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Annealing effect on the optical properties of organic semiconductor Alq_3: C_{60} blend thin films

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Abstract

The effect of heat treatment using different annealing temperatures on optical properties of bulk heterojunction blend (BHJ) Alq_3: C_{60} thin films which are fabricated by the spin coating technique were investigated in this study. The films have been coated on a glass substrate with speed of 2000 rpm for one min and treated with different annealing temperature (373, 423 and 473) K under vacuum. The optical properties and the chemical bonds structure of blends as-deposited and heat treated have been studied by UV-Vis spectroscopic and Fourier Transform-Infra Red (FTIR) measurements respectively. The results of UV visible show that the optical energy gap decreasing with increasing the annealing temperature for the ratio (100:1) while decreasing with increasing the annealing temperature for ratio (100:10). The FTIR spectra measurement were applied to know the type of the bonds of Alq_3: C_{60} BHJ thin films.

Key words

Organic semiconductor Alq_3: C_{60}, optical properties, heat treatment.

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تأثير التلدين على الخصائص البصرية لآغشية مزيج اشباه الموصلات العضوية Alq_3: C_{60} الرقيق

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الخلاصة

تم دراسة تأثير المعالجة الحرارية باستخدام درجات حرارة التلدين المختلفة على الخصائص البصرية لاغشية المتغاير الهجيني Alq_3: C_{60} الرقيقة التي تم تصنيعها بطريقة تقنية الطلاء البرمي. تم طلاء هذه الأغشية على قواعد زجاجية بسرعة 2000 دورة خلال دقيقة واحدة ومعالجتها بدرجات حرارة تلدين مختلفة (373، 423، 473) كلفن في الفراغ. تمت دراسة الخصائص البصرية وتركيب الاواصر الكيميائية للمزيج غيرالمعالج حرارياً والمعالج حرارياً بواسطة قياسات الأشعة فوق البنفسجية – المرئية (UV-Vis) وقياسات فوريير للتحويل - الأشعة تحت الحمراء (FTIR) على التوالي. تظهر نتائج الأشعة فوق البنفسجية المرئية أن فجوة الطاقة البصرية تتناقص بزيادة درجة حرارة التلدين للنسبة (100:1) وتتزايد بزيادة درجة حرارة التلدين للنسبة (100: 10). تم تطبيق قياس أطياف FTIR لمعرفة نوع وموقع الاواصر لاغشية المتغاير الهجيني Alq_3: C_{60}.

Introduction

Semiconductor materials can be divided into two parts: organic and inorganic materials. In the next years, inorganic materials are expected to be replaced by organic materials because of its properties [1]. In spite of organic semiconducting materials have been synthesized and studied the performance and stability of organic semiconducting materials were poor [2]. The performance of the organic materials can be increased by making improvement in the fabrication of the device rather than focusing on the complexity of the internal structure of the material [3]. Organic semiconductors can be classified according to the molecular size into two categories; small molecules and polymer [4]. Tris-(8-hydroxyquinoline) aluminum (Alq_3) is a π-conjugated small molecule (low-molecular weight) [5], and one of the most important materials between the class of organometallic compounds, which used as an active medium in organic light emitting diodes (OLEDs) [6] as shown in Fig.1(a).

Fullerenes (C_{60}) represent the third allotrope form of pure carbon, after graphite and diamond and have acquired an interest in many fields of science that range from bio applications to molecular electronics [7]. In this research, the optical properties of the blend Alq_3: C_{60} thin films were studied with different concentrations of C_{60}, as shown in Fig.1(b).

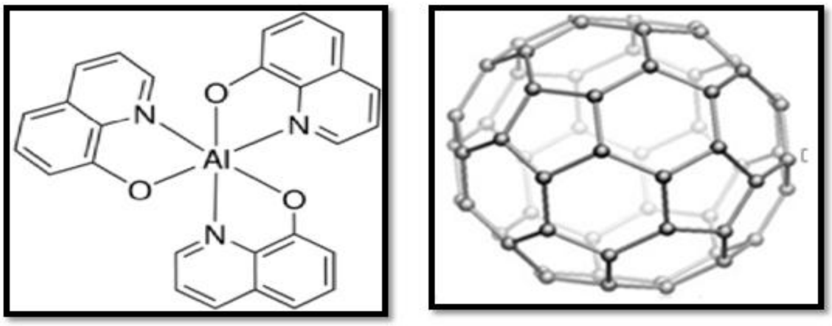

Fig. 1: Chemical structure of (a) Tris-(8-hydroxyquinoline) aluminum (Alq_3) (b) fullerene C_{60} [8, 9].

Experimental work

Tris-(8-hydroxyquinoline) aluminum (Alq_3) and Fullerenes (C_{60}) were purchased from Sigma-Aldrich and used without further purification. The molecular formula of Tris-(8-hydroxyquinoline) aluminum is $Al(C_9H_6NO)_3$ and has 459.441g/mol, while Fullerenes (C_{60}) is 720.66 g/mol. Before deposition the blend, the glass substrate cut to the size of 2.5 cm×2.5 cm after that cleaned in an ultrasonic bath for 10 min, to remove the dirt particles on the substrate surface using different steps with distilled water, liquid soap, a solution of ethanol and acetone. The first blend prepared by dissolving 15 g/ml for Alq_3 in chloroform with 100:1 weigh ratio and 0.15 g/ml C_{60} in toluene while the second blend prepared by dissolving 15 g/ml for Alq_3 in chloroform and 1.5 g/ml C_{60} in toluene with 100:10 weigh ratio. This solution put in a magnetic stirrer for 24 hours at 318 K. Then they filtered using 0.2 and 0.45 micrometer respectively. Finally, the two solutions of Alq_3 and C_{60} were blended together and developed on the stirrer again for 24 hours also to get a homogenous solution. Now the blended solution becomes ready to spin-coated method type CHEMAT SCIETIFIC SKW-4A2 spin coater on the pre-cleaned glass substrate for 2000 rpm for 1 min.

The prepared samples leaved in air for one day then putted in an oven at 343 K for 15min to remove the residual solvent may stay inside the film as Nano bubbles.

The prepared Alq_3: C_{60} thin films were then annealed in a vacuum oven at different temperatures (373, 423 and 473) K to about one hour.

The optical energy gap values (Eg^{op}) for (Alq_3: C_{60}) films have been determined using Tauc Eq.(1) [10]

$$\alpha E = B\left(E - E_g\right)^r \qquad (1)$$

where B is inversely proportional to amorphosity, 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, while r is equal to 2 and 3 for allowed and forbidden indirect transition respectively. While Fourier Transform-Infrared Spectroscopy (FTIR) for heat treatment blend (Alq_3: C_{60}) thin films have recorded the spectrum was over the range of (400-4000) cm^{-1} with resolution 4, the spectra obtained at room temperature and record in the transmittance mode using Thermo Scientific™ Nicolet™ IS™ 10 FTIR Spectrometer.

Results and discussion

The absorption spectra of BHJ blend (Alq_3: C_{60}) thin film spin coated at room temperature and heat treated films at temperatures (373, 423, 473) K were shown in Figs. 2 and 3. This absorption spectrum exhibits a wide absorption band from 365nm to 500nm with an intense absorption peak at around 404 nm. The maximum absorption was observed for BHJ film that as deposited attributed to the charge transition between the bonding and anti-bonding (π–π*). The BHJ film that annealed at 373K shows very low and broad absorption intensity than other annealed films. At higher annealing temperatures, the destabilization of quinoline bonding in the blend structure leads to quench of the absorption intensity [11-13].

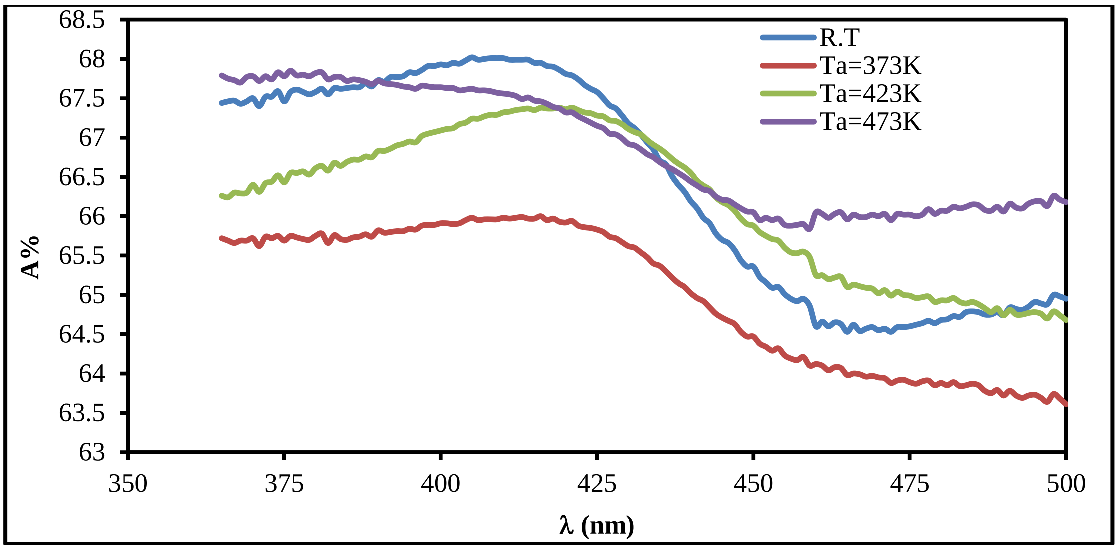

Fig. 2: Absorption spectra of as-deposited and annealed Alq_3:C_{60} thin films (100:1) at different Ta.

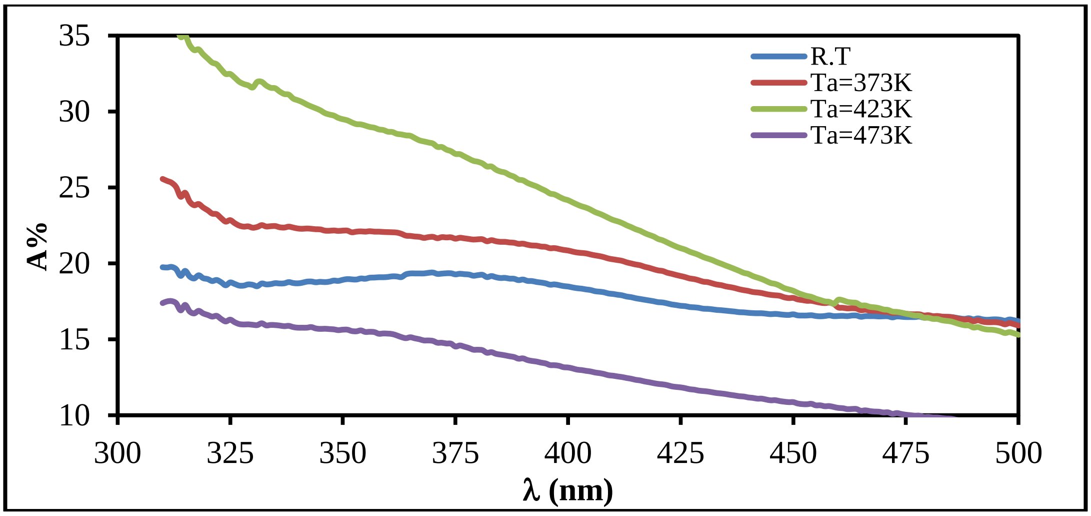

Fig. 3: Absorption spectra of as-deposited and annealed Alq$_3$: C$_{60}$ thin films (100:10) at different Ta.

From Fig. 3, one can note that there is a boarding in absorption peak in UV-region because of increasing in C$_{60}$ concentration which leads to more overlapping between Alq$_3$ and C$_{60}$ [14] Taus equations consider one of the most important means to determine the value of optical energy gap (E_g^{opt}) of the blend Alq$_3$:C$_{60}$. Figs. 4 and 5 show variation of (ahv)^2 as a function to photon energy (hv) of incident radiation for both mixed weight ratio (1:100) and (10:100).

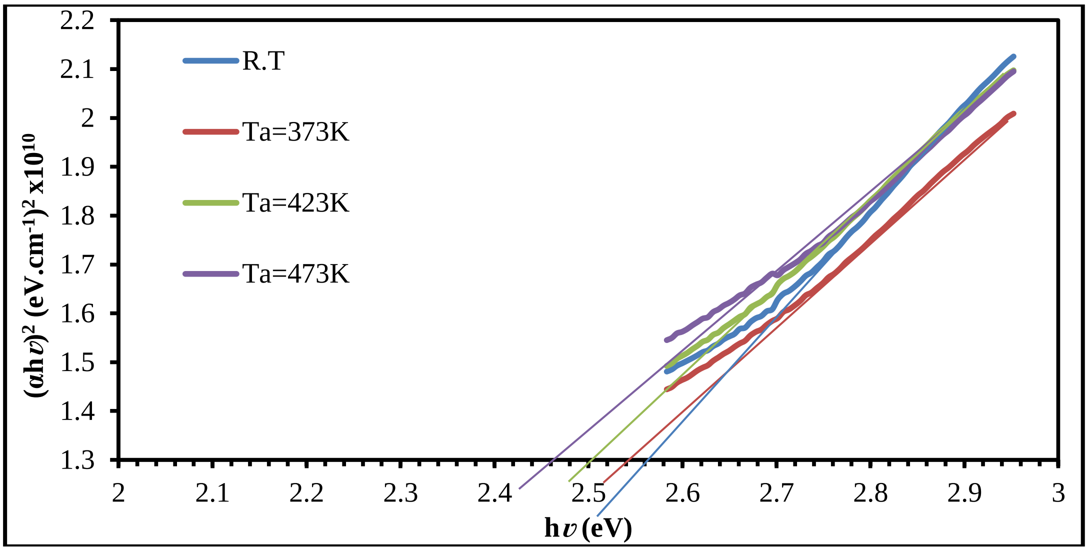

Fig. 4:** **(αhυ)^2 versus photon energy of incident radiation for as-deposited and annealed Alq$_3$:C$_{60}$ thin films (100: 1) at different Ta.

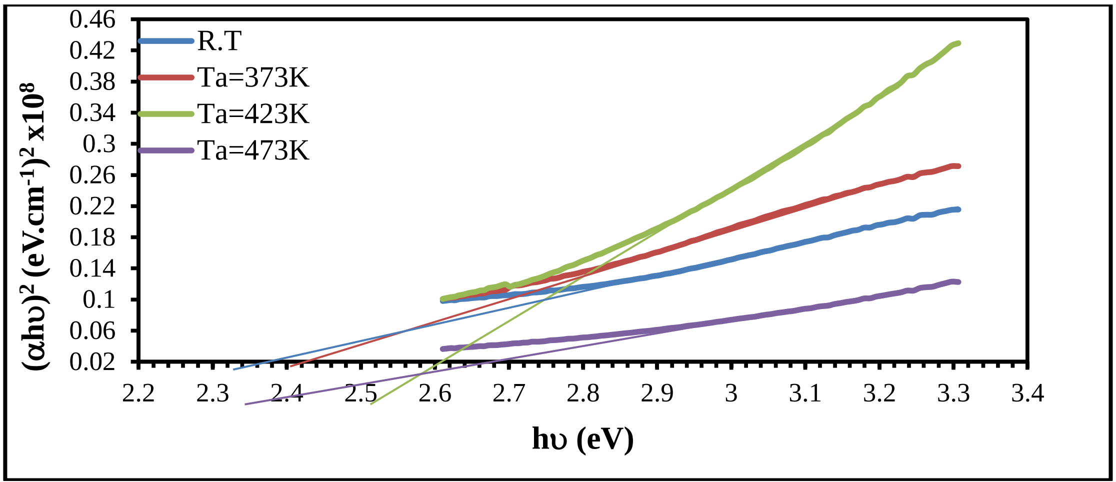

***Fig. 5:** $(\alpha h\upsilon)^2$ versus photon energy of deposited and annealed Alq_3:C_{60} thin films (100:10) at different Ta.*

From Fig.4 and Table 1, the optical energy gap was found slightly decreases with increasing annealing temperatures for the films prepared with a mixed ratio of (100:1) but still in the range between the energy gaps of the two compounds used in these films as indicated from the previous literature. The decrease in E_g attributed to the enhancement in the π–π intermolecular interaction, therefore, lowering the π–π* transition energy [13, 15, 16].

The second mixed ratio of (100:10) as-deposited and annealed thin films also indicate that an increase in optical energy gaps with increasing annealing temperatures from 2.36 eV at room temperature to 2.67 eV at 473 K as shown in Fig. 5 and Table 1.

The increasing in energy gap may be attributed to increasing the concentration of C_{60}, this is may be due to increasing the grain size caused by aggregation of C_{60} molecules in the blend [13, 15, 16].

***Table 1:** The optical energy gaps of as-deposited and annealed Alq_3:C_{60} thin films.*

Alq_3:C_{60}	T_a (K)	E_g (eV)
100:1	RT	2.56
	373	2.54
	423	2.50
	473	2.48
100:10	RT	2.36
	373	2. 42
	423	2. 60
	473	2. 67

The molecular structure of the Alq_3 was confirmed by the analysis of (FTIR) spectra.

Figs. 6 and 7 show the FTIR patterns for Alq_3: C_{60} thin films at both concentration (100:1) and (100:1) at room temperature and treated with different annealing temperatures (373, 423 and 473) K.

The FTIR absorption spectrum of Alq_3 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 between in Table 2 and 3 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}) [13, 15].

The film (100:1) that annealed at 423 K and 473 K indicates sharper C = C and C-N-C aromatic bonds. The blend displays that annealing at 373 K low intense characteristic bands of Alq_3 and C_{60} composite. The quinoline band noticed at 373 K has a lower intensity than the 423 K and 473 K annealed films, which evidence the degradation and partial sublimation of quinoline composites from its aromatic chain [13, 15], as shown in Fig. 6.

The film (100:10) that annealed at 423 K exhibit sharper peak intensity for C = C and C-N-C aromatic bonds. The blend displays low intense characteristic bands of Alq_3 and C_{60} composite that annealing at 373 K and 473K. The quinoline band noticed at 373 K and 473K has a lower intensity than the 423 K annealed films, which evidence the degradation and partial sublimation of quinoline composites from its aromatic chain [13, 15], as shown in Fig. 7.

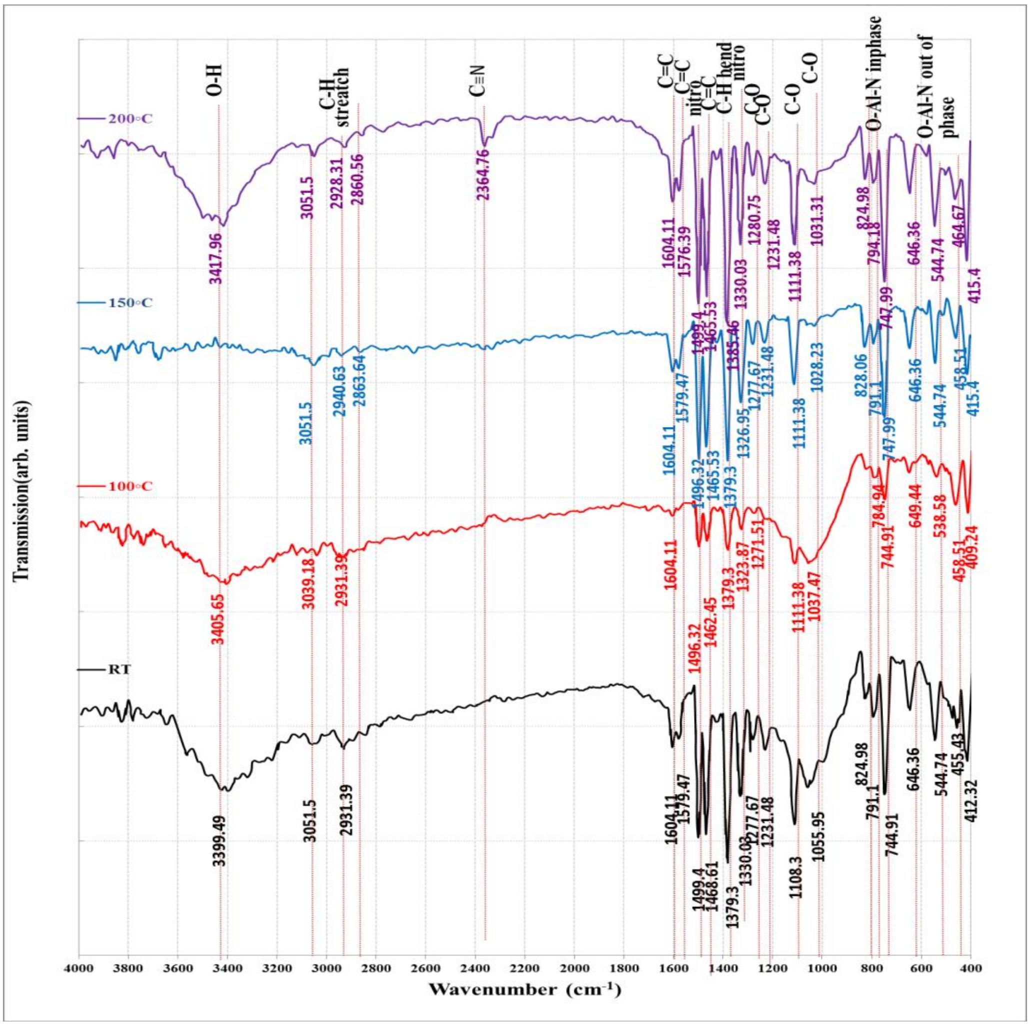

Fig. 6: FTIR for Alq_3: C_{60} thin films at 100:1 treated with different annealing temperatures.

Table 2: FTIR bonds for Alq_3: C_{60} (100:1) treated with different annealing temperatures.

	RT	373 K	423 K	473 K
Stretching Al-N vibration	**412.32**	**409.24**	**415.40**	**415.40**
Stretching Al-O vibration	**455.43**	**458.51**	**458.51**	**464.67**
Stretching Al-O vibration	**544.74**	**538.58**	**544.74**	**544.74**
Stretching Al-O vibration	**646.36**	**649.44**	**646.36**	**646.36**
C-H bending	**744.91**	**744.91**	**747.99**	**747.99**
C-H bending	**791.10**	**784.94**	**791.10**	**794.18**
C-H bending	**824.98**		**828.06**	**824.98**
C-O Strong Stretching	**1055.95**	**1037.47**	**1028.23**	**1031.31**
C-O Strong Stretching	**1108.30**	**1111.38**	**1111.38**	**1111.38**
C-O Strong Stretching	**1231.48**	**1271.51**	**1231.48**	**1231.48**
Aromatic amine	**1277.67**		**1277.67**	**1280.75**
Aromatic amine	**1330.03**	**1323.87**	**1326.95**	**1330.03**
Aromatic C=C bending	**1499.4**	**1496.32**	**1496.32**	**1499.4**
Aromatic amine	**1379.30**	**1379.30**	**1379.30**	**1385.46**
Aromatic stretching C=C	**1468.61**	**1462.45**	**1465.53**	**1465.53**
Aromatic C=C bending	**1579.47**	**1604.11**	**1579.47**	**1576.39**
Aromatic C=C bending	**1604.11**		**1604.11**	**1604.11**
C ≡N				**2364.76**
stretching vibration C-H	**2931.39**	**2931.39**	**2863.64**	**2860.56**
	3051.50	**3039.18**	**2940.63**	**2928.31**
			3051.50	**3051.5**
O-H stretching	**3399.49**	**3405.65**		**3417.96**

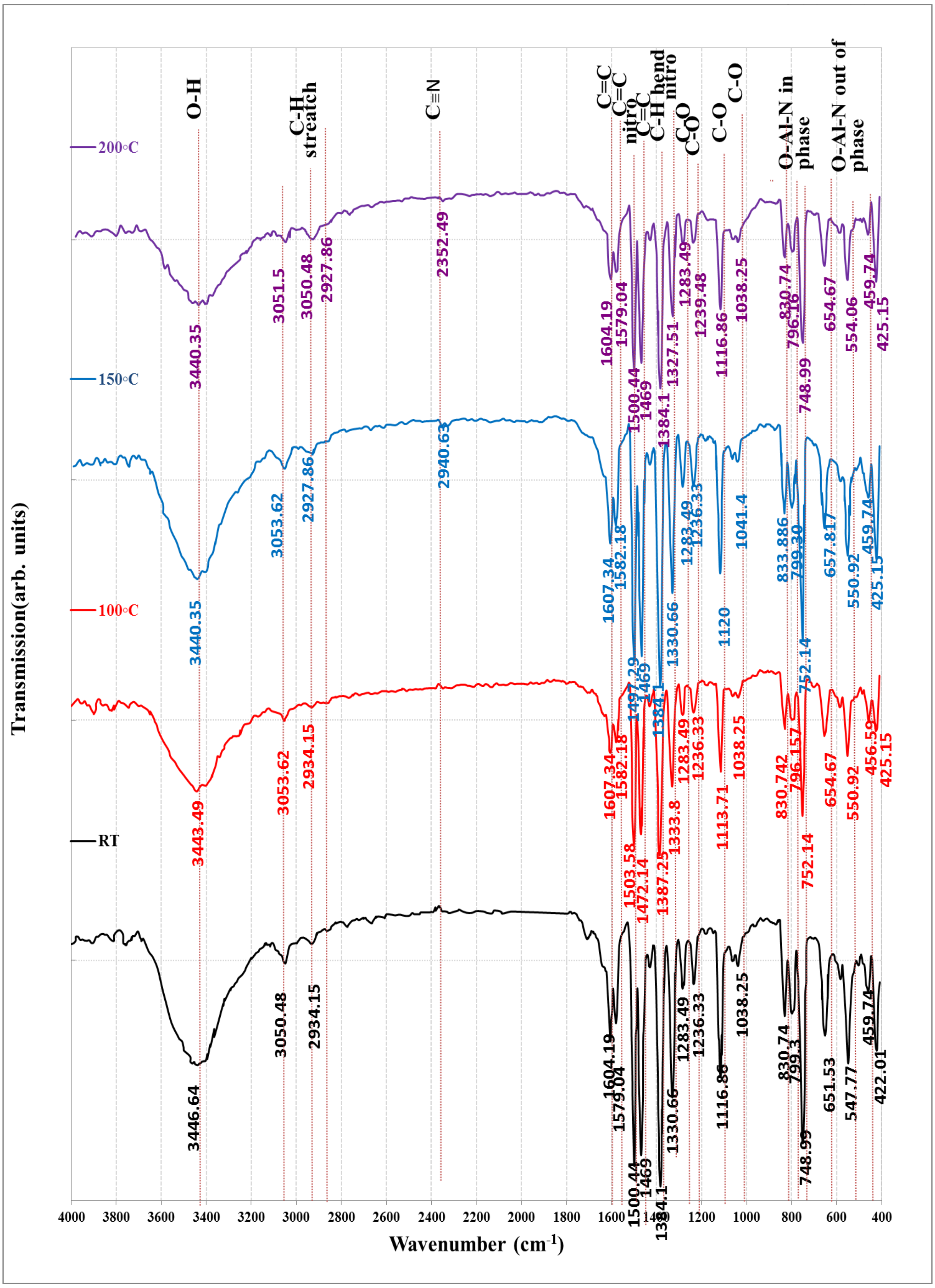

Fig. 7: FTIR for Alq_3: C_{60} thin films at 100:10 treated with different annealing temperatures.

Table 3: FTIR bonds in for Alq_3: C_{60} (100:10) treated with different annealing temperatures.

	RT	373 K	423 K	473 K
Stretching Al-N vibration	422.01	425.15	425.15	425.15
Stretching Al-O vibration	459.74	456.59	459.74	459.74
Stretching Al-O vibration	547.77	550.92	550.92	554.06
C-H bending	651.53	654.67	657.817	654.67
C-H bending	749.00	752.14	752.14	748.99
	799.30	796.16	799.30	796.16
	830.742	830.742	833.89	830.74
C-O strong stretching	1038.25	1038.25	1041.40	1038.25
C-O strong stretching	1116.86	1113.71	1120.00	1116.86
C-O strong stretching	1236.33	1236.33	1236.33	1239.48
Aromatic amine	1283.49	1283.49	1283.49	1283.49
Aromatic amine	1330.66	1333.80	1330.66	1327.51
Aromatic C=C bending	1500.44	1503.58	1497.29	1500.44
Aromatic amine	1384.10	1387.25	1384.10	1384.10
Aromatic C=C bending	1469.00	1472.14	1469.00	1469.00
	1579.04	1582.18	1582.18	1579.04
	1604.19	1607.34	1607.34	1604.19
C ≡N			2358.78	2352.49
C-H stretch	2934.15	2934.15	2927.86	2927.86
	3050.48	3053.62	3053.62	3050.48
O-H	3446.64	3443.49	3440.35	3440.35

Conclusions

- The heat treatment affected on the absorption and optical energy gap. The energy gap slightly decreases for the first mixed ratio of 100:1 and return increasing in the second mixed ratio of 100:10 with increasing annealing temperatures, this is may be due to increasing the grain size caused by aggregation of C_{60} molecules in the blend.
- The FTIR spectra measurement were applied to know the type of the bonds of Alq_3: C_{60} BHJ thin films at 100:1 and 100:10 ratio.

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