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ORIGINAL ARTICLE

Improved luminescence intensity and stability of thermal annealed ZnO incorporated Alq_3 composite films

M. Cuba[1] · **G. Muralidharan**[1]

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Abstract The 30 wt% of ZnO (weight percentage of ZnO has been optimised) incorporated tris-(8-hydroxyquinoline)aluminum (Alq_3) has been synthesised and coated on to glass substrates using dip coating method. The structural and optical properties of the Alq_3/ZnO composite film after thermal annealing from 50 to 300 °C insteps 50° has been studied and reported. XRD pattern reveals the presence of crystalline ZnO in all the annealed films. The films annealed above 150 °C reveal the presence of crystalline Alq_3 along with crystalline ZnO. The FTIR spectra confirm the presence of hydroxyquinoline and ZnO vibration in all the annealed composite films. The composite films annealed above 150 °C show a partial sublimation and degradation of hydroxyquinoline compounds. The ZnO incorporated composite films (Alq_3/ZnO) exhibit two emission peaks, one corresponding to ZnO at 487 nm and another at 513 nm due to Alq_3. The films annealed at 200 °C exhibit maximum photoluminescence (PL) intensity than pristine film at 513 nm when excited at 390 nm.

Keywords Tris-(8-hydroxyquinoline)aluminum · Photoluminescence · Film

Introduction

The luminescent organic metal complexes are promising materials for a wide range of applications such as organic light emitting diodes (OLEDs), lasers, organic field effect transistors (OFET), organic solar cells and fluorescent sensors [1]. Among these applications, OLEDs have progressed enormously on account of their high luminance, low fabrication costs, ease to fabricate large area devices and the ability to tune the emission wavelength. It is useful in wide display applications from small area telecom devices to large area displays. Generally metal-quinolates act as efficient electroluminescent material for OLED devices fabrication. Alq_3 is a metal chelate and it is known to be an excellent green emitting material. In 1987, Tang and Vanslyke first reported an efficient OLED using tris(8-hydroxyquinoline)aluminum (Alq_3) [2]. OLEDs based on Alq_3 are fluorescent solid state EL devices in which Alq_3 serves as both emitting and electron transport layer [3]. The OLEDs incorporating Alq_3 exhibit low stability and photoluminescence efficiency due to aging [4, 5]. One of the major factors causing device failure is the absence of encapsulation and thermal instability induced by the Joule heating during the operation of the device. The thermal studies of Alq_3 are used to understand the phase transition and the sublimation of the compounds [3, 6]. Various phases of Alq_3 with temperature were discussed by the research group of Colle and Brutting [7, 8]. Xu reported thermal stability of Alq_3. They could identify a glass transition at 130 °C and crystallization of a thin film at 185 °C [9].

Hybrid (organic/inorganic) materials are most suited for display devices, energy storage and biomedical applications [10, 11]. The addition of inorganic materials in an organic material enhances the mobility of charge carriers, stability and luminescence yield [12]. Chiang et al. [13] reported the thermal stability of hybrid material to increase with the addition of inorganic components than pure epoxy (polymer network). In the present work of preparing organic/inorganic (Alq_3/ZnO) composite film, we have selected ZnO metal oxide due to its higher charge mobility and stability [14, 15] at

✉ G. Muralidharan
muraligru@gmail.com

[1] Department of Physics, Gandhigram Rural Institute-Deemed University, Gandhigram, 624302 Tamil Nadu, India

ambient atmosphere. We have studied the role of ZnO in the PL of Alq_3 [16, 17]. We could identify that at 30 % ZnO incorporation, the best luminescence yield could be obtained from Alq_3. In continuation of the work, we have tried to optimize the temperature of annealing of these composite films. These results are presented and discussed in this paper.

In this work 30 wt% of ZnO incorporated Alq_3 (weight percentages have optimised) has been synthesised and coated on to a glass substrate using dip coating method [17]. The prepared Alq_3/ZnO composite films were annealed at different temperatures from 50 to 300 °C (in steps of 50 °C). Structural and optical properties of the annealed composite films have been optimised and we have investigated the stability of ZnO incorporated Alq_3 composite films and compared it with that of pristine Alq_3 films.

Experimental

Alq_3 and ZnO have been synthesized by precipitation method as reported elsewhere. The chemical reaction for the synthesis of Alq_3 [17, 18]:

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

Alq_3 and Alq_3/ZnO composite films were coated using dip coating method. The precursor solution was prepared by dissolving Alq_3 and ZnO (30 wt%) in 100 mL ethanol (C_2H_5OH) with addition of four drops (~0.2 mL) of conc. HCl. The solution was continuously stirred at 70 °C for an hour. Before coating the composite Alq_3/ZnO solution on to the glass substrate, the micro glass slides, were cleaned by chromic acid at 90 °C. Finally the substrates have been cleaned thoroughly with DD water and acetone using ultrasonic cleaner and dried at 150 °C. The prepared Alq_3/ZnO solution was coated on to the cleaned glass substrate at a withdrawal speed of 15 cm/min. After each coating the films (each layer) were dried in air for five minutes and treated in air at 150 °C for five minutes. Totally 10 layers have been coated and finally the multilayer films were annealed in air at different temperatures (50, 100, 150, 200, 250 and 300 °C) for an hour. Thickness of the film was estimated using ellipsometry. The measured thickness for 10 layer films is 220 nm. FTIR spectra have been recorded using Perkin-Elmer Spectrum BX-II spectrometer in the range of 400 to 4000 cm^{-1}. X-ray diffraction (XRD) analysis was performed using PANalytical XPERT-PRO X-ray diffractometer with Cu K_α incident beam (λ=0.1540 nm). Carl Zeiss MA/15 EVO scanning electron microscope was employed to investigate the morphology of Alq_3 films annealed at different temperatures. The absorption spectrum was recorded using Perkin-Elmer spectrophotometer in the range 200–1100 nm at room temperature. Photoluminescence studies were carried out using Perkin-Elmer LS 55 luminescence spectrometer in the region 200–900 nm at room temperature.

Results and Discussion

Figure 1 shows the XRD pattern of ZnO incorporated Alq_3 composite films annealed at different temperatures. The diffraction peak at 2θ=31.7° has been observed in all the annealed composite films. The observed diffraction peak corresponds to ZnO with preferential orientation along (100) plane (JCPDS card no. 36–1451), indicative of the formation of crystalline ZnO in the composite. The ZnO incorporated Alq_3 film annealed at 200 °C indicates the characteristic diffraction peak of Alq_3 at 2θ=18.9°. The composite film annealed at higher temperature (>200 °C) shows additional diffraction peaks due to crystalline Alq_3 at 2θ=10.35°, 18.7° and 23.46° along with crystalline ZnO planes (JCPDS No. 26–1550) [18]. XRD results reveal the formation of crystalline ZnO and crystalline Alq_3 in the case of films annealed above 200 °C. The XRD pattern of the pure Alq_3 film after thermal annealing from 50 to 300 °C in steps of 50° has been reported earlier [19]. It reveals the pure Alq_3 film annealed above 150 °C exhibits the crystalline nature. Similar results have been observed in the Alq_3/ZnO films when the films were annealed above 150 °C indicating the formation of crystalline Alq_3 and ZnO [20]. In addition it could be seen that the crystallinity of ZnO has increased with increase of annealing temperature as is evidenced by the increase in the diffraction intensity at 2θ=31.7° and by the reduction in the line width of this diffraction maximum.

FTIR spectrum of ZnO incorporated composite films annealed at different temperatures is shown in Fig. 2a. The band at 3047 cm^{-1} is due to stretching vibration of C–H bond in the Alq_3 aromatic ring. The bands in the region 1600 and

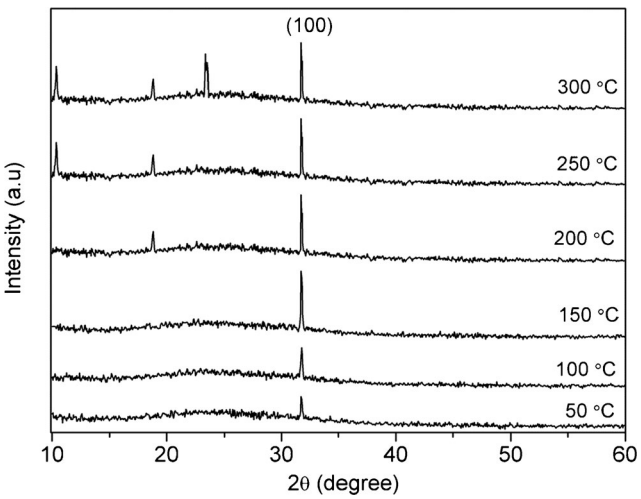

Fig. 1 XRD pattern of annealed Alq_3/ZnO films at different temperatures

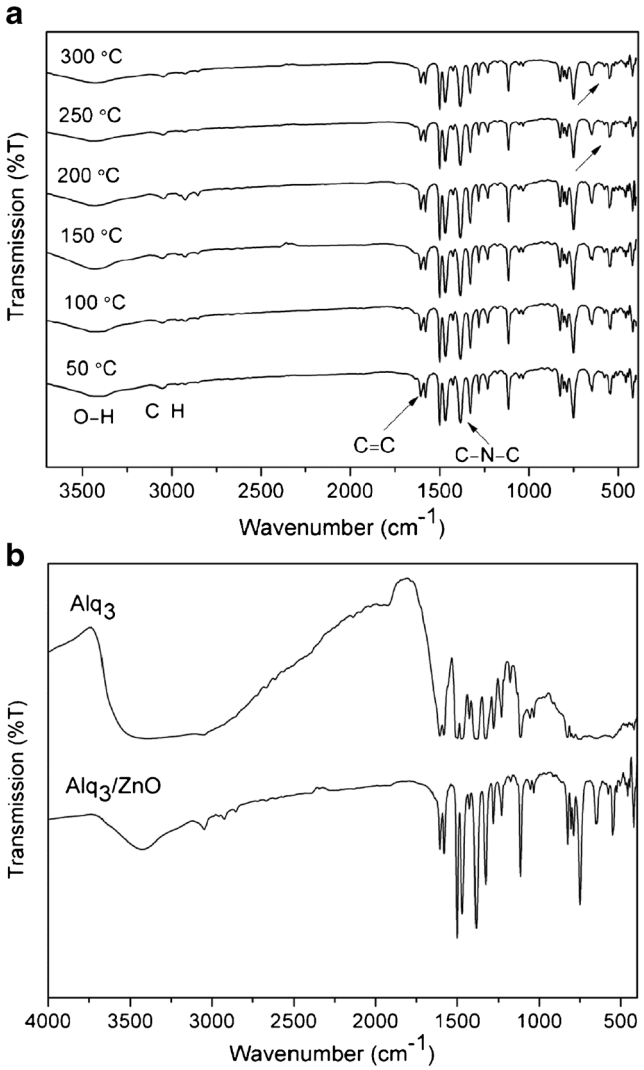

Fig. 2 **a** FTIR spectrum of annealed Alq_3/ZnO films at different temperatures. **b** FTIR spectrum of pure Alq_3 and Alq_3/ZnO films annealed at 300 °C

1551 cm^{-1} are assigned to C=C stretching vibration of composite films. The prominent bands at 1582, 1491 and 1425 cm^{-1} are due to conjugate action of aromatic rings in the composite film. The bands at 1380–1250 cm^{-1} are ascribed to aromatic amine resonance C–N–C bond [1]. The bands observed in the region 800–600 cm^{-1} are due to the vibration of quinoline and Al–O stretching [21]. The results confirm the presence of Alq_3 in the films annealed at different temperatures. The stretching vibration bands observed at 420 and 460 cm^{-1} indicate the presence of metal oxides (Zn–O) along with the corresponding vibration of quinoline and Al ion. Lu et al. [22] reported the vibration band of Zn–O in the region 400–500 cm^{-1}. The presence of ZnO and quinoline were observed in all the annealed composite films. The observed quinoline band of composite films at 250 and 300 °C has lower transmission intensity than 50 to 200 °C annealed Alq_3/ZnO films. This indicates the partial sublimation and degradation of quinoline compounds from its aromatic chain (250 and 300 °C). The result reveals the Alq_3/ZnO film annealed at 200 °C is thermally stable.

Cuba and Muralidharan [19] reported the pure Alq_3 film treated at 150 °C to be thermally stable. Compared to the previous report, the ZnO incorporated Alq_3 film indicates better stability than pure Alq_3 film (Fig. 2b). This shows the Alq_3 films containing ZnO film to be thermally and chemically stable. This is probably due to the caging effect of ZnO over the Alq_3 molecules [23]. Through structural studies we observed that the ZnO incorporated Alq_3 composite film is chemically stable than pure Alq_3 film.

The scanning electron microscopy (SEM) was used to investigate the morphology of Alq_3/ZnO composite films annealed at different temperatures with an acceleration voltage of 10 kV (Fig. 3). The Alq_3/ZnO film annealed at 50 °C indicates the smooth surface over the entire region. Distribution of some grains on the whole surface of the film could be observed for films annealed at 200 °C. The composite film annealed at 300 °C shows the uniform spherical morphology on the entire surface of the film. The morphology of the Alq_3/ZnO film seems to be completely modified as we increase the annealing temperature. Such a trend has been supported by XRD as well.

The thermogravimetric analysis (TGA) of preheated xerogel powder of pure Alq_3 and Alq_3/ZnO are shown in Fig. 4a and b. The TG studies were carried out from room temperature (RT) to 1000 °C at a heating rate 20 °C/min. A three step weight loss has been observed from RT to 1000 °C for both the samples. A minor weight loss of around 8 % has been observed in the interval from RT to 220 °C (Fig. 3a). It corresponds to the removal of volatile components of the precursor used for the preparation of the films and water molecules. The small step around 200 °C is indicative of the phase transition from amorphous to crystalline nature. This result is in good agreement with the structural studies (XRD) of previous work [19]. The second major loss of about 80 % was observed around 400 °C. This is attributed to the partial sublimation or degradation of the organic compound, namely Alq_3. The third weight loss is observed from 450 to 1000 °C. This is assigned to the total decomposition of the hydroxyquinoline compound. Similar results have been observed with ZnO doped Alq_3 films prepared in the present work. One may expect 30 % of residue after the total decomposition of hydroxyquinoline. But it should be understood that when the TG is started the material contains Alq_3 with ZnO along with water and certain degree of the precursor. This residue of around 27 % is acceptable, if the decomposition of the precursor and disintegration of Alq_3 are considered.

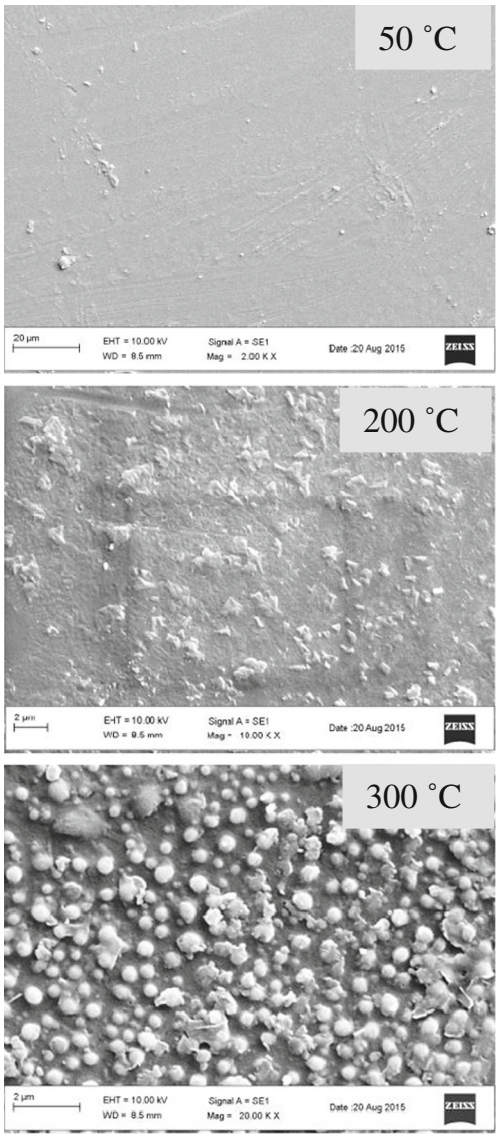

Fig. 3 SEM images of Alq_3/ZnO annealed films at different temperatures

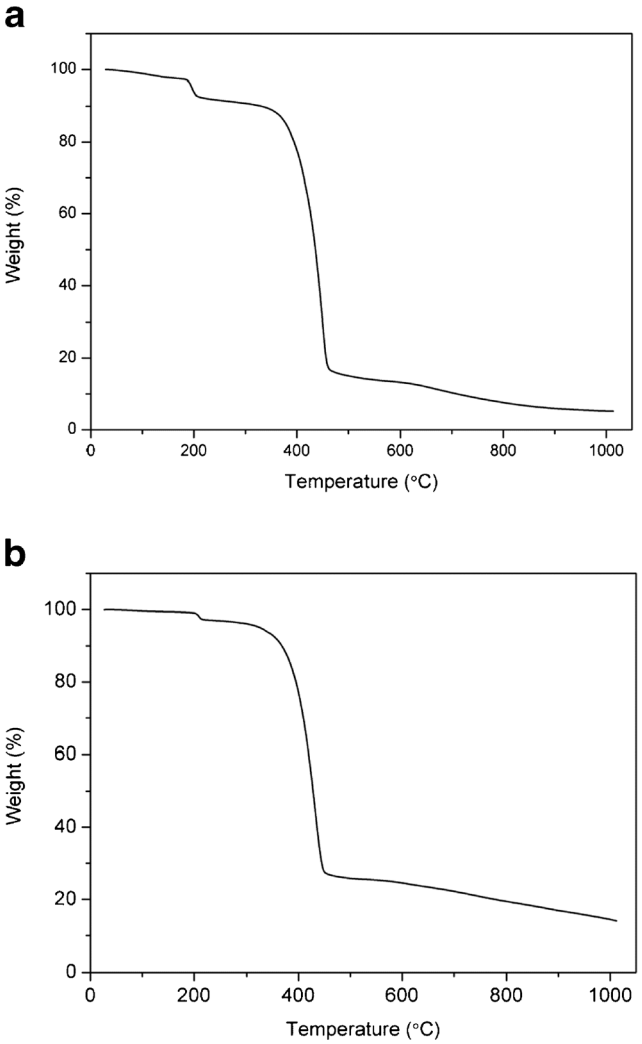

Fig. 4 TGA curve of preheated xerogel powder (**a**) pure Alq_3 and (**b**) Alq_3/ZnO

The absorption spectra of ZnO incorporated Alq_3 films annealed at different temperatures are shown in Fig. 5. Generally the absorption of photons by Alq_3 is due to the $\pi - \pi^*$ electronic transitions [24]. The annealed composite films exhibit an absorption band around 380 nm. The maximum absorption was observed for Alq_3/ZnO film annealed at 200 °C. The Alq_3/ZnO composite films annealed at 250 and 300 °C exhibit low absorption intensity. This may happen due to the destabilisation of quinoline bonding in Alq_3 structure which leads to a reduction in the absorption [20, 25]. From the FTIR spectra we could observe only a weak absorption in the quinoline region in the case of films annealed at 250 and 300 °C. The composite films treated at 200 °C show more than order improvement in absorption compared to pure Alq_3 films treated at the same temperature (inset Fig. 5). The composite films

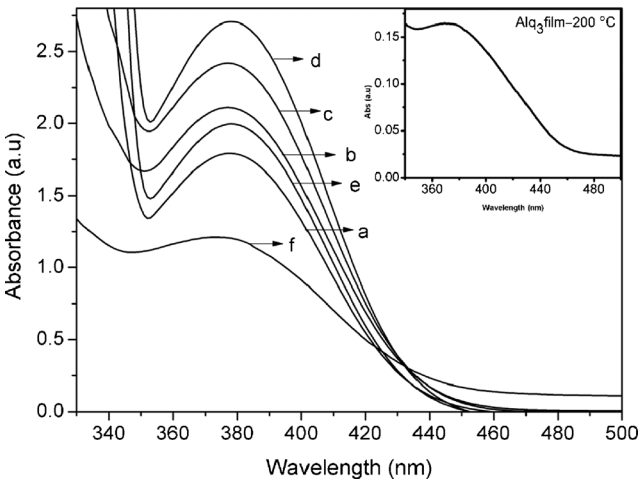

Fig. 5 UV-visible absorption spectrum of Alq_3/ZnO films annealed at (**a**) 50 °C, (**b**) 100 °C, (**c**) 150 °C, (**d**) 200 °C, (**e**) 250 °C and (**f**) 300 °C

treated at 200° revealed 60 % improvement absorption in contrast to the films annealed at 50 °C.

The relation between absorption coefficient and photon energy is given by Davis Mott [26]

$$\alpha h\nu = A\left(h\nu - E_g\right)^m \quad (1)$$

Where α is the absorption coefficient as a function of photon energy (hν), E_g is the optical band gap energy, hν is the incident photon energy, m is the index number and it depends on the nature of the transition. The value of m is 2 for indirect transition and m is ½ for direct transition. The Tauc plot of hυ Vs $(\alpha h\upsilon)^2$ is shown in Fig. 6. The extrapolation of the rising porting to zero absorption gives the energy gap (E_g) value. The energy differences (E_g) for annealed Alq_3/ZnO films are 3.28, 3.27, 3.26, 3.24, 3.26 and 3.28 eV. From these it could be seen that the annealing does not alter the band gap appreciably.

The photoluminescence behaviour of annealed Alq_3/ZnO composite films for the excitation of 390 nm is shown in Fig. 7. It shows that all the annealed ZnO incorporated Alq_3 films exhibit an emission in blue and green region. The emission peak observed at 485 nm corresponds to the characteristic wavelength of ZnO [27] and emission at 514 nm is due to Alq_3 molecules. This result indicates the presence of ZnO in hybrid Alq_3/ZnO films. This may happen due to the compatible energy levels and electron–hole recombination of both organic and inorganic components [16, 28]. The Alq_3/ZnO film annealed at 200 °C shows maximum luminescence intensity. It yields five times stronger luminescence than the pure Alq_3 films annealed at 200 °C (inset Fig. 7). The incorporated ZnO may act as a shield among the Alq_3 molecules, which suppress the internal conversion or intersystem crossing in the excited state [23].

The partial destabilisation of quinoline chain (in the films annealed beyond 200 °C) leads to quenching of emission intensity in higher temperature annealed composite films. Similar results has been reported for pristine Alq_3 [29] and other organic semiconductors [20] and polymers [30]. These results

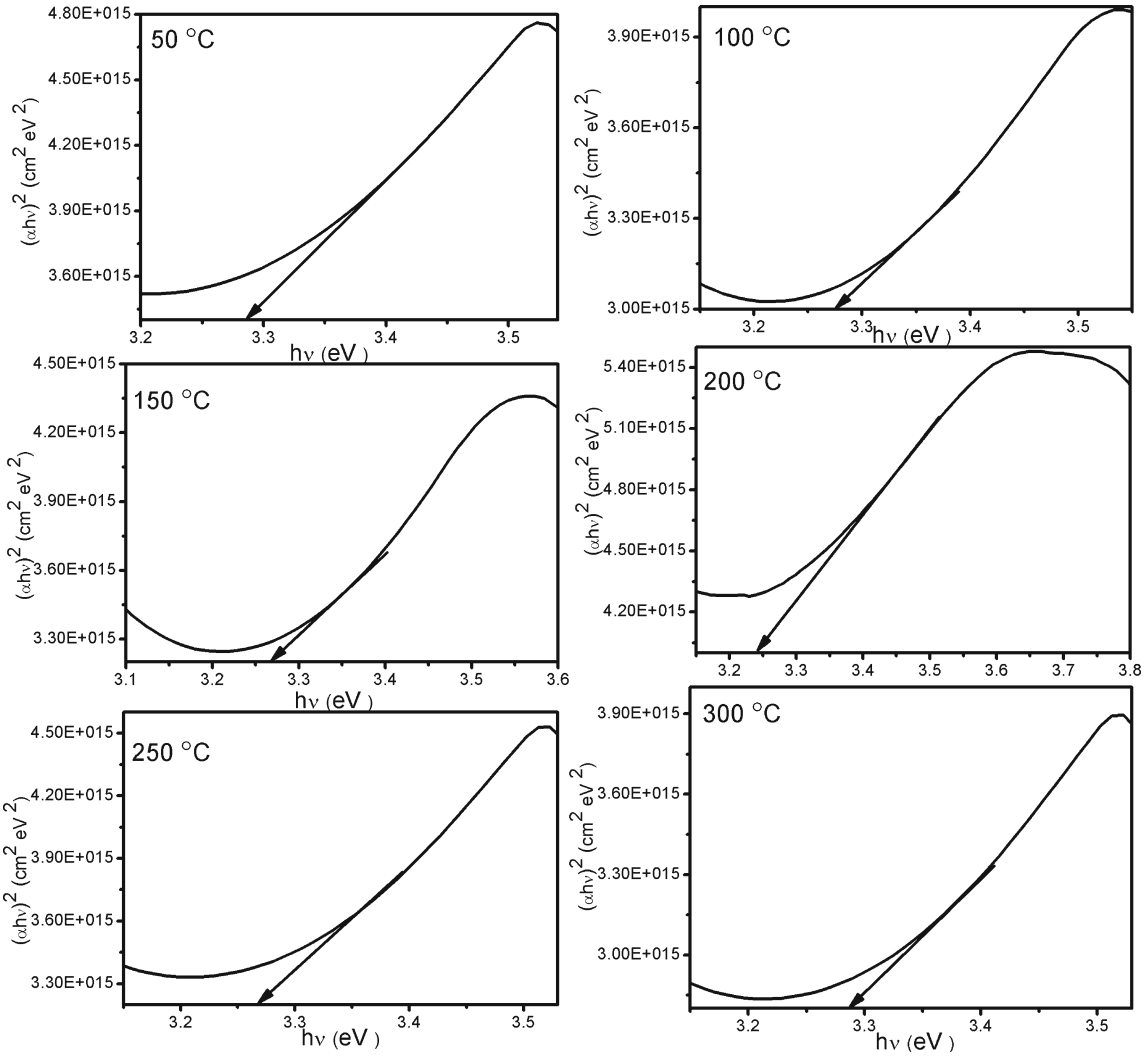

Fig. 6 Tau plot of Alq_3/ZnO films annealed at different temperatures

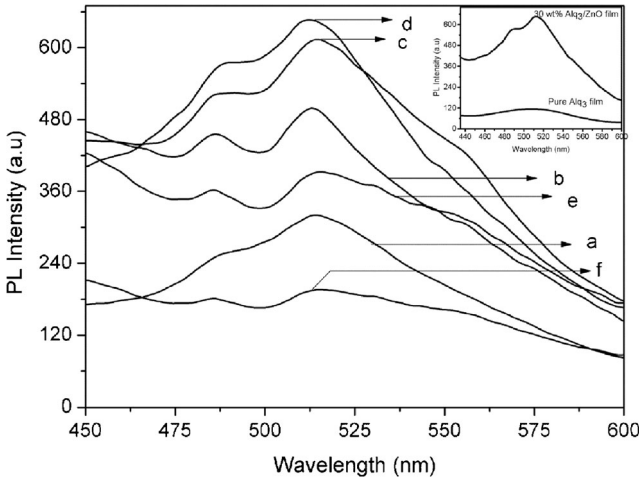

Fig. 7 PL emission spectrum of Alq_3/ZnO films recorded at room temperatures for films annealed at (**a**) 50 °C, (**b**) 100 °C, (**c**) 150 °C, (**d**) 200 °C, (**e**) 250 °C and (**f**) 300 °C. Inset: Pure Alq_3 and Alq_3/ZnO films annealed at 200 °C

suggest the ZnO incorporated Alq_3 composite films annealed at different temperatures is more thermally stable than pure Alq_3 annealed film. The measurements made in this work indicate that the best luminescence performance is obtained from the films annealed in air at 200 °C.

Conclusion

The 30 wt% of ZnO incorporated Alq_3 has been synthesised and coated on to a glass substrate using dip coating method. The structural studies confirm the presence of ZnO in the Alq_3 compounds. The Alq_3 films containing ZnO (Alq_3/ZnO) show green and blue emission, which is characteristic of both the components of the composite films. The Alq_3/ZnO film annealed at 200 °C exhibits nearly five times stronger than of pure Alq_3 film at 200 °C. Compared to the pure Alq_3 matrix, the ZnO incorporated Alq_3 shows enhance thermal stability and luminescence behaviour. This occurs due to the caging effect of crystalline ZnO over the Alq_3 molecules. From these studies it is suggested that the best possible luminescence yield can be obtained through the incorporation ZnO into the Alq_3 at 200 °C other than pure matrix.

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