2214

Morphological Study of Aluminium *tris(*8-hydroxyquinoline) using IR and Raman Spectroscopy.

R.J. Curry. Optoelectronic Research Centre, University of Southampton, Southampton, SO17 lBJ, United Kingdom.

W.P. Gillin. Department of Physics, Queen Mary, University of London, London E1 4NS, United Kingdom.

J. Clarkson and D.N. Batchelder. Department of Physics and Astronomy, University of Leeds, Leeds, LS2 9JT, United Kingdom.

Abstract

We present a study of aluminium *tris*(8-hydroxyquinoline) (Alq_3) films using infra-red (IR) absorption and Raman spectroscopy. Evidence is given that upon sublimation a disordered phase, γ-Alq_3, may be obtained. Upon annealing of these films at temperatures above 200°C crystallisation of the films is observed along with evidence for an increase in the presence of the α-Alq_3 polymorph. The results of IR absorption measurements on the sublimed films could be interpreted as evidence that thermal interconversion between the *mer* and the *fac* isomers had taken place during annealing at 300°C. These two results appear to be in contradiction and so the use of IR spectroscopy to identify the two isomers of Alq_3 is questioned.

Aluminium *tris*(8-hydroxyquinoline) (Alq_3) has become one of the most widely used molecules in organic light emitting diodes (OLEDs) following the demonstration by Tang and VanSlyke of an efficient device utilising the molecule [1]. In addition to the earlier studies of Alq_3 [2-6], this use of the molecule for OLED applications has lead to a number of more recent studies of its [7-19] properties. Despite all this research the role of the morphology of Alq_3 films on the performance and stability of OLEDs incorporating them is still not clear.

Two geometric isomers of Alq_3 exist, *mer* (C_1 symmetry) and *fac* (C_3 symmetry), and thermal interconversion between the two has previously been suggested [5]. Evidence suggests though that such interconversion is not a prerequisite for obtaining amorphous films [16]. However, it is thought that the two isomers co-exist in the amorphous state, a result of which may be an increase in the stability of this state [18]. Identification of the two isomers has been attempted using IR absorption spectroscopy and peaks at ~442, 456 and 472 cm^{-1} have been assigned to the *mer* isomer and at 398 and 419 cm^{-1} to the *fac* isomer [4,8].

Three polymorphs of the *mer* isomer, labelled α-Alq_3, β-Alq_3, and γ-Alq_3, have been identified [16]. Of these characteristic Raman ‘fingerprints’ were found for the α-Alq_3 at 117 and 155 cm^{-1}, and β-Alq_3 at 109 and 183 cm^{-1}.

In the work presented here we give detailed IR and Raman spectra of Alq_3 powder and films annealed at temperatures ranging from ambient to 300 °C. The Raman spectra clearly show that under annealing there is a re-arrangement of the Alq_3 film that is similar to that observed by Brinkmann *et al.* [16]. Under the same conditions we also observe a change in the IR spectra which could be interpreted as evidence for some thermal interconversion between the isomers of Alq_3. We then discuss these results in the context of previous studies.

The Alq_3 powder was obtained from Alderich and used without further purification. Films of Alq_3 were sublimed under a vacuum of ~ 10^{-6} mbar from a degassed boron nitride crucible at a rate of 1-2 Å/s onto WSi_2 and KBr substrates. The substrate temperature was not controlled and the resulting Alq_3 film thicknesses were 635 nm on the WSi_2 and 50 nm on the KBr substrates, measured using a calibrated quartz crystal thickness monitor.

The annealing of the films was carried out under a flowing nitrogen atmosphere using a barrel furnace. Each anneal was for 1 hour at a temperature of 50°C, 100°C, 150°C, 200°C, 225°C, 250°C or 300°C.

The KBr discs incorporating Alq_3 powder for IR absorption measurements were pressed with a weight ratio of 0.1 % Alq_3 in KBr. The IR absorption spectra were obtained using a Perkin Elmer 2000 FTIR spectrometer with a resolution of 0.5 cm^{-1}.

The anti-Stokes Raman spectra were obtained using a Renishaw Raman microscope system fitted with a Leica DMCN microscope incorporating a CCD camera. The resolution of this system was better than 1 cm^{-1}. The images of the Alq_3 sublimed films were obtained using the CCD camera on the microscope using a × 20 objective. All Raman spectra were taken using a × 50 objective.

Figure 1 shows the Raman spectra of Alq_3 powder, a sublimed film of Alq_3 (on a Wsi_2 substrate) and various areas of sublimed films annealed at 225°C and 300°C over the range –500 to –70 cm^{-1}. Figure 2 shows microscope images of the regions of the sublimed films that the spectra shown in figure 1 were taken from. The Raman spectrum of the Alq_3 powder shows a main broad peak centred at 109 cm^{-1} with a shoulder at ~95 cm^{-1}. Within this broad peak lie two of the Raman 'fingerprints' used to identify the α-Alq_3 and β-Alq_3, at 117 and 109 cm-1 respectively [16]. In addition to the main peak two other peaks are visible at 154cm^{-1} and 168 cm^{-1}. The former of these peaks coincides with the second Raman 'fingerprint' of α-Alq_3 [16] and both have been assigned to ring wagging modes of the ligands [13]. The position of the main peak and the peak at 154 cm^{-1} suggests that the powder contains both α-Alq_3 and β-Alq_3. If we compare the Raman spectra of the Alq_3 powder and sublimed film that has not been annealed, shown in figure 2a, there are some obvious differences. Firstly the main broad peak has moved from 108 to 95 cm^{-1} upon sublimation of the Alq_3. In addition to this the peak at 154 cm^{-1} has reduced in intensity whilst a peak at 194 cm^{-1} has emerged. The reduced intensity of the 154 cm^{-1} peak along with the movement of the main peak would suggest a reduction in the α-Alq_3 polymorph upon sublimation. The movement of the main peak to 95 cm^{-1}, past the Raman 'fingerprint' of β-Alq_3 at 109cm^{-1}, also suggests that there may be a reduction in this polymorph upon sublimation. Brinkmann *et al.* [16] found that X-ray diffraction evidence indicated that the α-Alq_3 was formed preferentially in thin films. They also suggested that a new disordered phase, γ-Alq_3 originally obtained by heating crystals of the α polymorph at ~395°C, was possible through freezing of the molecular positions whilst cooling. Such a process may have taken place upon sublimation of our films resulting in a reduction in the amount of the α-Alq_3 and β-Alq_3 polymorph and so movement of the main peak as observed.

As has been previously noted [13] we observed no change in the Raman spectra upon annealing of the sublimed films at temperatures up to 200°C. At temperatures above this however the films are seen to start crystallising as expected from thermal analysis of Alq_3 [9]. The Raman spectra of three areas of a film annealed at 225°C, figure 2b, are shown in figure 1. The Raman spectrum of the featureless area of the film, labelled 'flat' area, as expected is similar to that of the un-annealed film. However, changes can be seen in the spectra obtained from a crack in the film and a needle like crystal (similar to that described by Brinkmann *et al.* [16]). In both of these spectra the main peak has moved back from 95 cm^{-1} towards the position observed in the spectrum obtained from the Alq$_3$ powder. Furthermore, the peak at 155 cm^{-1} has re-emerged. Finally, figure 1 shows the Raman spectrum of the film annealed at 300°C, shown in figure 2d. This film is comprised of many needle like crystals. The Raman spectrum shows the characteristic α-Alq$_3$ 'fingerprint' at 154 cm^{-1} and a shoulder in the main peak at ~ 120 cm^{-1} indicates the presence of the second fingerprint of this polymorph. The main peak can be seen to consist of two further peaks centred at 109 cm^{-1} (thus suggesting some of the β-Alq$_3$ polymorph is also present) and 100 cm^{-1}.

Crystals of α-Alq$_3$ obtained by sublimation have been shown to consist of the *mer* isomer of Alq$_3$ and so the γ-Alq$_3$ obtained from these crystals was thought to be comprised of the same isomer [16]. However, this conclusion was only inferred, as the presence of the *fac* isomer could not be ruled out from X-ray diffraction data. Figure 3 shows the IR spectra of Alq$_3$ powder dispersed in a KBr disc and two sublimed films of Alq$_3$ (on KBr substrates) one of which has been annealed at 300°C. The IR spectrum of the powder has peaks located about the characteristic peaks of the *mer* isomer and there are also some peaks indicating the possible presence of the *fac* isomer. Upon sublimation the resulting film shows a significant increase in the intensities of the peaks located at 398 and 419 cm^{-1} along with a slight reduction in intensity of the peaks located at 443, 455 and 466 cm^{-1}. Following annealing at 300°C these changes are even more striking. If these peaks can be used to identify the two geometrical isomers of Alq$_3$ then these results would appear to give evidence for some thermal interconversion between the *mer* and the *fac* isomer upon sublimation and annealing. Sano *et al.* showed that with heating it was possible to produce denatured Alq$_3$ which has a broad absorption peak ~ 420 cm^{-1} which covers both of the *fac* isomer absorption peaks [8]. Whilst the denatured Alq_3 absorption peak coincides with the peak observed here at 419 cm^{-1}, the narrow width of this peak in conjunction with the peak observed at 398 cm^{-1} precludes the possibility of this explanation for the changes observed upon annealing.

It should be noted that the films deposited onto KBr substrates did not show the same degree of crystallization as those deposited onto WSi_2. The reason for this could be related to the thickness of the sublimed film in each case with the thinner film constraining the crystal growth.

The Raman spectrum and IR absorption spectrum in the region 500 to 2000 cm^{-1} was also obtained for each sample. Upon sublimation and annealing of the films no change in these spectra were observed.

The apparent increase in the *fac* isomer upon annealing is in contrast to the growth of the α-Alq_3 crystals obtained during the same process that have been shown to be comprised of the *mer* isomer [16]. If the Alq_3 films contained a racemic mixture of the two isomers of Alq_3 then this would act to inhibit the growth of crystals in the film. As a result we are left with the possibility that either the α-Alq_3 polymorph contains a mixture of the two isomers or that the IR absorption peaks cannot be used to identify the two isomers. The detailed work of Brinkman *et al.* [16] seems to preclude the first of these suggestions and so we are left to question the reliability of identification of the isomers of Alq_3 using IR spectroscopy. This would appear to be in agreement with calculations that have shown that the activity of the vibrations used to identify the isomers is too low to allow the isomers to be distinguished using this method [18]. However, further work needs to be undertaken before this is fully understood.

In conclusion we have given evidence that sublimed films of Alq_3 may contain a disordered phase, γ-Alq_3. Upon annealing of these films at temperatures above 200°C crystallisation of the films is observed along with evidence for an increase in the presence of the α-Alq_3 polymorph. The results of IR absorption measurements on the sublimed films could be interpreted as evidence that thermal interconversion between the *mer* and the *fac* isomers had taken place during annealing at 300°C. These two results appear to be in contradiction and so the use of IR spectroscopy to identify the two isomers of Alq_3 is questioned.

References

1) C.W. Tang and S.A. VanSlyke. Appl. Phys. Lett., **51** (12), 913 (1987).

2) K.G. Stone. J. Am. Chem. Soc., **76**, 4997 (1954).

3) R.G. Charles, H. Freiser, R. Friedel, L.E. Hilliard, and W.D. Johnston. Spectrochimica Acta, **8,** 1 (1956).

4) R. Larsson and O. Eskilsson. Acta. Chem. Scand., **22**, 1067 (1968).

5) B.C. Baker and D.T. Sawyer. Anal. Chem., **40** (13), 1945 (1968).

6) P.J. Milham, A.W. Hudson, M.J. Maguire, K.S. Haddad, and C.C Short. Appl. Spectrosc., **33** (3), 298 (1979).

7) I. Fujii, N. Hirayama, J. Ohtani, and K. Kodama. Anal. Sci., **12**, 153 (1996).

8) K. Sano, Y. Kawata, T.I. Urano, and Y. Mori. J. Mater. Chem., **2** (7), 767 (1992).

9) K. Naito and A. Miura. J. Phys. Chem., **97**, 6240 (1993).

10) I. Fujii, N. Hirayama, J. Ohtani, and K. Kodama. Anal. Sci., **12**, 153 (1996).

11) E. Han, L. Do, N. Yamamoto, and M. Fujihira, Thin Solid Films, **273**, 202 (1996).

12) J.D. Anderson, E.M. McDonald, P.A.Lee, M.L. Anderson, E.L. Ritchie, H.K. Hall, T. Hopkins, E.A. Mash, J. Wang, A. Padias, S. Thayumanavan, S. Barlow, S.R. Marder, G.E. Jabbour, S. Shaheen, B. Kippelen, N. Peyghambarian, R.M. Wightman, and N.R. Armstrong. J. Am. Chem. Soc., **120**, 9646 (1998).

13) M.D. Halls and R. Aroca. Can. J. Chem., **76**, 1730 (1998).

14) A. Curioni, M. Boero, and W. Andreoni. Chem. Phys. Lett., **294**, 263 (1998)

15) R.J. Curry and W.P. Gillin. J. Appl. Phys., **88** (2), 781 (2000).

16) M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi, and A. Sironi. J. Am. Chem. Soc., **122**, 5147 (2000).

17) G.P. Kushto, Y. Iizumi, J. Kido, and Z.H. Kafafi. J. Phys. Chem. A, **104**, 3670 (2000).

18) A. Curioni and W. Andreoni. IBM J. Res. And Dev., **45** (1), 101 (2001).

19) H. Ichikawa, T. Shimada, and A. Koma. Jpn. J. Appl. Phys., **40**, L225 (2001).

Figure captions.

Figure 1. The 632 nm excited Raman spectra of Alq_3 powder, a 635 nm Alq_3 film as deposited, three areas of a 635 nm Alq_3 film annealed at 225 °C for 1 hour, and a 635 nm Alq_3 film annealed at 300 °C for 1 hour.

Figure 2. Optical microscope images of A) an as deposited 635 nm Alq_3 film, B) a 635 nm Alq_3 film annealed at 225 °C for 1 hour, C) a 635 nm Alq_3 film annealed at 250 °C for 1 hour and D) a 635 nm Alq_3 film annealed at 300 °C for 1 hour. Each image was taken using a x 20 objective.

Figure 3. The IR transmission spectra of Alq_3 powder dispersed in a KBr disc, a sublimed film of Alq_3 and a sublimed film of Alq_3 following annealing at 300°C.

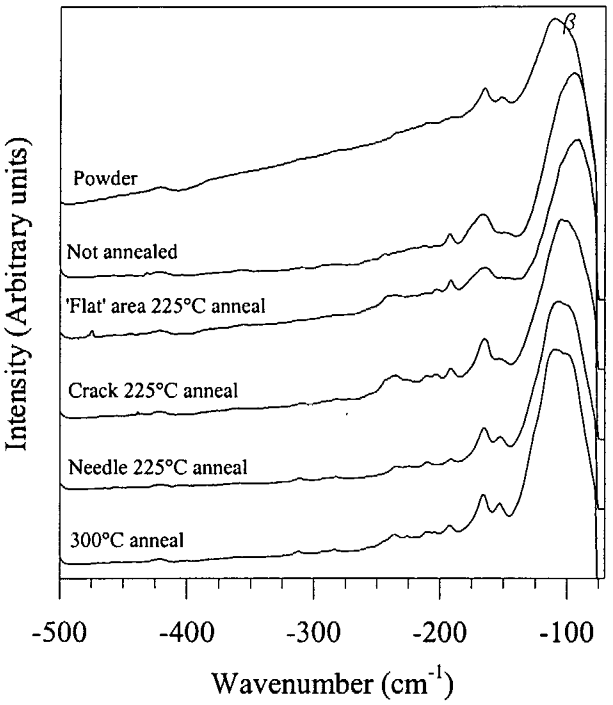

Figure 1. R.J. Curry *et al.*

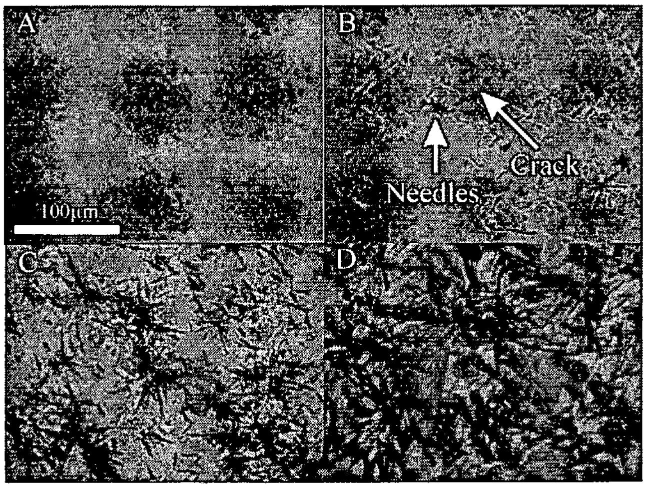

Figure 2. R.J. Curry *et al.*

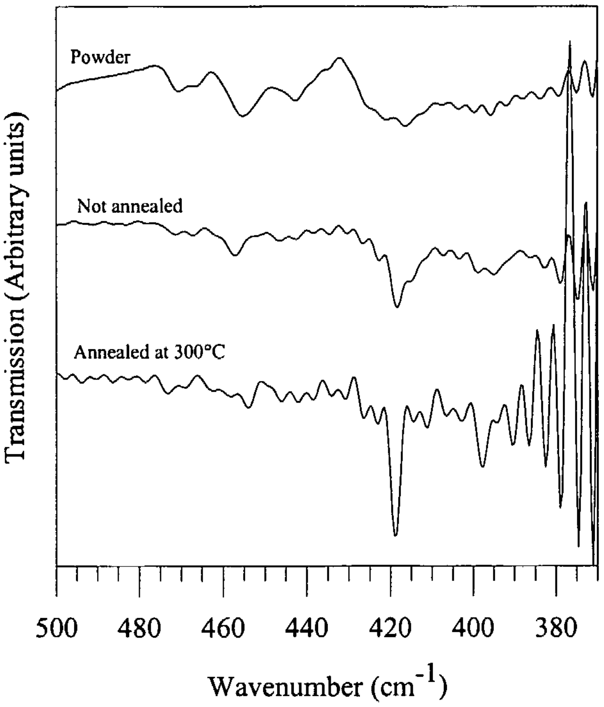

Figure 3. R.J. Curry *et al.*