Performance of Synthesized Metal Chelate Complex of Tris- (8-hydroxyquinoline) Aluminum (Alq_3) in Fabrication of OLEDs

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Abstract:

The metal chelate complex of aluminum 8-hydroxyquinolines (Alq_3) is an important electro-luminescent (EL) material used in fabricating organic light emitting (OLEDs). In this work, diodes / displays using in house synthesized Alq_3 and simple structure have been fabricated. It is demonstrated that luminance of 12460 cd/m^2 and efficiency of 3.1 cd/A are achievable in these fluorescent devices. Possible degradation effects are analyzed.

1. Introduction

The synthesis of better materials, understanding of physics behind the EL, experiments with device structure and developments of better encapsulation schemes have led to improved efficiency and lifetime in OLEDs. The lifetime of more than 2,20,000 hours operating at brightness of 150 cd/m^2 have been reported [1]. These are positive developments and further understanding and improvements will take this technology in the realm of real commercial world. Alq3 is an important basic material used in organic devices. Since the first report of EL in Alq_3 by Tang and VanSlyke [2], this material has proved itself to be an important one in fabrication and understanding the physics of OLEDs. Basically, it is an organic semiconductor with strong electroluminescence in green region of visible spectrum. It has also found applications as a good electron transport material in electro-phosphorescent devices. Further, it acts as an efficient host material for both fluorescent and phosphorescent dyes [3] in the singlet and triplet spin statistics study experiments. Above all, it is quite easy to synthesize this material in few steps in comparison to tedious routes generally followed in the synthesis of polymers.

In this work, Alq_3 has been synthesized using a simple route as given in a report [4]. The electronic structure and interaction of Alq_3 molecules have been studied using a combination of spectral investigations such as FTIR and NMR, PL and EL spectra. The OLEDs have been fabricated using the synthesized material and their I-V, L-V characteristics are evaluated with respect to their effect on the performance of devices. It is demonstrated that the technology provides low cost solutions for low information content displays like 7-segment displays.

2. Results

2.1 Synthesis

The chemical structure of the Alq_3 molecule is shown in Fig.1. Alq_3 is a metal chelate composed of one metal aluminum ion (Al^{3+}) and three 8-hydroxyquinoline (HQ) molecule. In Alq_3 molecule, the electron structure of Al^{3+} is $1s^2 2s^2 2p^6$, a metal ion structure similar to inert gas atom, so Alq_3 has good stability in dry atmosphere.

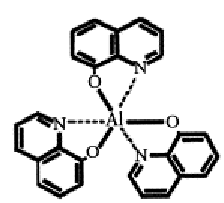

Fig. 1. The structure of Alq_3

The fundamental principle of the synthesis of Alq_3 is to combine HQ anion with Al^{3+} in its aqueous solution. Alq_3 is precipitated under the optimum condition by adjusting pH value of solution. The aqueous solution of aluminum nitrate was chosen as Al^{3+} ion. Liquor Ammonia was used to adjust the pH value of the solution. The degree of chemical reaction depends on the acidity and alkalinity of reactive materials. The pH value of approximately 8 is maintained during complete precipitation of Alq_3. The chemical reaction during the synthesis of Alq_3 is given below.

$$C_9H_7NO + Al^{3+} + OH^- \longrightarrow C_{27}H_{18}AlN_3O_3\downarrow + H_2O$$

The end product yield is more than 90%. The IR and ^{1}HNMR spectra of the material are given in Fig 2 and 5 respectively which are in broad agreement with standard Alq_3 spectra.

2.1.1 The infrared (IR) spectra of Alq3

The IR spectra of Alq3 are shown in Fig. 2. The broad characteristic peak at 3366 cm^{-1} corresponding to OH^- stretching vibration confirms that the Al-O bond is coordinate and not ionic. The peak centered at 3052 cm^{-1} is attributed to the stretching vibration of C- H

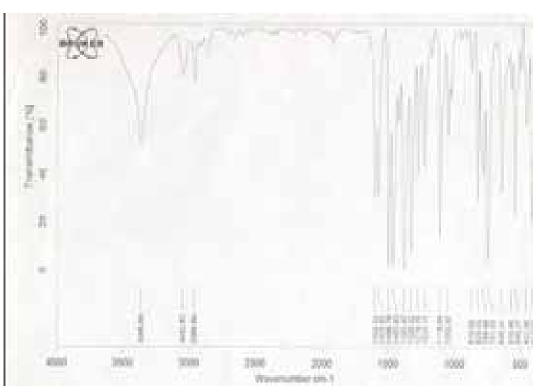

Fig. 2 Infrared Spectra of Alq_3

bond in aromatic ring. Another vibrational mode at 1670 and 1604 cm^{-1} are assigned to the skeleton stretching vibration of - C= C- bond in aromatic ring. The prominent peaks at 1588, 1550, 1467 and 1400 cm^{-1} which are characteristic of the absorption vibration of the aromatic ring. The peaks at 1390 and 1328 cm^{-1} are attributed to the stretching vibration of -C-N bond. C- O at 1279 and 1251 cm^{-1} are weaker and narrower than the homologous peaks of HQ. The characteristic peaks of quinolinic rings from 600 to 800 cm^{-1} labeled the existence of quinolinc rings.

2.1.2 The hydrogen nuclear magnetic resonance(^{1}HNMR) spectra of Alq3

In order to study the local molecular structure of this chelate and interaction between Al^{3+} and the ligand in Alq_3 molecule, the investigation of ^{1}HNMR of Alq_3 and HQ were performed by using the Joel Jmm Lamda- 400 nuclear magnetic resonance spectrometer with a test frequency of 400MHz at room temperature. The solvent is deuterium chloroform solution ($CDCl_3$). The ^{1}HNMR spectra of HQ used in the synthesis is shown in Fig. 3.

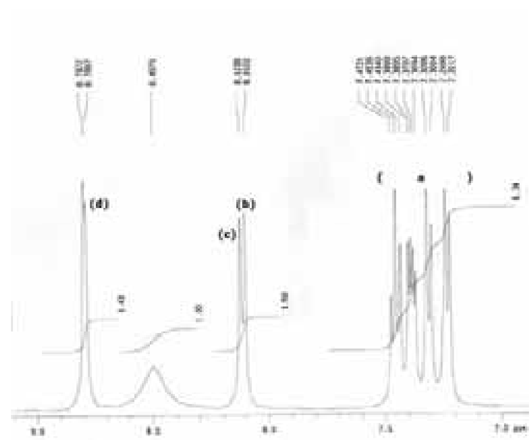

Fig. 3 ^{1}HNMR spectra of HQ

There are four environments of H atoms in HQ molecule, namely a, b, c and d, [5] as shown in Fig.4. These environments are represented by corresponding peaks as marked in ^{1}HNMR spectra of HQ shown in Fig. 3.

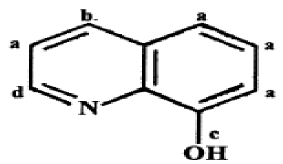

Fig. 4 Structure of HQ

The [1]HNMR spectra of Alq_3 synthesized from same material is shown in Fig. 5.

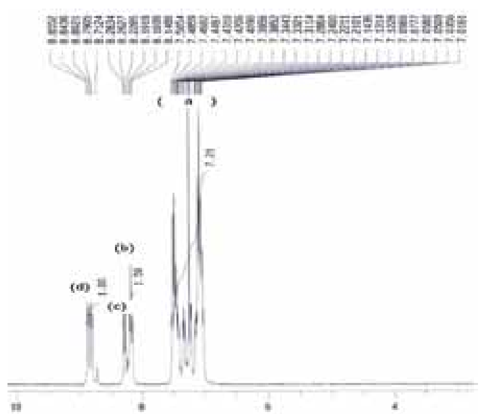

Fig. 5 [1]HNMR spectra of Alq_3

The peaks corresponding to different HQ sites are also present in this spectrum. There is little positive chemical shift in d (0.06), c (0.16), b (0.12) and a (0.03) signifying their interaction with Al^{3+} ion. There are few extra peaks observed in the NMR spectra of Alq_3. Some of these are also present in the spectra of HQ.

2.1.3 PL & EL spectrum of Simple OLED

Simple devices having structure of ITO/PEDOT/Alq_3/Ca/Al using the synthesized material have been fabricated to see the effect of pure material on electro-luminescence. The primary EL peak is observed at 524 nm. This primary EL peak has been seen varying its position from 521 to 546 nm in different run of synthesis. There is also a secondary peak observed at 503 nm as seen from the EL Spectrum in Fig.6.

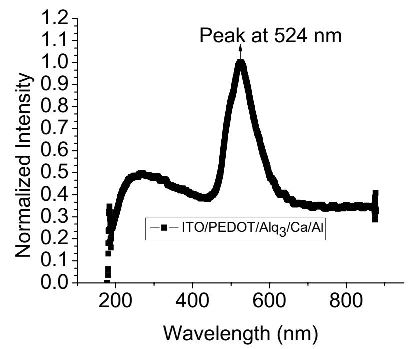

Fig.6 EL Spectrum of ITO/PEDOT/ Alq_3/Ca/Al OLED

Similar peaks are observed in the PL spectrum as shown in Fig.7.

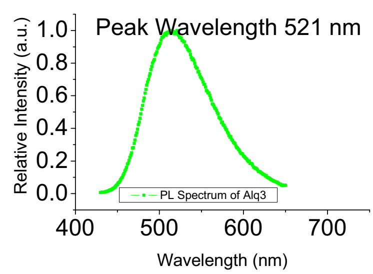

Fig.7. PL Spectrum of Thin Film of Alq_3

This signifies the presence of two electroluminescence species formed during synthesis. Pure Alq_3 gives peak luminance at 510 nm. The isomers of Alq_3 giving these peaks are yet to be identified.

2.2 Device Fabrication:

A general device structure used in the following experiments is shown in Fig. (8). ITO/SiO_2 coated glass substrates have been commercially obtained. These have been cut as per device/display sizes and patterned using usual photolithography steps. Substrates were scrub cleaned using common liquid detergent, rinsed in DI water thoroughly and then boiled in 5:1:1 :: DI water : Hydrogen Peroxide : Ammonia Solution for 20 minutes & then rinsed thoroughly in DI water again. After being spin dried, these were treated with ozone plasma for 10 minutes. The hole transport and injection layer PEDOT:PSS mixed with 10% isopropyl alcohol was spin coated and then substrates were vacuum annealed for 1 hour at 120°C. The small molecules Alq_3, HTL films were deposited in vacuum of 1-5x10^{-6} mbar. The metals were evaporated in 1x10^{-6} mbar vacuums. To analyze the effect of voltage and current levels on light intensity, OLEDs with different active layer thicknesses of Alq_3 with and without hole transport layer (HTL) have been fabricated.

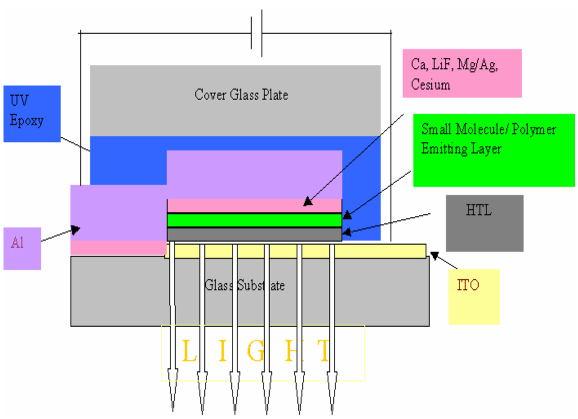

Fig. 8 Simple Device Structure

On completion of cathode deposition, the devices were sealed in air using a plane glass plate and UV cured epoxy. The UV epoxy is applied uniformly over the glass plate and cured under UV lamp. The devices were found quite stable for few months when operated <10V. With epoxy applied on the perimeter of the glass plate, the devices degraded very fast during measurement itself.

2.3. Measurements & Characteization

The light emitting diodes fabricated from small molecule Alq_3 are shown in Fig. 9. There are number of working LEDs in a row but only few of them have been connected. The current-voltage (IV) and light-voltage (LV) characteristics have been obtained using Keithley SMU 236 and DMM 196 interfaced with PC using Lab-View.

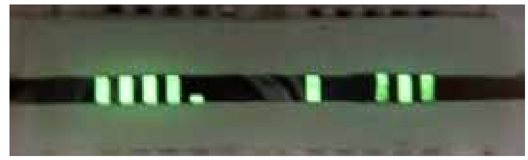

Fig. 9 OLEDs fabricated from Alq_3

The luminance (Cd/m^2) vs Current (mA/Cm^2) and Current efficiency (Cd/A) vs Voltage (V) of these devices are shown in Fig. 10 and 11 respectively. The maximum luminance of 12460 Cd/m^2 at 14V and 700 mA/cm^2 has been recorded. The luminance of 4912 cd/m^2 is achieved at 8V and 155.5 mA/cm^2 as shown in Fig.10

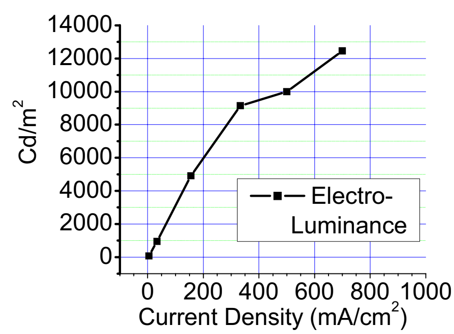

Fig.10 Luminance–Current Density (mA/cm^2)

The peak efficiency of 3.16 Cd/A is also achieved at 8V as shown in Fig. 11. There is decrease in luminance and efficiency at higher voltages.

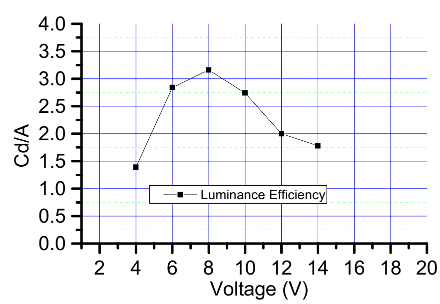

Fig.11 Current Efficiency (Cd/A)–Voltage

A study has been made to see the effect of voltage and current levels on EL. The EL of same device has been measured from 0-8V, 0-10V and 0-12V in Fig. 12. The current and luminance have been plotted on log scale as to see their effect on longer range. As seen from the Fig 12, there is little degradation in luminance and current levels in successive measurements. The light intensity increases as the current and voltage are increased.

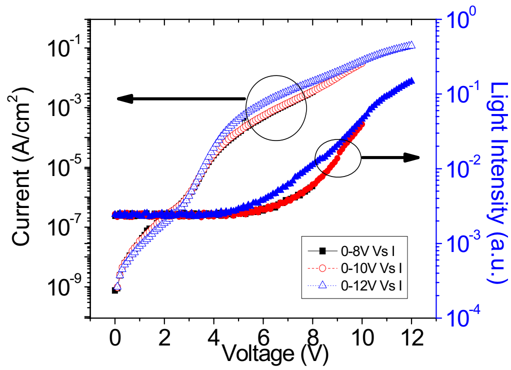

Fig. 12 I-L-V from 0-8V, 0-10V and 0-12V.

In Fig. 13, the successive I-L-V on the same device has been measured for 0-14V, 0-16V, 0-18V, 0-20V and 0-22V. The EL starts decreasing beyond 14V, however, there is no corresponding decrease in current. The current at high voltage is still increasing. It seems that radiative recombination is transformed into non-radiative one at high intensity. The EL efficiency of the material is affected at such higher voltage and current levels.

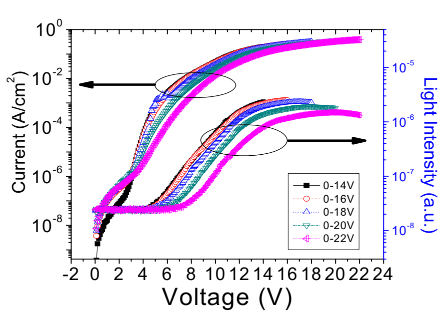

Fig. 13 I-L-V from 0-14V, 0-16V, 0-18V, 0-20V and 0-22V.

To investigate the degradation of EL at higher voltage, devices with active layer thickness of 20 nm and 120 nm with HTL (40 nm) were fabricated. The I-V and L-V characteristics of these devices are shown in Fig. 14. As seen from the Fig.14, minimum threshold voltage of 2.3V is achievable in 20 nm, Alq_3 active layer devices. Light starts decreasing beyond 10V. Maximum Light intensity is obtained from 60 nm Alq_3 active layer. Increasing the active layer thickness to 120nm, results in higher threshold voltage of 6V. Noticeable degradation in light intensity is observed at higher voltages. This decrease in light intensity shifts to higher voltages in thicker devices. The onset voltage of light degradation also shifts beyond 18V in thicker devices.

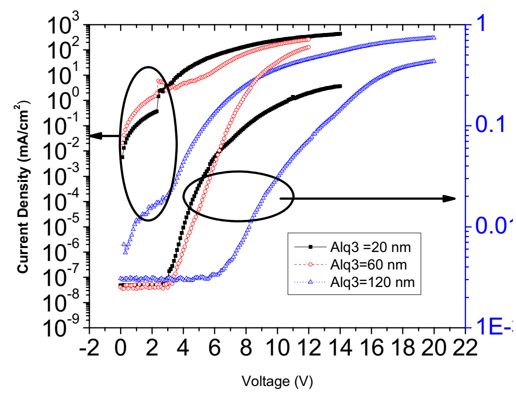

Fig. 14 I-V & LV of OLEDs with Alq_3 (20, 60 nm, 120 nm) and with 40 nm HTL

To further find out the cause of degradation in performance and failure, devices with active layer thickness of 60 nm and with out having HTL were fabricated. IV and LV are shown in Fig. 15. The EL of these devices is quite low in comparison to devices having HTL layer and it starts decreasing beyond 8 V. There is a catastrophic failure at 12 V.

The above experiment shows that the efficiency and onset of degradation is also related to device structure. The HTL layer besides providing hole transport to active layer also plays important in the stability of devices.

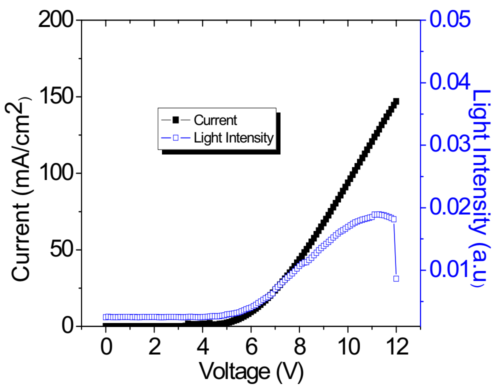

Fig. 15 IV and LV of simple ITO/ PEDOT/ Alq3/Ca/Al OLED

3. Impact

Small molecule Alq_3 material has been synthesized by simple route using locally available LR grade raw materials. The material shows EL peaks varying from 503 – 546 nm in different run of synthesis with overall good luminescence in the yellow-green region of visible spectrum. Highest EL of 12460 cd/m^2, is attained in these simple devices. It is shown that there is little degradation in device performance if these are operated less than a certain voltage. The optimized thickness in terms of threshold voltage and maximum EL is found around 60 nm. The experiments with different device configurations show the importance and relevance of different layers. Devices without using HTL show feeble EL and degradation/failure of device sets in at comparatively lower voltages. The technology can be utilized in realizing cost effective low information content displays like General displays, 7-segment and dot matrix displays where high luminance and thus high voltage and current levels are not so much demanding. Using the above device structure, few simple bright displays as shown in Fig. 16 have been fabricated.

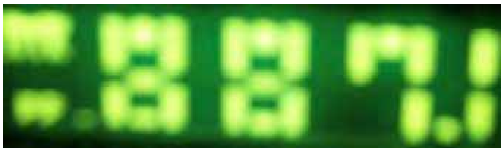

Fig. 16 Low Information Content Alfa-numeric Displays

5. CONCLUSION :

The low cost electro-luminescent material Alq_3 has been synthesized with good yield from locally available LR grade raw materials. The light emitting diodes having simple structure show good over all characteristics. The process & technology as demonstrated is quite economical for low information content displays.

ACKNOWLEDGEMENT

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Reference

[1] Philipp Wellmann, Michael Hofmann, Olaf Zeika, Ansgar Werner, Jan Birnstock, Rico Meerheim, Gufeng He, Karsten Walzer, Martin Pfeiffer and Karl Leo, Journal of the SID Vol 13, 5, 393, (2005).

[2] C.W. Tang and S.A. VanSlyke, Applied Physics Letters vol. 51, p.913, (1987).

[3] Baldo M A, O'Brien D F, Thompson M E and Forrest S R *Phys. Rev.* B 60**,** 14422–8 (1999).

[4] G. Baldacchini, S. Gagliardi, R.M. Montereali, A. Pace, R.B. Pode, A Report Prepared and Distributed by Servizio Edizioni Scientifiche – ENEA Centro Ricerche Frascati, Rome, Italy.

[5] Hairong Li, Fujia Zhang, Yanyong Wang, Daishun Zheng, Material Science and Engineering, B100, 40-46, (2003).