

Tunable Photoluminescence from tris (8-hydroxyquinoline) aluminum (Alq₃)

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Abstract: *Blended thin films of Alq₃ embedded in polymethyl methacrylate (PMMA) matrix at different concentrations are investigated.. We have recorded PL characteristics of blended thin film of Alq₃: PMMA at concentration ratio of 100:100,10:100,1:100. From the obtained excitation and emission spectra it is revealed that the emission wavelength as well as the intensity shift to the blue side with the decrease in concentration of Alq₃. The emission can thus be tuned by changing the relative concentration of Alq₃ in PMMA. We propose that the blue shift of emission wavelength may be attributed to cross relaxation.*

Keywords: Alq₃; PL; OLED; PLLCD.

Introduction

Recently, a new generation of optoelectronic devices based on inexpensive organic light-emitting diodes have been reported. The rapid progress in performance and lifetime make organic light-emitting diodes (OLEDs) suitable candidates for flat panel display applications. Since the first report of efficient and stable OLEDs [1,2], tris (8- hydroxyquinoline) aluminum (Alq₃) –which is used as the emission and electron transport layer, the interest in this archetype material is persistent. Properties such as relative stability, easy synthesis, good electron transport, and emitting properties result in extensive application of Alq₃ in OLED design. Tang and co-workers discovered Alq₃-based multi-layer thin-film electroluminescent devices in 1987[1]. Alq₃ still continues to be the workhorse among the class of low molecular weight materials for OLEDs. Research into organic materials for use in OLEDs has mostly focused on conjugated polymers or low molecular weight materials [3]. However, so far comparatively few investigations have been devoted to the electronic and optical properties of the material, in particular in the crystalline state. Recently, a systematic study of the optical properties of solution, amorphous films, and different polymorphic crystalline phases of Alq₃ was published [4].

Three Crystalline phases i.e. α , β , γ phase of Alq₃ were identified in 2002 by Brinkmann and co-workers [4]. In 2003 M.Colle and co-workers reported new crystalline phase of Alq₃ i.e. δ -phase, which was obtained by thermal sublimation in a horizontal glass tube [5]. The α and δ -phase of Alq₃ characterized by photoluminescence characterization. M.Colle and co-worker also investigated the thermal properties of Alq₃ in order to understand the forming process of new δ -phase of Alq₃

and reported an efficient method to obtain blue luminescent Alq₃ by a simple annealing process [5]. In 2006, Levichkova et. al. [6] reported vacuum deposited thin films of Alq₃ embedded in SiO₂ matrix at concentration corresponding to single –molecule distribution and dilution of Alq₃ in the matrix leads to blue shift of the luminescence compared to pure Alq₃ layers. In this paper, we have investigated the photoluminescence characterization of Alq₃ embedded in polymethyl methacrylate (PMMA) at different concentration and we are reporting how to synthesize green to blue tunable photoluminescent thin films which can be very useful for Organic Light Emitting Diode (OLED), Photoluminescent Liquid Crystal Display (PLLCD) and Solid State Lighting applications. We propose that tunable blue shift of emission wavelength may be attributable to cross-relaxation.

Experimental

Synthesis: 8-Hydroxyquinoline (Merck, 5gram) was dissolved in a Mixture of 25mL double distilled water and 25mL of acidic acid, stirred it well till orange transparent solution is obtained. Al (NO₃)₃ 9H₂O (LOBA chem., 4.3069 gram) was dissolved in double distilled water, stirred it well till crystal transparent solution is obtained. Add these two mixtures and resulting suspension was stirred for 10 min. Now, pour solution of (NH₄OH) Ammonium Hydroxide (precipitating agent) to this solution drop by drop with continuous stirring. Yellow-green precipitate was filter out. Wash this PPT 8-10 time with double distilled water and keep it for evaporation to dryness.

Blended thin film of Alq₃: PMMA at concentration ratio 100:100 can be obtained in the following way:-

Take 1gram of PMMA & dissolve it with 20mL of chloroform in a stainless steel plate. To this paste like solution, pour the solution of 1gram Alq₃ in 10mL chloroform, stir it & keep it for evaporation to dryness. Blended thin film of Alq₃: PMMA at concentration ratio 100:100 is obtained. Similarly blended thin film of Alq₃: PMMA at concentration ratio 10:100, 1:100 can be obtained.

Characterization: X-ray diffraction patterns for Alq₃ powder were recorded on Philips PANalytical X'pert Pro diffractometer. PL characteristics for Alq₃ powder and blended thin films were studied using a Hitachi F-4000 spectrofluorometer, at room temperature, using 1.5 nm spectral slit width in the range 200-700 nm.

Results and discussions

Although the phases have been clearly distinguished by X-ray diffraction measurements, some small admixtures of a few percent can not be excluded [7]. XRD pattern of α - phase of meridional isomer Alq₃ reported by Michael Colle et.al.[4] closely matched with the XRD pattern of our sample shown below in fig. 1

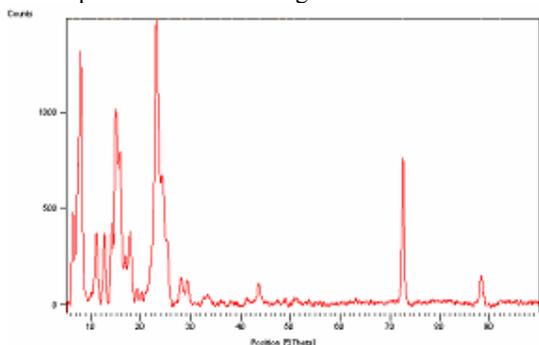


Figure1. XRD pattern of Yellowish –Green Alq₃ powder

Figure 2 shows the photoluminescence (PL) emission spectrum of Alq₃ powder by excitation wavelength is 385nm. The prominent PL emission peak is observed at 520nm in green region of the spectrum. Colle et.al. [5] and Levichkova *et.al.* [6] reported that the green emission of yellowish- green Alq₃ powder is attributable to α - phase of meridional isomer of Alq₃

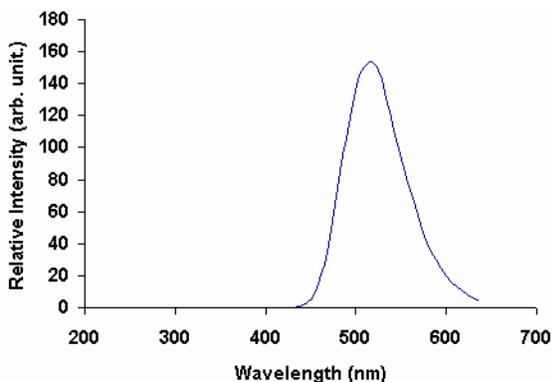


Figure 2. Emission Spectrum of yellowish- green Alq₃ powder, excited at 385nm, emission wavelength is 520nm

From the above discussion, as per the XRD and PL results are concerned, the prepared yellowish green Alq₃ powder in our laboratory at room temp.is α –phase , out of four phases reported in the literature [5,6].

The PL excitation spectrum of yellowish green Alq₃ powder is shown in fig. 3. It shows the prominent shoulder at 385nm (λ_{em} =520nm). The excitation peak at 385nm reveals that the prepared yellowish-green Alq₃ not only suitable for organic light emitting diode (OLED) but also for photoluminescent liquid crystal display (PLLCD) and solid state lighting application.

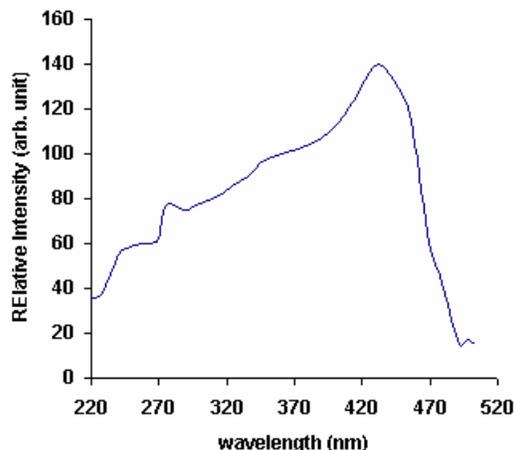


Figure 3. Excitation spectrum of Yellowish green Alq₃ powder λ_{em} =520nm

Figure 4 shows the PL emission shifted from green region to blue region of the spectrum in case of blended thin film of Alq₃ embedded in polymethyl methacrylate (PMMA) matrix at different concentration of Alq₃. The emission can thus be tuned by changing the relative concentration of Alq₃ in PMMA

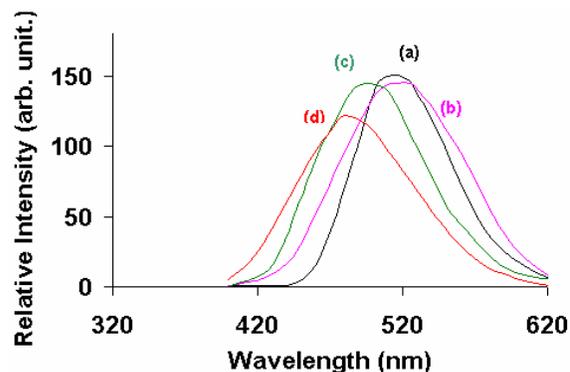


Figure 4. Emission spectrum of various % of Alq₃ in thin film of Acrylic

(a) = 100% Alq₃ in Acrylic, (b) = 10% Alq₃ in Acrylic, (c) = 1% Alq₃ in Acrylic, (d) = 0.1% Alq₃ in Acrylic

Figure 4 (d) shows that at 0.1% concentration of Alq₃ in PMMA, the prominent PL emission peak is at 480nm, which is in the blue region of the spectrum when excitation wavelength is 385nm. This reveals that 0.1% concentration of Alq₃ in PMMA thin film can be used for blue emitting OLED and PLLCD display where as 100% concentration of Alq₃ in PMMA thin film {Fig. (4) (a)} can be used for green emitting OLED and PLLCD display.

M.colle and co-workers show [4,5] the new crystalline phase of Alq₃ i.e. δ -phase of Alq₃, which was obtained by thermal sublimation in a horizontal glass[4]. Its optical properties have been tentatively discussed in terms of the isomerism of the Alq₃ molecule. As

compared to the α -phase, the δ -phase of Alq₃ shows the strong blue shift PL characterization. This result shows that, using train sublimation method at high temperature i.e. 410°C, Alq₃ observed in δ -phase and this δ -phase structure is responsible for blue emission. Levichkova et al. [6] concluded that a blueshift of the PL maximum corresponding to isolated Alq₃ molecules in a SiO₂ matrix. He further reported that formation of facial isomer form meridional isomer of Alq₃ molecule is responsible for blue emission. Two parameters influence the presence of facial molecules: First, local heating of Alq₃ molecules during film growth causes meridional to facial isomer transformation. Second, the rigid matrix supports the conservation of the already transformed fac-Alq₃ molecules. In our case of blended thin film of Alq₃: PMMA with different concentration ratio, neither annealing nor sublimation at high temperature was performed. Hence structure of Alq₃ molecule remains same in blended thin film as it was in Alq₃ powder and still we observed blue shift in blended thin film. The observed blue shift of emission may be attributed to cross relaxation. The concentration dependence of the emission colour reminds us the luminescence of Tb³⁺. At low concentration, the luminescence is blue due to ⁵D₄→⁷F₆ transition. For higher concentrations, this emission is quenched due to cross relaxation and the green emission arising from ⁵D₄→⁷F₅ transition becomes dominant [8]. We propose that similar cross relaxation is responsible for the concentration dependence of Alq₃ emission.

Conclusion

From the XRD and PL study we conclude that, the prepared yellowish green Alq₃ powder in our laboratory at room temp. is α -phase, out of four phases. From this yellowish green Alq₃ powder blended thin film of Alq₃: PMMA at concentration ratio of 100:100, 10:100, 1:100 are synthesized without providing heat treatment. The emission can be tuned by changing the relative

concentration of Alq₃ in PMMA and not by any annealing process. Thus the prepared blended thin film can be a suitable candidate for green and blue emitting OLED, PLLCD and solid state lighting application.

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References

1. C. Tang and S. VanSlyke, *Appl. Phys. Lett.* 51, 913 (1987).
2. Stefan Berleb and Wolfgang Brütting *Phys Rev Lett.* 89, 286601 (2002)
3. John E. Knox, Mathew D. Halls, Hrant P. Hratchian and H. Bernhard Schlegel, *Phys. Chem. Chem. Phys.*, 8, 1371 (2006)
4. M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi, A. Sironi, *J. Am. Chem. Soc.* 122, 5147 (2000)
5. Michael Colle, Jürgen Gmeiner, Wolfgang Milius, Harald Hillebrecht, and Wolfgang Brütting, *Adv. Func. Mat.* 13 (2)-108 (2003)
6. M. M. Levichkova, J. J. Assa, H. Fröb, and K. Leo *Appl. Phys. Lett.* 88, 201912 (2006)
7. M. Cölle, S. Forero-Lenger, J. Gmeiner and W. Brütting, *Phys. Chem. Chem. Phys.*, 5, 2958 (2003).
8. G. Blasse *Prog. Solid State Chem* 18 79 (1988)