Blended thin films of tris-(8-hydroxyquinoline) aluminium (Alq_3) embedded in polymethyl methacrylate (PMMA).

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Abstract. Alq_3 is widely used in organic light emitting diodes (OLEDs) as emission and electron transport layer. During the fabrication of OLEDs the current trend is to use solution-processing; however, Alq_3 must be vacuum deposited. One possible way to overcome this problem is to use different polymers containing the Alq_3. In this study blended thin films of Alq_3 embedded in a PMMA matrix at different molar concentration ranging from 0.5% to 5% was investigated. The photoluminescence (PL) characteristics of the blended films of Alq_3:PMMA was obtained. This was done by exposure of the films to 355 nm UV light. Emission peaks were obtained at ~ 515 nm for the Alq_3:PMMA films, corresponding to the peak observed for Alq_3 in the solid state. Scanning electron microscopy and atomic force microscopy were done on the samples to investigate the surface morphology and structure of the samples.

1. Introduction

Since its first report in 1987 by Tang and Van Slyke [1] Alq_3 is used as the emission and electron transporting layer in organic light emitting diodes (OLEDs). The current trend during the fabrication of OLEDs is to use solution-processing. However, with this technique Alq_3 must be vacuum deposited [2]. A possible solution to this problem is to dope different polymers with Alq_3. These polymers should contain the optical properties of Alq_3 while the processability of a polymer is maintained. This will allow for low cost manufacturing techniques such as ink-jet printing and solution processing [3]. In this study polymethyl methacrylate (PMMA) is doped with different mole % of Alq_3 ranging from 0.5 - 5 %. The effect of the different concentrations of Alq_3 on the photoluminescence (PL) intensity and emission wavelength is investigated. The morphology and structure of the blended films are studied to see what will be the effect of surface roughness on the PL intensity

2. Experimental

2.1 Synthesis

Alq_3 phosphor powder was synthesized using the co-precipitation method [4]. 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. It was stirred for 15 minutes. 0.5 g $Al(NO_3)_3$ was added to 20 ml H_2O and was 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 mixture was stirred for 15 minutes. 5 ml of NH_4OH was added drop wise to the mixture while

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stirring. A yellow green precipitate formed. The precipitate was filtered and washed 8 times with distilled water. The precipitate was left to dry overnight at 80°C. After drying the precipitate was grinded to get a fine powder. The powder was dissolved in 10 ml acetone and left to recrystalize in atmosphere at room temperature.

A blended thin film of Alq_3:PMMA at a concentration ratio of 1% was obtained in the following way: 2g of PMMA was dissolved in 25ml of chloroform. A solution of 0.026 g Alq3 in 15 ml of chloroform was added to the PMMA solution. The blend was stirred and poured into a stainless steel dish were it was left to dry in atmosphere for 24 hours. The films were then cut into 1x1 cm pieces for further characterization. The blended thin films of Alq3:PMMA at concentration ratios of 0.5% - 5% can be obtained in a similar way.

2.2 Characterization

The structure and morphology of the samples were determined by scanning electron spectroscopy (SEM) using a Shimadzu SSX550 at the Centre for microscopy (CCEM) at the University of the Free State and atomic force microscopy (AFM) by using the Shimadzu SPM – 9600 system. The PL emission data was collected with a Cary Eclipse fluorescence spectrophotometer equipped with a Xenon flash lamp.

3. Results and discussion

Figure 1 shows the SEM images of the 1% Alq_3:PMMA film at x1000 and x5400 magnification. Small holes can be seen scattered all over the film. These holes are formed when gasses escaped during the evaporation of chloroform (the solvent). At higher magnifications it can be seen that the holes are not all the same size. Bigger holes had formed early in the solidification process due to rapid rate of evaporation of the solvent. The smaller holes formed almost at the end when the amount of solvent was less and the rate of evaporation slowed down. A smoother surface can be obtained if the rate of evaporation of the solvent can be slowed down. This can be acieved by keeping the samples in a cooler environment during the drying process. Small chunks with no holes can be seen at x1000 magnification. This is peaces of PMMA that did not completely dissolved during the chemical reaction. By increasing the time allowed for the PMMA to dissolved in chloroform these chunks might dissapear.

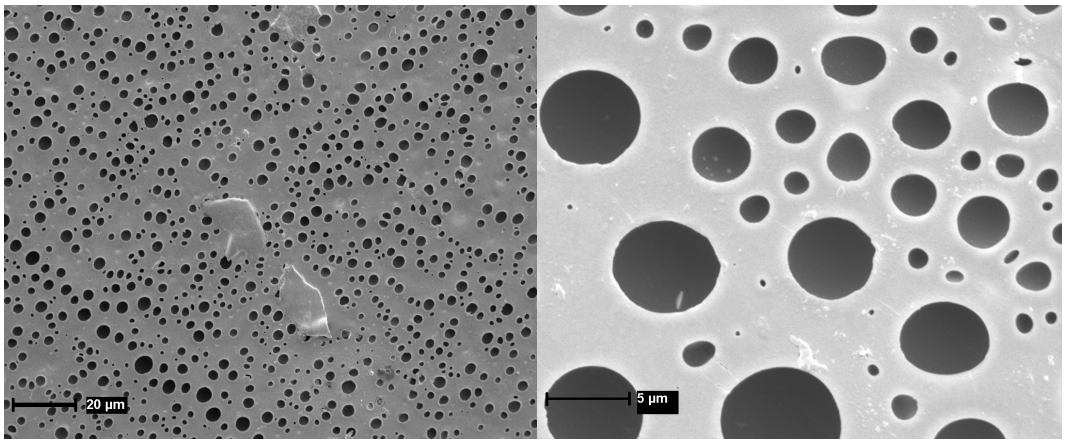

Figure 1: SEM images of 1% Alq_3:PMMA at x1000 and x5400 magnifications. Holes that had formed during the evaporation of the solvent can clearly be seen.

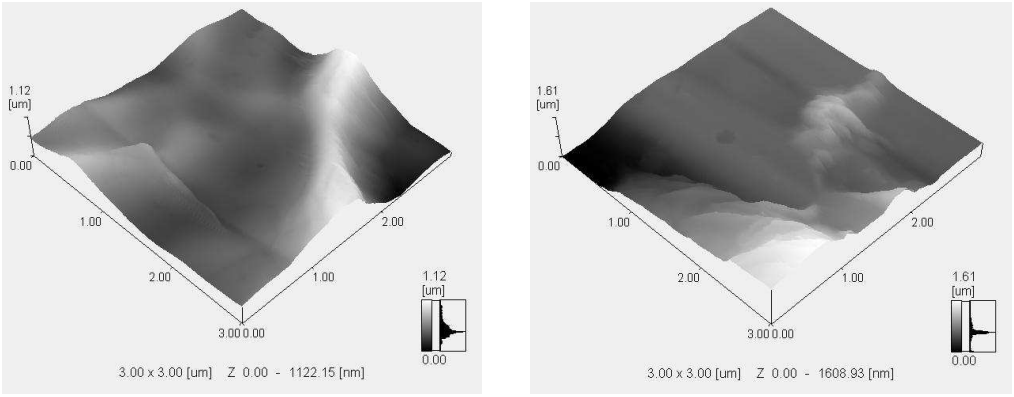

Figure 2: AFM images of two different spots on the 1% Alq_3:PMMA film.

Figure 2 shows the AFM images of two different spots on the 1% Alq_3:PMMA film. From the images it can be seen that the surface of the films is not very smooth. Outcrops can be seen ranging between 1-2 µm in height. No distinct particles can be seen confirming that the Alq_3 powder have completely mixed with the PMMA

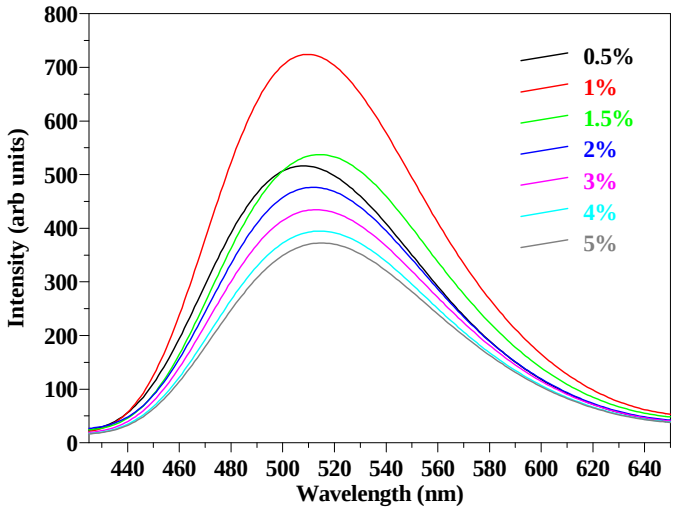

Figure 3: Photonluminescent spectra of different concentrations of Alq_3 in a PMMA matrix, just after synthesis.

Figure 3 shows the PL spectra of different concentrations of Alq_3 in a PMMA matrix just after synthesis of the films. The films were excited at 355 nm. All the peaks show a broad spectrum with a maximum in intensity at around 515 nm (figure 4(a)). This corresponds to the emission of Alq_3 in the solid state [5], demonstrating that the optical properties of Alq_3 are preserved within the PMMA matrix.

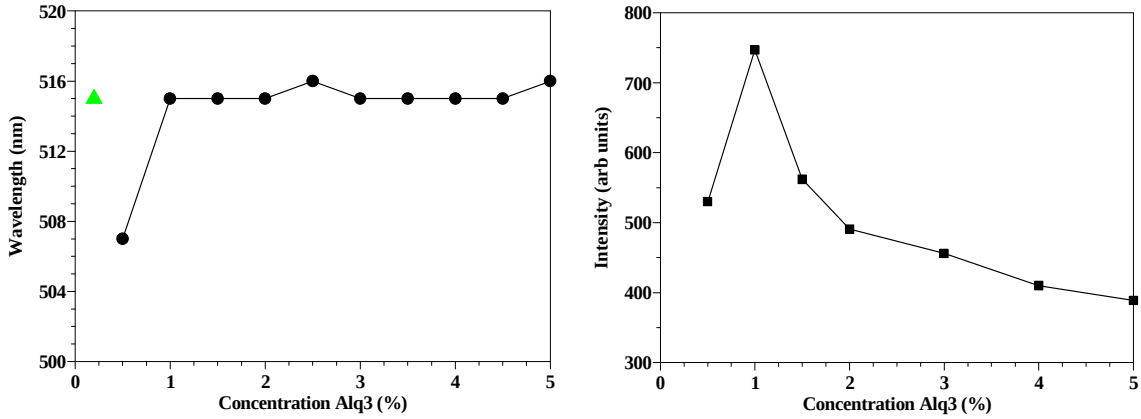

Figure 4: (a) A plot of the emission wavelength at maximum intensity as function of the Alq_3 concentration. The triangle represents the emission of Alq_3 in the solid state. (b) Plot of PL maximum intensity as a function of concentration of Alq_3.

The peak of the 0.5% sample has a blue shift of 8 nm. Previous reports by Cölle et. al. [6] and Levichkova et.al. [7] contribute the blue shift to either the formation of the δ-phase of Alq_3 or the transformation of the meridional form of Alq_3 to the facial form. For the δ-phase to form a processing temperature of 410°C is required [8]. In this study all synthesis were performed at room temperature and the XRD analysis done on Alq_3 in the solid state shows that it is in the α-phase (JCPDS 26-1550). For Alq_3 to transform from the meridional form to the facial form, local heating of the Alq_3 molecules are needed during film growth [4]. As already mentioned no heating was applied during the processing of the Alq_3:PMMA films. The observed blue shift in the emission spectrum of the 0.5% sample may however be attributed to cross relaxation. Blasse reported that the luminescence of Tb^{3+} is concentration dependant [9]. At low concentrations the emission is due to the $^5D_4$-$^7F_6$ transition of Tb^{3+} and is blue, but at higher concentration of Tb^{3+} this emission is quenched due to cross relaxation and the $^5D_4$-$^7F_5$ transition becomes dominant and this gives rise to green emission. A similar cross relaxation might be responsible for the concentration dependence of the Alq_3 emission. Alq_3 is known to be a singlet emitter [10]. The emission of solid state Alq_3 is due to the relaxation of an excited electron from the S_1-S_0 level. A lot of S_n levels exist above the S_1 level. At low concentrations the emission is most probable due to relaxation from the S_n-S_0 level causing a blue shift in the emission. At higher concentrations this emission is quenched due to cross relaxation and the S_1-S_0 transition becomes dominant. Figure 4(b) shows that the sample doped with 1% of Alq3 has the highest intensity. The intensity then decreases with an increase in concentration. This same decrease in intensity was reported by Meyers and Weck [2].

As can be seen from the SEM images that the surface of the samples on a macro scale is full of holes and therefore fairly rough. The AFM images also show on a micro scale that the surface is rough with a “hills and valleys” structure. Coetsee et. al. reported that the luminescence from a thin film normally results in a lower intensity due to the internal reflection of the light exciting the layer. A rougher surface would therefore result in a better light output [11]. This might be one of the reasons that a high luminescence intensity is observed for samples doped with low concentrations of Alq_3.

4. Conclusion

Blended thin films of Alq_3:PMMA were successfully synthesized. The morphology and structure measurements of the films showed that the surface had a lot of holes, where the trapped gas had

escaped. The AFM images showed that the surface of the films was not smooth, but rather rough with a lot of “hills and valleys”. This rough surface contributed to the high luminescence intensity that was observed due to less internal reflection that occurred within the film. A broad emission band was observed, with its maximum at 515 nm when excited with 355 nm photons. This corresponded to observed emissions of Alq_3 in the solid state. A blue shift in the emission was observed for the 0.5% sample. This blue shift might be due to cross relaxation. The 1% sample showed the highest intensity and the intensity then decreased with an increase in doping concentration.

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