown in Fig.2b

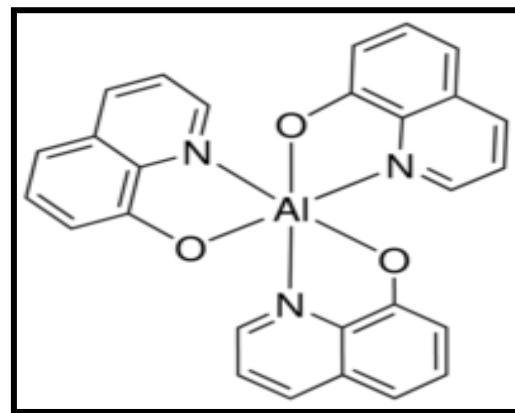
At first, the glass substrate was cleaned in an ultrasonic bath for 10 min using distilled water, followed by rinsing with acetone and alcohol respectively and finally distilled water used again in an ultrasonic bath for

10min. The substrate was dried using nitrogen gas.

The two compound NiPcTs and Alq₃ were grinding using get mortar to get a fine powder, then the powder dissolved in Dimethyl sulfoxide (DMSO) 20 mg/ml, as 10 mg/ml respectively to obtain blend (NiPcTS/Alq₃) solution then putted on a magnetic stirrer for 5 hour by using heat 60 °C. After that using 0.2 μm filters. And it heat plate magnetic stirrer with temperature of 60 °C for 5 hours to get a homogenous solution.



a



b

Fig.2: Strutral formula a. Molecular structure of nickel (II) phthalocyanine tetrasulfonic acid tetrasodium salt (NiPcTs). b. Tris-(8-hydroxyquinoline) aluminum (Alq₃) [11].

Thin film prepared using the CHEMAT SCIENTIFIC SKW-4A2 spin coater. The pattern of X-Ray Diffraction has been plotted the intensity as a function of Bragg's angle .this analysis Using X-ray diffractometric system typ Shimadzu XRD 6000.

The source of radiation was NiPcTs /Alq₃ Cu(K_α) with wave length= 1.5405 Å, the current was 30.0 mA and the voltage 40 kV. The scanning angle 2θ varied in the range of (0-60°).

The lattice parameters of the films were calculated using the Bragg's formula [12]:

$$n\lambda = 2d \sin\theta \quad (1)$$

where n: spectrum order (1, 2, 3...),
λ: wavelength in (nm), d: interplaner spacing, θ: Bragg's angle.

The grain size (G.S) of the crystallites was calculated from the XRD using Scherer's relation [13]:

$$G.S \text{ (nm)} = 0.9\lambda/\beta \cos\theta \quad (2)$$

where: β: Full Width at Half Maximum.

To examine the optical properties of the as-deposited and heat treated BHJ blend (NiTsPc/Alq₃) thin films, Split Beam (internal double beam design) beam Metertech SP-8001UV-Vis NIR spectrophotometer was used in the range (300–800) nm.

The optical energy gap values (E_g^{opt}) for NiPcTs/Alq₃ films have been determined by using Tauc Eq.(1). [14]

$$\alpha E = B(E - E_g)^r \quad (3)$$

where B is a constant, r is a constant whose value depends on the type of transition, where r is equal to 1/2 and 3/2 for allowed and forbidden direct transition, respectively. The constant r is equal to 2 and 3 for allowed and forbidden indirect transition, respectively.

While Fourier-transformed Infrared (FTIR) spectrum for as-deposited and annealed blend (NiTsPc/Alq₃) thin films were recorded the spectrum over the range of 400-4000 cm⁻¹ with resolution 4, the spectra obtained at room temperature and recorded in the transmittance mode using Thermo Scientific™ Nicolet™ iS™10 FTIR Spectrometer.

Results and discussion

The X-Ray diffraction spectra of as-deposited and heat treated BHJ blend (NiPcTs/Alq₃) thin films which are

prepared by spin coating at room temperature were recorded by X-ray diffraction for 2θ in the range between 0 to 60° as shown Fig. 3.

For this figure, one can see that the as-deposited and film annealed at 373 K film show amorphous, structure while the films annealed at 423, 473 K have polymorphism structure, i.e mix between amorphous and polycrystalline structure. The value of the crystallite size was estimated using the Equation:

$$L = \frac{K\lambda}{\beta \cos \theta}$$

where, L is the mean crystallite size, K is the Scherer constant with value 0.94, λ= 1.542 Angstroms is the X-ray source wavelength and β is the FWHM value.

The full width at half maximum (FWHM), interplane distance (d) and crystallites size (G.S) of as-deposited and annealed blend (NiPcTs/Alq₃) thin films are listed in Table 1. It is clear that annealing the sample to 423K decreases the crystallite size.

Table 1: The structural parameters of blend NiPcTs/Alq₃ structural thin films.

T _a k	2θ (exp.) (deg)	FWHM	d (exp.) (Å ^o)	G.S (nm)
RT	Amorphous			
273	Amorphous			
373	26.559	0.187	3.3535	78
473	26.532	0.278	3.3568	42

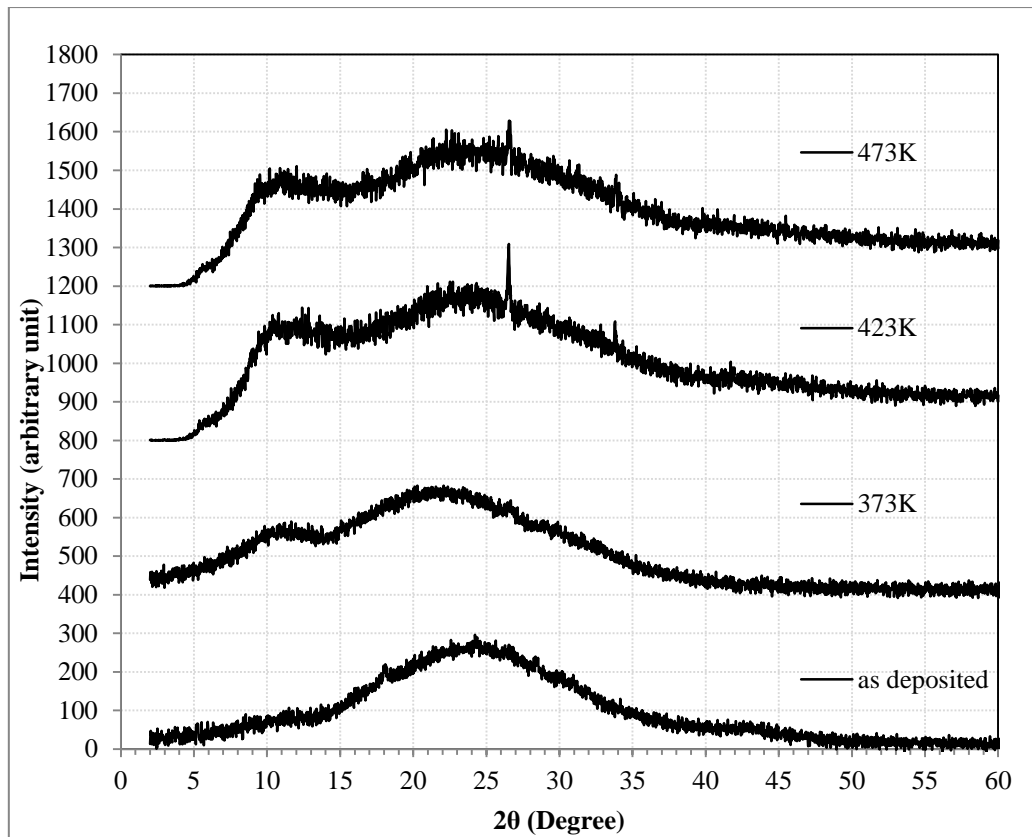


Fig.3: XRD pattern of as-deposited and annealed blend NiPcTs/Alq₃ thin films.

Absorption spectra of the as-deposited and annealed BHJ blend NiPcTs/Alq₃ thin films are shown in Fig. 4. The absorption spectra exhibit two peaks which are B and Q bands. In the Q-band, an intense absorption peak (RT, 373, 423 and 473) K around (614, 611, 613 and 615) nm respectively is due to the transition between the bonding and antibonding ($\pi-\pi^*$) at the

dimer part of the phthalocyanine molecule. While the B-band an intense absorption peaks (RT, 373, 423, 473)K around (343, 335, 342, 345) nm respectively [15].

The absorbance decrease strongly with annealing temperature. The sample to 373 K while returned to increase with further annealing to 423K.

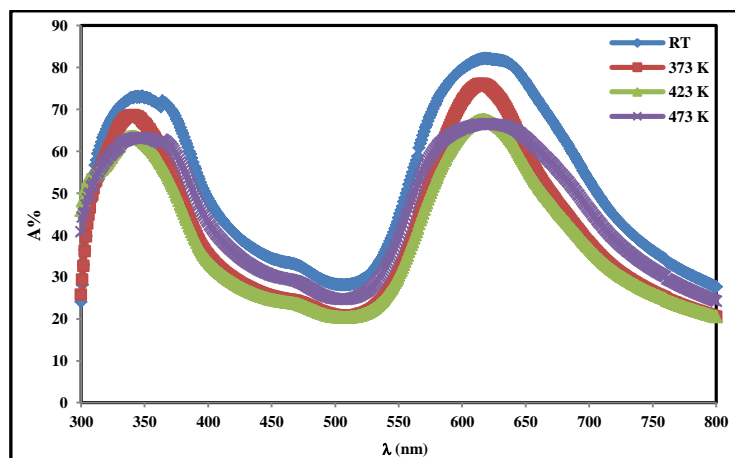


Fig.4: Absorption spectra of as-deposited and annealed blend NiPcTs/Alq₃ thin films.

Some researchers utilized similar research work to enhance the absorption capability of the thin films [16, 17].

The values of E_g^{opt} has been determined using Tauc equation to find transition type by plotting $(\alpha h\nu)^r$ where $r=1/2$ for direct allowed versus photon energy $(h\nu)$ and select the optimum linear part intersect the $h\nu$ axis.

Before heat treatment (E_g^{opt}) belonged to Q and B band respectively is equal to (1.64) eV and (3.04) eV increases to (1.76) eV and (3.26) eV as a result of annealing the sample at 373K.

The optical energy gap for Q-band decreased to (1.74, 1.68) eV with increased annealing temperature to 423 and 473 K as show Fig. 5; the same behavior observed in B-band, the optical energy gap increased from (3.26) eV when the temperature increases to 373 K, while the optical energy gap return to decreased to (3.1, 3.04) eV after increasing the temperature to 423, 473 K respectively although it still above the value of room temperature as show Fig. 6.

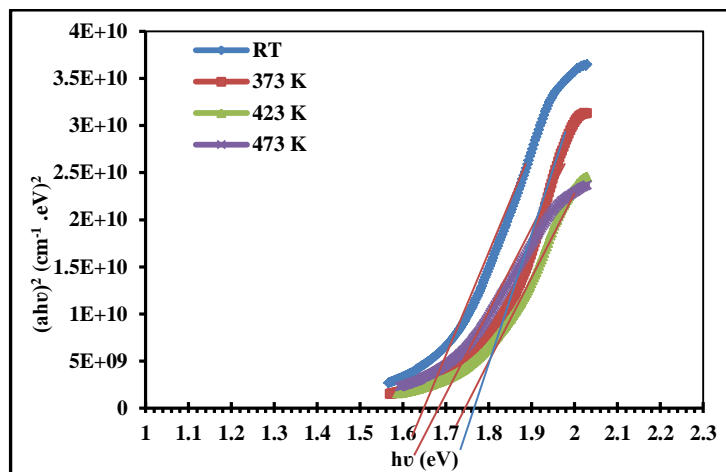


Fig.5: $(ah\nu)^2$ versus photon energy of incident radiation for as-deposited and annealed Blend NiPcTs/Alq₃ thin films (Q-band).

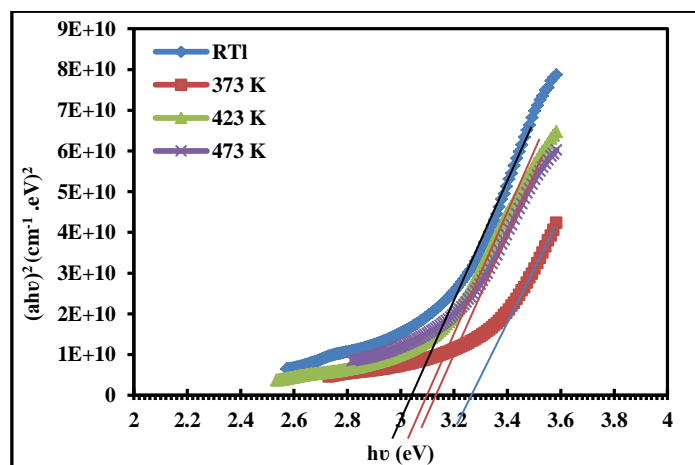


Fig.6: $(ah\nu)^2$ versus photon energy of incident radiation for as-deposited and annealed blend NiPcTs/Alq₃ thin films (B-band).

The FT-IR spectra Fig. 7 for as-deposited and annealed BHJ blend NiPcTc/Alq₃ thin films were measured at different temperatures. FT-IR for blend NiPcTc/Alq₃ thin films shows the bond bending represented by the range (400- 2000) cm⁻¹ while the bond stretching represented by the range (2000-4000) cm⁻¹. One can see a weak peak in the range (400-600) cm⁻¹.

The FTIR absorption spectrum of Alq₃ displays all the characteristic absorbance of quinoline and the Al ion with ligands. For example, the characteristic bands centered at 600-800 cm⁻¹ come from the vibrations of

quinoline, and the band at 400-600 cm⁻¹ can be attributed to the stretching vibration of Al ion with ligands. Compared with the normal FTIR absorption spectrum of quinoline, the intensive band of C-O at 1114.8 cm⁻¹ and the weaken band at 1280.6 cm⁻¹ indicated that the Al-O bond had formed, transformations of aromatic stretching (C=C, 1600–1450 cm⁻¹) and aromatic amine resonance (C–N–C, 1370–1250 cm⁻¹) [18].

The Table 2 shows the types of bonds to the bulk heterojunction blend (NiPcTs/Alq₃) and compare it each compound bonds.

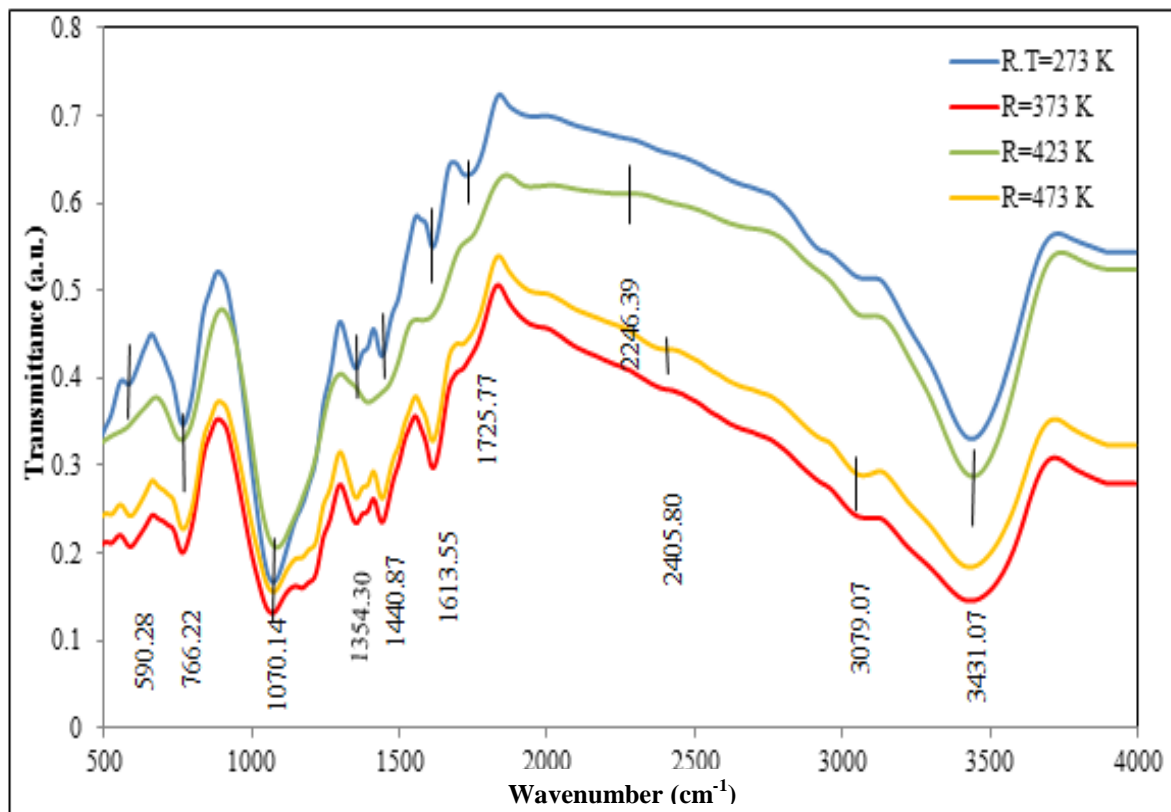


Fig.7: FTIR spectra for as-deposited and annealed blend NiPcTs/Alq₃ thin films.

Table 2: List of the type bond FFIR for blend NiPcTs/Alq₃ films [19-22].

NiPcTs (Tem.) cm ⁻¹	Bond type	Alq ₃ cm ⁻¹	Bond type	Bland (NiPcTs + Alq ₃) cm ⁻¹	Bond type
621.70	Benzene rings	544.86	Ring de., Al-O stretching	590.28	(Nickel – Nitrogen) bond vibration
1064.67	S=O & C-C	644.82	Ring def., Al-O starching	766.22	C-H bond of benzene
1200.29	C-H stretching bond	764.57	Al-O starching vibration	1070.14	PO ₂ symmetric stretching vibration
1402.03	Stretching bonds of Benzene	1039.97	PO ₂ symmetric stretching vibration	1354.30	C-C-H bending vibration
1630.62	C-C aromatic	1246.25	C-O stretching	1440.87	C=C aromatic stretching
2347.23	O-H	1359.68	C-C-H bending vibration	1613.55	C=C aromatic stretching
3439.30	O-H	1473.22	C-O stretching vibration	1725.77	C=C bond
		1595.63	C-C stretching vibration	2246.39	CH ₃ and-CH stretching
				3079.07	C-H and aromatic stretching
				3431.07	C-H and aromatic stretching

Conclusions

- The heat treatment affected on the absorption and energy gap. The energy gap increase at 373K and return decrease at 423, 473K.
- The X-Ray pattern of the prepared hertojunction blend (NiPcTs/Alq₃) also effect by annealing temperature where the structure changing from amorphous to polymorphism.
- The FTIR spectra measurement was applied to know the type of the bonds of NiPcTs/Alq₃ bulk heterojunctions blend thin films.

References

[1] A. Köhler and H. Bässler. Electronic Processes in Organic

Semiconductors: An Introduction. John Wiley & Sons, 2015.

[2] J. J. M Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, Nature, 376 (1995) 498-500.

[3] V.D. Pokhodenko and N. F. Guba. Theoretical and Experimental Chemistry 30, 5 (1995) 203-226.

[4] Y. Gang, J. Gao, Jan C. Hummelen, F. Wudl, A. J. Heeger, Science 270, 5243 (1995) 1789.

[5] N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, G. Stucky, F. Wudl. Applied Physics Letters, 62, 6 (1993) 585-587.

[6] B. R Weinberger, M. Akhtar, S. C. Gau., Synthetic Metals 4.3 (1982) 187-197.

- [7] J. M. G. Cowie and V. Arrighi. Polymers: chemistry and physics of modern materials. CRC press, 2007.
- [8] S. Sono, K. Tashiro, N. Gose, K. Imanishi, M. Izuchi, M. Kobayashi, M. Imai, M. Ohashi, Y. Yamaguchi, K. Ohoyama, Polymer Journal, 31, 8 (1999) 677-686.
- [9] C. Müller, J. Bergqvist, K. Vandewal, K. Tvingstedt, A. S. Anselmo, R. Magnusson, M. I. Alonso. Journal of Materials Chemistry, 21, 29 (2011) 10676-10684.
- [10] J. Kalinowski, V. Fattori, P. Di Macro. Chem. Phys., 266 (2001) 85.
- [11] A. Curioni, W. Andreoni, R. Treusch, F. J. Himpsel, E. Haskal, P. Seidler, C. Heske, S. Kakar, T. Van Buuren, L. J. Terminello. Applied physics letters, 72, 13 (1998) 1575-1577.
- [12] H. P. Myers. Introductory Solid State Physics. Taylor & Francis. ISBN 0-7484-0660-3 (2002).
- [13] E. Pungor and G. Horvai, A practical guide to instrumental analysis. CRC press, 1994.
- [14] S. M. Hasan and R. A. Ahmed. AIASR, 5, 5 (2014) 122-138.
- [15] M. M. El-Nahass, K. F. Abd-El-Rahman, A. A. M. Farag, A. A. A. Darwish. International Journal of Modern Physics, B 18, 03 (2004) 421-434.
- [16] S. Karan and B. Mallik. Solid State Communications 143, 6 (2007) 289-294.
- [17] B. E. Schuster, T. V. Basova, V. A. Plyashkevich, H. Peisert, T. Chassé. Thin Solid Films, 518, 23 (2010) 7161-7166.
- [18] R. J. Curry, W. P. Gillin, J. Clarkson, D. N. Batchelder. Journal of applied physics, 92, 4 (2002) 1902-1905.
- [19] M. Cölle, S. Forero-Lenger, J. Gmeiner, W. Brütting. Physical Chemistry Chemical Physics, 5, 14 (2003) 2958-2963.
- [20] T. Gavrilko, R. Fedorovich, G. Dovbeshko, A. Marchenko, A. Naumovets, V. Nechytyaylo, G. Puchkovska, L. Viduta, J. Baran, H. Ratajczak. Journal of molecular structure, 704, 1 (2004) 163-168.
- [21] C. D. Kanakis, P. A. Tarantilis, C. Pappas, J. Bariyanga, H. A. Tajmir-Riahi, M. G. Polissiou. Journal of Photochemistry and Photobiology B: Biology, 95, 3 (2009) 204-212.
- [22] D. H. Park, N. Kim, C. Cui, Y. K. Hong, M. S. Kim, D. -H. Yang, D. -C. Kim, H. Lee, J. Kim, D. J. Ahn, J. Joo, Chem. Commun., 2011, 47, 7944.