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Green Emitters for White Light Emitting Diodes: A Comparative Study

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Abstract : In the present study, a comparative analysis was carried out on the luminescent properties of metaloquinolates of Zinc, Cadmium, Aluminium and the complexes have been used for the testing of white light emission in order to apply in phosphor converted White Light Emittting Diodes (pcLEDs). Initially, the resulting metaloquinolates were characterized by using Infrared, UV-Visible spectra, Thermogravimetry, Photoluminescence, and CIE Chromaticity Coordinates. The white light emission was realized by mixing each metaloquinolate with a red and blue emitters respectively. The results show that the complex, bis(8-hydroxyquinolinato)zinc(II), Znq_2, can be used as excellent luminescent green emitter for phosphor converted white LEDs (pcLEDs), realizing better white light emission than the other two metaloquinolates.
Key words : Metaloquinolate, Photoluminescence, White light emission, Green emitters, CIE Chromaticit.

Introduction

Phosphors are solid state luminescent materials that absorb energy acting on them and subsequently emit the absorbed energy as light, usually in the visible range. Recently, phosphor converted white light emitting diodes (pcLEDs) is gaining great importance in the illumination industries because of huge energy saving[1-3]. For the generation of white light in the LEDs, the powder phosphor materials are generally coated above the LED chips and these phosphors are excited by near UV or blue light and emit white light by combination of two or three emissions[4-6]. However, the phosphor materials are prepared by cumbersome solid state method which involves various intermittent processes. So that in the recent days, luminescent metal complexes are gaining great importance in photonic industries. The importance of the metal complexes are because of the simplicity in synthesis procedures, ease of fabrication, high thermal stability, high quantum yield, high fluorescence, excellent electron-transporting mobility and the wide spectral response[7-9]. The metal

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complexes consist of a metal ion and its chelating luminescent ligand as a sensitizer which can transfer excitation energy to the encapsulated metal ion by efficient energy transfer.

Zn and Cd metal complexes based small molecules are used in organic light emitting diodes (OLED), devices as electron, hole transport layers and an emissive layer because of their wide spectral response in the visible region[10,11]. Tris(8-hydroxyquinolinato) aluminium(III), Alq_3,complex was reported as one of the most widely used materials for electron transport and green emission for organic light emitting diodes (OLEDs) owing to its excellent stability, luminescent properties and high quantum yield[12,13]. Extensive research work is going on in various laboratories to synthesize new metal complexes containing new ligands to produce a number of novel luminescent zinc complexes as emitters[14-17] and electron transporters[18-20] in OLED research. However, no work has been reported to our knowledge based on using of metaloquinolates for phosphor converted white light emitting diodes. One way of generation of white light is pumping of red, green, and blue phosphor blend using UV LED to realize white light emission.

In this present work we carried out a comparative study on the luminescent properties of green light emitting metaloquintolates, sucs as Znq_2, Cdq_2, Alq_3 and made an attempt to develop white light emitting diodes (LEDs) by mixing each metaloquinolate with a red and blue phosphors.

Experimental

Preparation of bis(8-hydroxyquinolinato)M(II) (M = Zn, Cd)

8-Hydroxyquinoline (8-Hq) 0.29 g (2 mmol) solution was prepared in 50 ml absolute ethanol and stirred with a magnetic stirrer for one hour at a constant temperature of 60°C in an oil bath. A solution of zinc acetate or cadmium acetate (1 mmol) in 2 ml of deionised water was added drop wise to the reaction mixture. After 2 h stirring a yellowish green precipitate of the complex was separated from the reaction mixture which was filtered and dried in vacuum oven for 24 h.

Preparation of Tris(8-hydroxyquinolinato)aluminium(III), Alq_3

A similar procedure as described above was followed with 8-Hydroxyquinoline (8-Hq) (3 mmol) solution of ethanol and aluminium salt solution . The resulting yellowish green precipitate of the complex was separated from the reaction mixture which was filtered and dried in vacuum oven for 24 h.

Analytical and physical measurements

All the reagents and solvents employed were commercially available high-grade purity materials (E-merck) used as supplied without further purification. The metaloquinolates were characterized by using FT-IR, TGA-DTA, Photoluminescence and CIE Chromaticity Coordinates. Universal V4. 3A TA Thermal Sciences instrument was used for the thermogravimetric analysis. The heating rate of the furnace was fixed at 20°C per minute. About 5mg of the sample was taken in porcelain crucible for each thermogravimetric experiment. The UV–Visible absorption spectrum was recorded using a Shimadzu 2401 PC spectrophotometer. Photoluminescence emission and excitation spectra were recorded using fluorolog spectrophotometer (Scientific equipments, USA). USB - 2000 Ocean optics spectrophotometer was used to analyze the LED excited spectra and the intensity. The Commission International de l'Eclairage (CIE) chromaticity coordinates were measured using OOIrrad software, USB 2000 (Ocean Optics, USA). All the optical measurements were carried out at room temperature.

To get white light emission, the three phosphors (red, green and blue light emitters) are coated on LED chip which is encapsulated using epoxy resin in a dome shape. After application of external source to the LED, emits near UV light which is absorbed by the three phosphors to emit in red, green and blue regions. These colours combined with the source wavelength (390nm) result in white light eimission.

Results and Discussion

Infrared and Thermal characterization

The wavenumbers near at 1601, 1574, 1389 and 1322cm^{-1} were assigned to the quinoline group of metal 8-hydroxyquinoline complexes. The bands near at 1499 and 1464cm^{-1} are corresponding to both the pyridyl and phenyl groups of the complexes[21]. The spectra show the characteristics peaks of aromatic ring stretching near at 742 cm^{-1}, 789 cm^{-1} and 820 cm^{-1}, which supports the existence of quinolinic rings in all the complexes.. The water of hydration in the samples was readily identified by the presence of a broad infrared absorption band in the region from 3000 to 3400 cm^{-1}

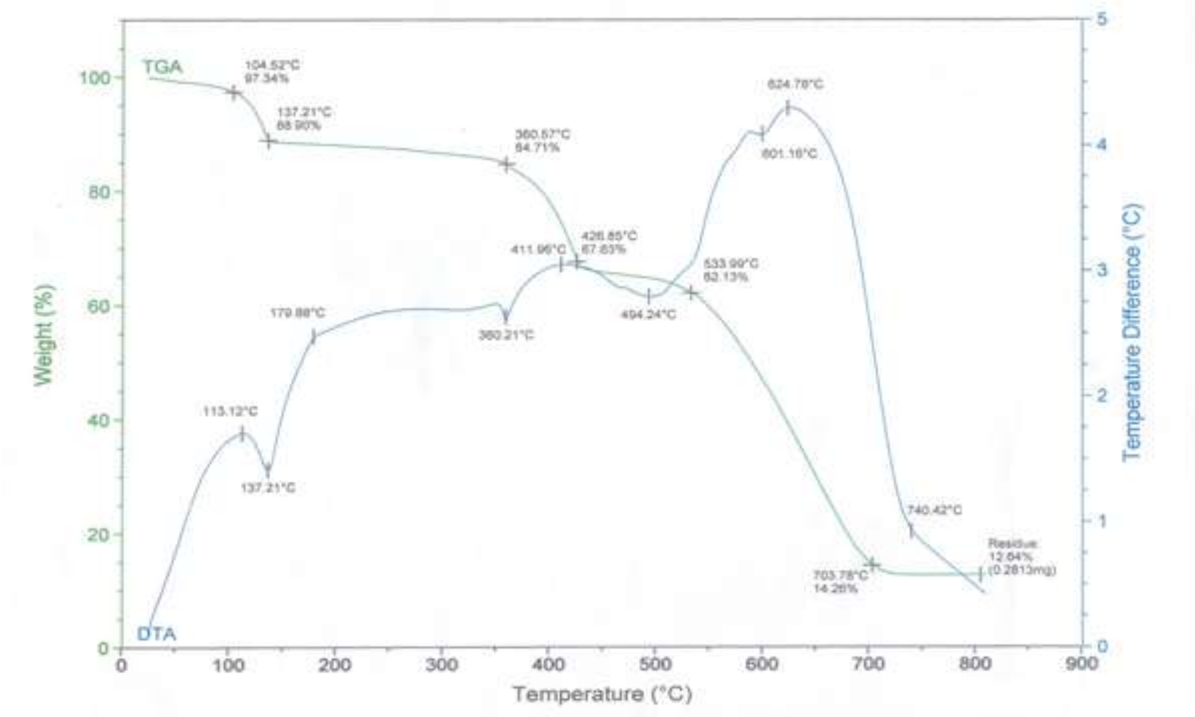

Fig. 1.TG-DTA of Bis(8-hydroxyquinolinato)zinc(II)complex

The initial mass loss occurs up to 137° C in the TGA curve and it is ascribed to the loss of water in all the complexes. An endothermic peak in the DTA curve also correspond to the water loss process. After water loss, decomposition pattern of the sample were observed, which are consistent with the literature. All the metaloquinolates show higher thermal stabilities. The high thermal stability in nitrogen, which is attributed to the highly polarized M-N bond. The high thermal stability of the complexes is as an advantage in the fabrication of light emitting device for getting greater longevity. The TGA and DTA results for the Znq_2 complex are shown in Fig.1.

Absorption and emission studies

The absorption maxima from UV-Visible spectra were observed at 384, 382 and 380 nm respectively for the complexes Znq_2, Cdq_2 and Alq_3 respectively. The maxima are due to the aromatic ring based $\pi-\pi^*$ transition. Fig.2 shows the photoluminescence (PL) emission spectra of metaloquinolates by excitation wavelength 395nm. The PL emission peaks are observed nearly at 540 nm in all the complexes .

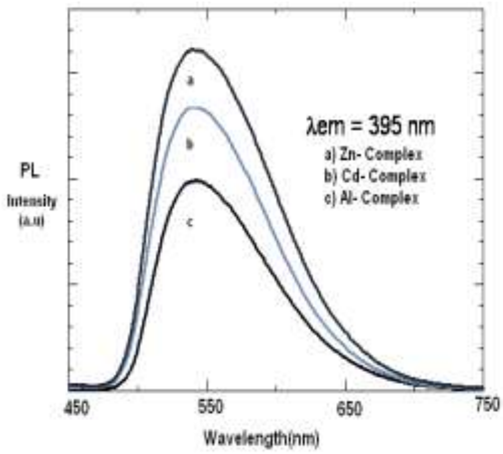

Fig. 2 PL emission spectrum (excited at λem = 395nm) of Zn, Cd and Al complexes

The optical transition responsible for the photoluminescence is due to a transition from electron rich phenoxide ring (location of the highest occupied molecular orbital (HOMO) to the electron deficient pyridyl ring (location of the lowest unoccupied molecular orbital (LUMO)[22]. The PL emission spectra show a broad emission peak with an emission maximum at 540 nm . Among the three metaloquinolates, Znq_2 is showing the higher PL intensity than the other two metaloquinolates. It is very important to note that the broad emission which covers from blue to red region is very useful for the LED lighting applications to get high color rendering index LED lamps. The excitation peak at 395 nm reveals that the prepared greenish yellow complexes not only suitable for organic light emitting diode (OLED) but also for photoluminescent liquid crystal display (PLLCD) and solid state lighting application.

Near UV LED excitation

Fig. 3 shows a electroluminescent (EL) emission spectra of the complexes excited at near UV (406 nm) LED wavelength. EL emission spectra recorded using a 406 nm LED show wide band in each case, which covers the entire visible region, consisting of two bands located in bluish green and greenish yellow regions with a full width at half maximum (FWHM) of 90 nm. It is noted that Znq_2 is showing the higher intensity than the other two metaloquinolates. The EL spectra suggest a promising greenish yellow emitting material for solid state light emitting devices application.

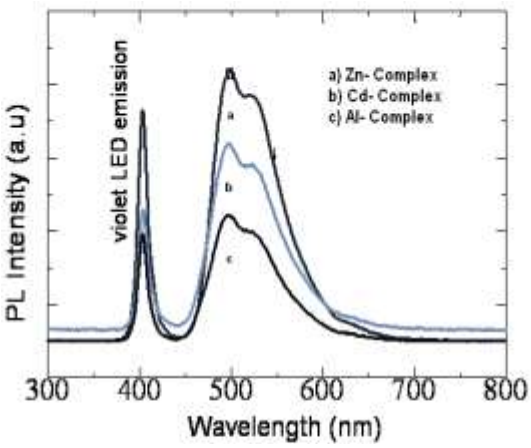

Fig. 3: Near UV LED excited spectrum of Zn, Cd and Al complexes

CIE chromaticity co-ordinates

The complex shows a bright green emission with CIE co-ordinate of (0.253, 0.453) which is very close to the standard green light. It is very important to mention at this juncture that this phosphor can be mixed with a blue and red phosphor to obtain a white light emission for the LED lighting applications. CIE chromaticity co-ordinates (x,y) of Znq_2 are shown in Fig. 4..

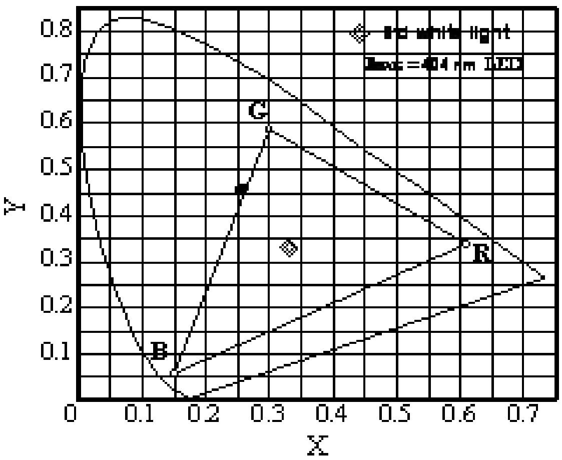

Fig.4: CIE color co-ordinate of Znq_3 complex at the excitation of 404 nm LED emission

White light emission

For the white light generation, each green emitter was mixed in appropriate ratio with red and blue phosphors. The resulting phosphor blend was coated on LED chip which is encapsulated using epoxy resin in a dome shape. After application of external source to the LED, emits near UV light which is absorbed by the three phosphors to emit in green, red, and blue regions. These colours combined with the source wavelength (390nm) and resulted in white light emission. Comparatively better performance has been observed with Znq_2 .

Conclusion

The green emitters have been synthesized and characterized. Photoluminescence spectra recorded at room temperature at the exicitation of near UV LED revealed a broad green emission peak at 540nm in all the three complexes. Thermogravimetric studies show that the complexes are thermally stable for the photonic applications. The CIE chromaticity showed that the coordinates were found very close to the standard green light,which supports the suitability of the complexes for lighting lighting applications. An a ttempt to realize white light emission by combining each green emitter with a red and blue emitters using UV LED was carried out. The results of the investigation prove that the above metaloquinolates can be used as green emitters for pcLEDs. The studies also prove that the Znq_2, can be used as excellent luminescent green emitter for pcLEDs, realizing better white light emission than the other two metaloquinolates

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