The effect of nano sized Alq_3 on the external quantum and power conversion efficiencies of OLEDs

M M Duvenhage[1], O M Ntwaeaborwa[1], E Wrzesniewski[2], J Xue[2] and H C Swart[1,3]

[1]Physics Department, University of the Free State, P.O. Box 339, Bloemfontein, 9300, South Africa
[2]Department of Materials Science and Engineering, University of Florida, USA

[3]Email: swarthc@ufs.ac.za

Abstract Alq_3 is widely used in organic light emitting diodes (OLEDs) as emission and electron transport layer. Commercial Alq_3 is normally used in the fabrication of OLEDs. In this study nano sized Alq_3 was synthesized using a co-precipitation method and it was purified using temperature gradient sublimation. The Alq_3 was then used to fabricate a simple two layer OLED with a device structure: ITO/NPB/Alq_3/Cs_2CO_3:Al. The electroluminescence (EL) spectrum of the device consisted of a broadband with a maximum at ~520 nm and was similar to the photoluminescence (PL) spectrum observed from the synthesized Alq_3 powder. The luminance (*L*)–current density (*J*)–voltage (*V*) characteristics of the device showed a turn on voltage of ~ 2V, which was lower than the current density of the device fabricated using the commercial Alq_3. The external quantum efficiency (η_{EQE}) and the power conversion efficiency (η_P) of the device were 1% and 2 lm/W, respectively.

1. Introduction

Since its first report in 1987 by Tang and Van Slyke [1], tris-(8-hydroxy-quinoline) aluminium (Alq_3) has been used in organic light emitting devices (OLEDs) both as a green light emitting material and an electron transporting layer (ETL). An OLED device consists of an electroluminescent (EL) medium of thin organic layers (<0.2 µm) sandwiched between two electrodes. Some organic layers transport holes and others electrons. When a potential difference is applied between the anode and the cathode the holes and electrons will migrate towards the oppositely charged electrode. Holes and electrons will then be transferred to the emitting material forming tightly bound excitons which emit photons upon relaxation. These photons are then capable of escaping from the device architecture through the transparent anode and out the glass substrate.

In this study we have synthesized nano-sized Alq_3 for use in fabricating OLEDs by thermal evaporation process. Thermal evaporation utilizes high vacuum and direct heating of materials to deposit nanoscale layers of material onto a desired substrate and is an ideal technique for the deposition of organic small molecules due to the fine control and relatively gentle method of deposition. A description of this method and the tools necessary are presented.

In this study Alq_3 was used as both the ETL and emitting layer (EML) of the OLED, while commercial N,N'-di(naphthalen-1-yl)-N,N'-diphenyl-benzidine (NBP) was used as the hole transporting layer (HTL). Indium tin oxide (ITO) coated onto a glass substrate was used as the anode, while the Al:Cs_2CO_3 top electrode was used as the cathode. The devices fabricated using the synthesized Alq_3 are compared with those fabricated using the commercially available Alq_3. Furthermore, the current-voltage-luminance characteristics were also measured and the external quantum and power efficiencies of the two devices are compared.

---

[3] To whom any correspondence should be addressed.

2. Experimental

2.1 Synthesis and purification of Alq_3

Alq_3 phosphor powder was synthesized using the co-precipitation method. 0.625g of 8-hydroxyquinoline (8-Hq) was added to a mixture of 6.5 ml H_2O and 6.5 ml of glacial acetic acid. The mixture was stirred for 15 minutes. 0.5 g of $Al(NO_3)_3$ was added to 20 ml of H_2O and this mixture was also stirred for 15 minutes. The $Al(NO_3)_3$ solution was added drop wise to the 8-Hq solution with vigorous stirring. The resulting brown solution was stirred for 15 minutes. 5 ml of NH_4OH was added drop wise to the solution while stirring vigorously. A yellow green precipitate was formed. The precipitate was filtered and washed 8 times with distilled water. The precipitate was dried in an oven overnight at 80°C. After drying, the precipitate was ground to get a fine powder. The powder was dissolved in 10 ml acetone and left to recrystalize in air at room temperature.

During purification of Alq_3, three quartz tubes (segments) were used. These tubes were placed in an outer quartz tube. 0.394 g of raw material was loaded in the first segment. The outer quartz tube was sealed with quartz wool to prevent any solids from entering the vacuum pumps. The tube was connected to a roughing pump and turbo molecular pump and was evacuated to a pressure of 2×10^{-6} Torr. The second segment was heated to 150 °C in 90 minutes. The first segment was heated to 50 °C above this temperature and segment three was heated to 50 °C below this temperature, yielding a temperature gradient of 100 °C over the segments. The setup was left for 24 hours. After that the heaters were switched off and the system was allowed to air cool back to room temperature. Impurities were left in the first segment and had a dark brown color, while the purified Alq_3 crystals were collected in the second segment (bright yellow color). Almost no material was present in the third segment. Segment two was harvested for purified material and 0.140 grams (35.53%) of the material was yielded. The impurities yielded almost 15% and 50% of the raw material was lost during the purification.

2.2 Fabrication of OLEDs

Glass substrates precoated with an indium tin oxide (ITO) anode (sheet resistance ~ 20 Ω/sq) were degreased in detergent and de-ionized water, and cleaned with ultrasonic baths of acetone and isopropanol consecutively for 15 minutes each. The substrates were then exposed to an ultraviolet-ozone ambient for 15 minutes immediately before loading into a high vacuum thermal evaporation system (base pressure ~ 3×10^{-7} Torr). All the organic and metal layers were deposited successively without breaking the vacuum. The device structure consisted of ITO/NPB/Alq_3/Cs_2CO_3:Al layers and they are shown in figure 1. The NPB and Alq_3 layers were 50 nm thick each, the Cs_2CO_3 layer was 1nm and the Al layer was 80 nm thick.

Figure 2 shows the energy level diagram of the fabricated OLED device [2]. A barrier for electron injection is commonly present at the metal-organic contact when the work function of the metal is larger than the lowest unoccupied molecular orbital (LUMO) of the organic materials, the use of a low work function metal is highly desirable to facilitate the injection of electrons. By adding sub-monolayer amounts of LiF or Cs_2CO_3 between the cathode and ETL, the work function of the metal can be decreased dramatically [3]. Electrons are injected from the cathode (Al:Cs_2CO_3) into the Alq_3 layer, which acts as the ETL. The hole-injecting contact requires a metal of high work function to match the highest occupied molecular orbital (HOMO) of the organic hole transporting layer. This contact must also be transparent to permit light to exit the device in an effective manner. Most OLEDs rely on the transparent and conductive indium tin oxide (ITO) as the anodic material to facilitate the hole-injection. The work function of ITO ranges from 4.5 to 5.0 eV [4] and is strongly dependant on the methods of surface treatment. Treatment of ITO glass substrates using UV-ozone substantially increases its work function and also enhances the hole-injection from the ITO anode into the HTL. Holes are simultaneously injected from the anode (ITO) into the NPB layer, which acts as a hole transporting layer. The Alq_3 layer acts as the emissive layer and electron-hole recombination takes place just next to the interface between Alq_3 and NPB on the Alq_3 side. During recombination photons with the wavelength of 520 nm are released.

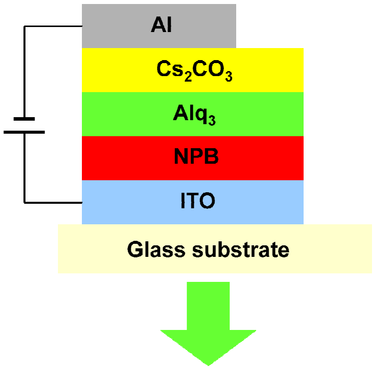

Figure 1: Schematic illustration of the device structure.

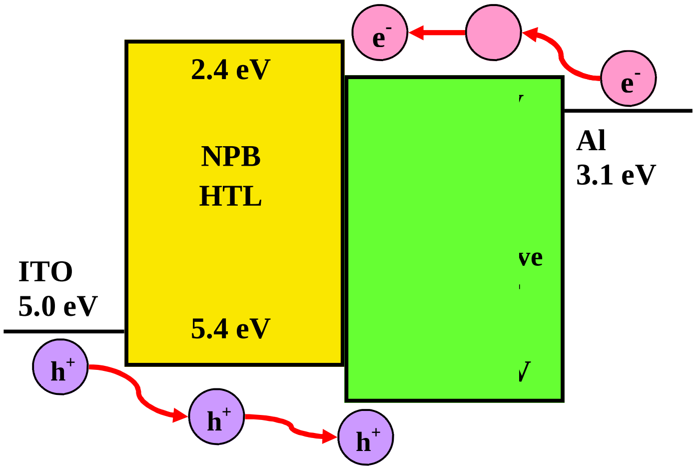

Figure 2: Energy level diagram of the fabricated OLED.

2.3 Characterization

The average particle size of the samples was estimated from the XRD data recorded using a Bruker D8 Advance Diffractometer equipped with a Cu Kα source. Luminance (*L*)–current density (*J*)–voltage (*V*) measurements were conducted in ambient conditions using an Agilent 4155C semiconductor parameter analyzer and a Newport 818-UV photodetector. The luminance of the OLEDs was calibrated using a Konica Minolta LS-100 luminance meter assuming a Lambertian emission pattern. Electroluminescence (EL) spectra were recorded using an Ocean Optics Jaz spectrometer.

3. Results

The crystallanity of the Alq_3 powders was determined by XRD and the spectrum is shown in figure 3. The peaks are in agreement with the data reported by Mao et al [5], confirming that the chemical compund we synthesized was indeed Alq_3. The standard data available on various XRD databases for Alq_3 does not match with the sample, because the standard data that was reported by Taylor et. al. [6] in 1973 was for tris(quinolin-8-olato)titanium(III) (Tiq_3) and not for Alq_3. There is therefore a mismatch between the standard data referenced in JCPDS 26-1550 with the Alq_3 sample prepared in this study. Peaks marked with an arsterik (*) are not yet identified at present. The average particle size determined by using Schrerrer's equation was found to be 40 ± 4 nm.

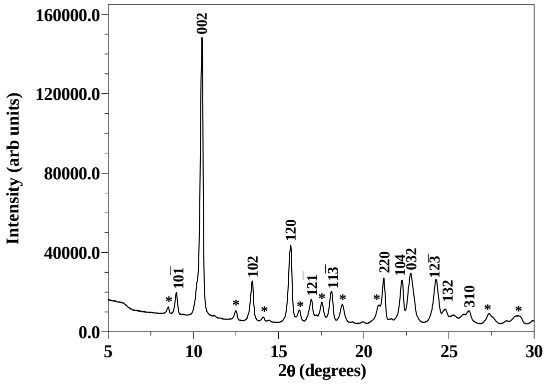

Figure 3: XRD spectra of Alq_3 after recrystalized in acetone.

A potential difference of 4 V was applied to the OLED at a constant current of 400 µA and the electroluminescence (EL) of the device was measured. The device's EL was compared to a device fabricated with commercial Alq_3. The normalized EL curves are shown in figure 4. Both devices show emission at 520 nm. This emission is consistent with the photoluminescence (PL) data reported previously [7] for nano sized Alq_3 powder.

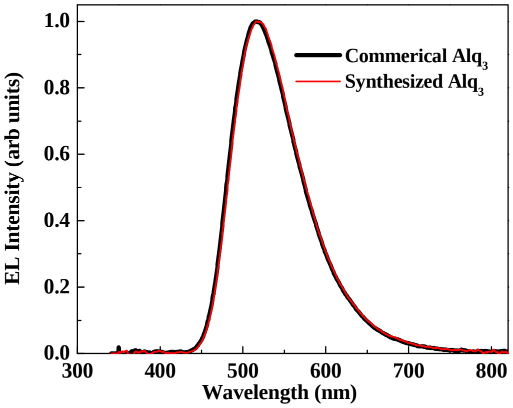

Figure 4: The EL spectra of commercial and synthesized Alq_3, both are showing a broad emission peak with a maximum at 520 nm.

Figure 5 compares the *L-J-V* characteristics of OLED devices fabricated using the synthesized and commercial Alq_3. Both devices were found to have a turn on voltage of ~ 2 V. The current density of the device fabricated using the commercial Alq_3 was higher than that of the one fabricated with the synthesized Alq3. The luminance of the commercial Alq_3 device was 1.5× more intense than that of the synthesized Alq_3 device. The luminance of both devices dropped to 0 cd/m^2 at 10 V, pointing to a complete breakdown of the device. The external quantum efficiency (η_{EQE}) and power conversion efficiency (η_P) were calculated based on the methods recommend by Forrest et al [8] and the plots of η_{EQE} and η_P versus luminance are shown in figure 6. Both devices show a maximum η_{EQE} of just above 1%. This is consistent with other η_{EQE} values reported for devices fabricated with commercial Alq_3 [9]. The η_P value at 100 cd/m^2, which is an important luminance level for display devices, was about 2.5 lm/W for the commercial Alq_3 device and it dropped to 2 lm/W for the synthesized Alq_3 device. This is an indication that the synthesized Alq_3 layer degrades faster, especially under high voltages. This might be due to some impurities like hydroxyquinoline and Al-O compounds which were probably still present in the Alq_3 even after purification.

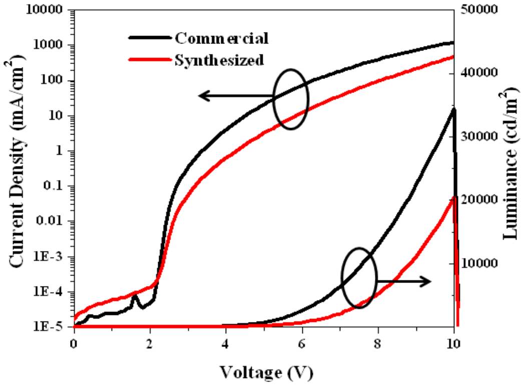

Figure 5: *L-J-V* characteristics of the OLEDs.

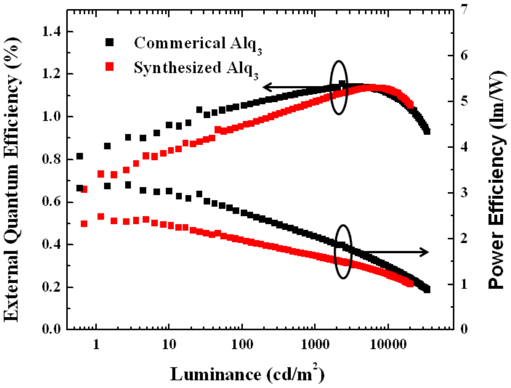

Figure 6: η_{EQE} and η_P as a function of luminance for the two devices.

4. Conclusion

Alq_3 powder was successfully synthesized using the co-precipitation method. The XRD measurements confirmed that Alq_3 with an average particle size of 40 ± 4 nm was synthesized successfully. Both devices' normalized EL spectra showed emission at 520 nm and this corresponds with reported PL results. Both devices have a turn on voltage of 2 V. The synthesized Alq_3 device has lower current density, luminance and η_P values compared to the commercial Alq_3 device. These lower values are an indication that the synthesized Alq_3 layer degrades faster, especially under higher voltages. The reason for the degradation could be due to residual impurities that could not be removed by purification. The η_{EQE} and η_P can be increased by using Alq_3 just as ETL and using a host like 4,4'-bis(9H-carbazol-9-yl)biphenyl (CBP) doped with a green dopant like tris(2-phenylpyridine)iridium (Ir(ppy)3).

Acknowledgements

The authors wish to thank the National Research Foundation (NRF), the Cluster program of the University of the Free State and the Photonic Initiative of South Africa (PISA) for their financial support.

5. References

[1] Tang C W and Vanslyke S A 1987 *Appl. Phys. Lett.* **51** 913
[2] Lin T C, Hsiao C H and Lee J H 2005 *Proc. of SPIE* **5937** Q1
[3] Shabeen S E, Jabbour G E, Morrell M M, Kawabe Y, Kippelen B and Peyghambarian N 1998 *J. Appl. Phys.* **84** 2324
[4] Hung L S and Chen C H 2002 *Mater. Sci. Eng.* **R 39** 143
[5] Mao C J, Wang D C, Pan H C and Zhu J 2011 *J. Ultrason. Sonochem.* **18** 473
[6] Taylor F and Wilkins J 1973 *Chem. Soc. Dalton Trans.* **1** 87
[7] Duvenhage M M, Ntwaeaborwa O M and Swart H C 2012 *Physica B-Condensed Matter* **407** 1521
[8] Forrest S R, Bradley D D C and Thompson M E 2003 *Adv. Mater.* **15** 10
[9] Lee Y H, Kim W J, Kim T Y Jung J, Lee J Y, Park H D, Kim T W and Hong J W 2007 *Curr. Appl. Phys.***7** 409