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Preparation and characterization of blue luminescent tris(8-hydroxyquinoline)aluminum (Alq$_3$)

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Abstract

Using differential scanning calorimetry (DSC) measurements in combination with structural and optical characterization we have investigated the formation conditions of different phases of tris(8-hydroxyquinoline)aluminum (Alq$_3$). We have identified the δ-phase as a high temperature phase of Alq$_3$ being composed of the facial stereoisomer and report an efficient method to obtain blue luminescent Alq$_3$ by a simple annealing process. This allows to prepare large amounts of pure δ-Alq$_3$ choosing appropriate annealing conditions, which is the prerequisite for further characterization of this blue luminescent phase and offers the possibility to fabricate blue organic light emitting devices (OLEDs) from this material.

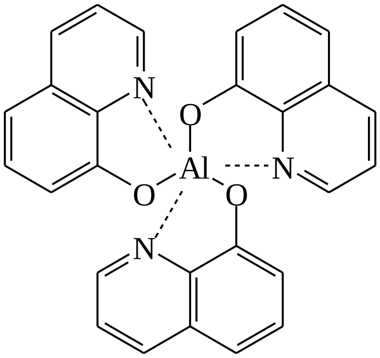

Figure1: Chemical structure of tris(8-hydroxyquinoline)aluminum (Alq_3)

Introduction

Since the discovery of tris(8-hydroxyquinoline)aluminum (Alq_3)-based multilayer thin-film electroluminescent devices by Tang and co-workers in 1987[1] much progress has been made in organic light emitting devices (OLEDs), that are of interest in various display applications. Alq_3 (chemical structure shown in Figure 1) is a stable metal chelate complex that can be sublimed to yield amorphous thin films and stands as one of the most successful organic materials used in OLEDs. After more than 15 years of intense research and development, Alq_3 still continues to be the workhorse among the class of low-molecular weight materials for OLEDs. However, so far comparatively few investigations have been devoted to the material's electronic and optical properties - in particular in the crystalline state. Recently, a systematic study of the optical properties of solutions, amorphous films and different polymorphic crystalline phases of Alq_3 was published.[2] Three new crystalline phases (α-, β- and γ-Alq_3) were identified. The vibronic structure of the fluorescence was resolved for the first time in α- and β-phase crystals at low temperature and a correlation between the molecular packing and the spectral features of the fluorescence was shown. Although crystallographic data were presented for the γ-phase, no x-ray spectra and no optical characterization or investigation of this high temperature phase have been published so far.

Another unresolved issue concerns the isomery of the Alq_3 molecule.[3-5] It is well-known that octahedral complexes of the type MN_3O_3, where M is a trivalent metal and N and O stand for the nitrogen and oxygen atoms in the quinoline ligands, can occur in two different stereoisomers: meridional and facial. However, up to now experimental investigations have given no evidence for the presence of the facial isomer in one of the known phases of Alq_3. Therefore, it is generally believed that the meridional isomer is predominant, both in amorphous films and crystals of Alq_3.

Recently, we have reported a new crystalline phase of Alq_3 (δ-Alq_3) which was obtained by thermal sublimation in a horizontal glass tube.[6] Its optical properties have been tentatively discussed in terms of the isomery of the Alq_3 molecule. As compared to the α-phase the δ-phase is characterised by a strong blue-shift of the photoluminescence maximum of about 0.2eV.[6] However, using the train sublimation method, only small amounts of blue luminescent δ-Alq_3 (some mg) were obtained. Furthermore, the material was embedded between the neighbored phases and thus it was difficult to obtain a pure phase. While the forming conditions of α- and β-Alq_3 from evaporation and solution, respectively, are well known, this is not the case so far for the δ-phase. Obviously temperature has a significant influence on the formation of blue luminescent Alq_3. Therefore we have investigated the thermal properties of Alq_3 in order to understand the forming process of this new phase. By doing so, we found out how to prepare large amounts of pure δ-Alq_3 which is necessary for further characterization and for the preparation of blue luminescent thin films or OLEDs.

Results

Figure 2 shows the DSC measurement of polycrystalline Alq_3 powder taken with a heating rate of 20° C/min. One observes a coupled endothermic and exothermic phase transition at about

395°C prior to the large melting transition at 419°C. This additional phase transition has also been reported in the literature and has been attributed to polymorphism of the crystalline material.[2,8] It is very pronounced at fast heating rates (above 15°C/min). For slow heating rates the endothermic and exothermic transitions become broader which comes along with a less intense peak with respect to the strong melting peak. They start to intermingle and are slightly shifted to lower temperature as shown in the inset of Figure 2 for heating rates of 20°, 10°, 5° and 2°C per minute. This behaviour is similar to known irreversible monotropic solid-solid transitions.[7] Typically, the monotropic transition is very slow and is therefore mostly observed a few degrees below the melting point. Thus it is advisable to measure the monotropic transition isothermally at very slow heating rates. At higher heating rates (here above 2°C/min) it is easy to "run over" the slow transition and so reach the melting temperature of the metastable low-temperature phase giving the endothermic melting peak that merges directly into the exothermic crystallization peak leading to the high-temperature phase. Although we did not investigate this process in detail, we think that the described scenario can explain the behaviour shown in Figure 2.

We find that increasing the temperature above 430°C results in decomposition of the material. Furthermore we note that a small broad transition at 320°C reported by Sapochak et al.[8] was not observed in our samples. In the following we used a slow heating rate of 2°C/min, where the shift of the peak temperatures is rather small (see Figure 3) and where it is possible to stop the process at a defined temperature. By this procedure we could specify the conditions for the preparation of different Alq_3 phases by a controlled thermal annealing process.

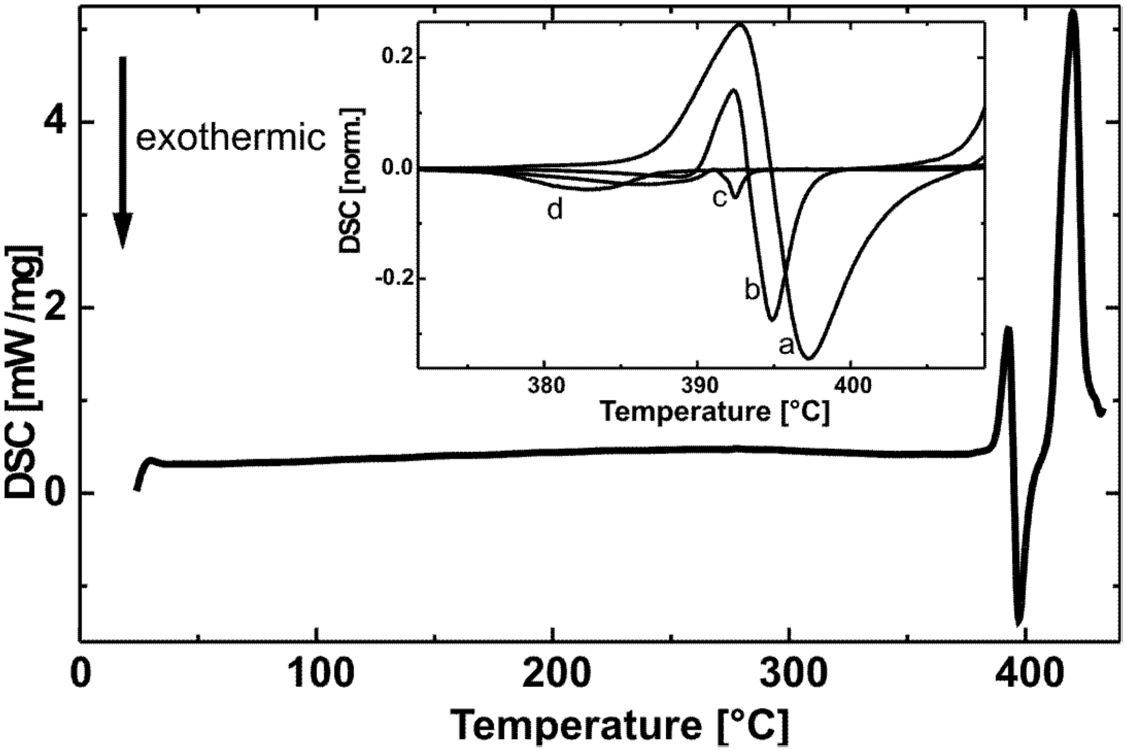

Figure 2: DSC trace of Alq_3 with pronounced thermal transitions at 393°, 396° and 419°C measured with a heating rate of 20°C/min. Inset: Broadening and intermingling of the endothermic and exothermic transition around 395°C in the DSC signal related to the sweep speed (a: 20°C/min, b: 10°C/min, c: 5°C/min, d:

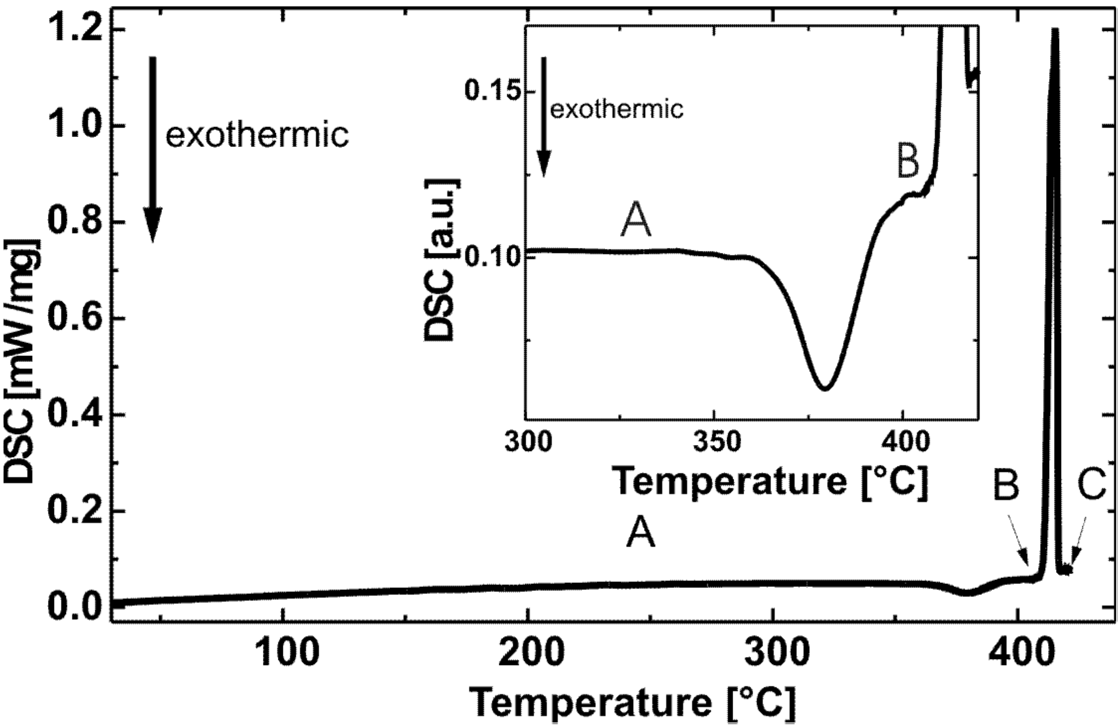

Figure 3: DSC trace of Alq_3 measured with a heating rate of 2°C/min. The clearly pronounced exothermic phase transition at 380°C prior the melting point is zoomed out in the inset, as it becomes broad and less intense with respect to the melting peak for this slow heating rate. A, B and C mark the regions of yellowish-green Alq_3, blue Alq_3 and melt, respectively.

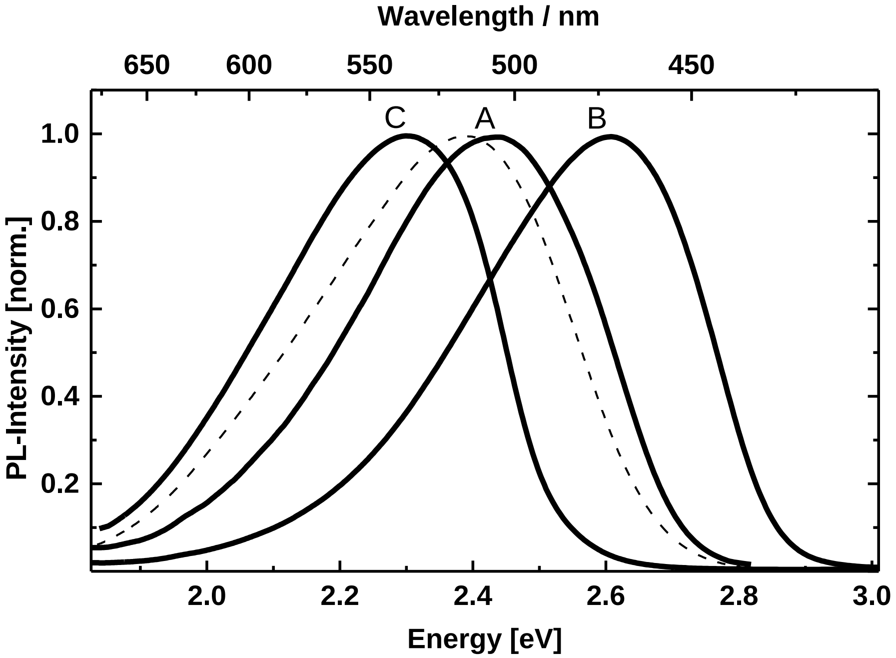

Figure 4: PL spectra of Alq_3 samples taken from the regions A, B and C of Figure 3 respectively, excited at 350nm. For comparison the PL of an evaporated Alq_3 film is shown (dashed line).

We could distinguish three different phases of Alq_3 in these slow DSC measurements (see Figure 3): First the usual yellowish-green powder (A) before the exothermic phase transition, second a whitish powder (B) (hereafter called "blue Alq_3") between this phase transition and the melting peak and third the glassy state of Alq_3 (C). This glassy state of Alq_3 was obtained by quenching the melt in liquid nitrogen. Its highly amorphous character was verified by using x-ray powder diffraction measurements and using an image plate detection system (IPDS). Cooling down the liquid melt slowly, results in yellowish-green powder (A) again, as discussed in [9]. All of these phases are stable at room temperature.

Figure 4 shows the PL spectra of annealed polycrystalline Alq_3 powder from regions A and B as well as of the quenched amorphous melt (C). For annealing temperatures up to 365°C Alq_3 is a yellowish-green powder with a PL maximum at 506nm (curve A). After the exothermic transition at about 380°C, there is a big blue shift of 0.18eV (37nm), associated with a slight change in the shape of the PL spectrum (curve B), which is less symmetric for the blue Alq_3. The rise at the high energy side becomes steeper and the tail at low energies is more pronounced. The quenched melt (curve C) is clearly red shifted (0.14eV) compared to the yellowish-green Alq_3-powder (curve A). The strong difference in the emission color can be seen in Figure 5, where samples of the quenched melt, yellowish-green and blue Alq_3 are shown at daylight (a) and under UV-irradiation (b), respectively. The emission color is shifted from green (CIE coordinates: x=0.27, y=0.5) to blue (x=0.16, y=0.26). From Figure 5 one can also see the relatively low PL intensity of the quenched melt compared to the very intense PL emission of blue Alq_3. This is due to the high PL quantum efficiency of crystalline Alq_3 (blue Alq_3: 51%, yellowish-green powder: 40%,

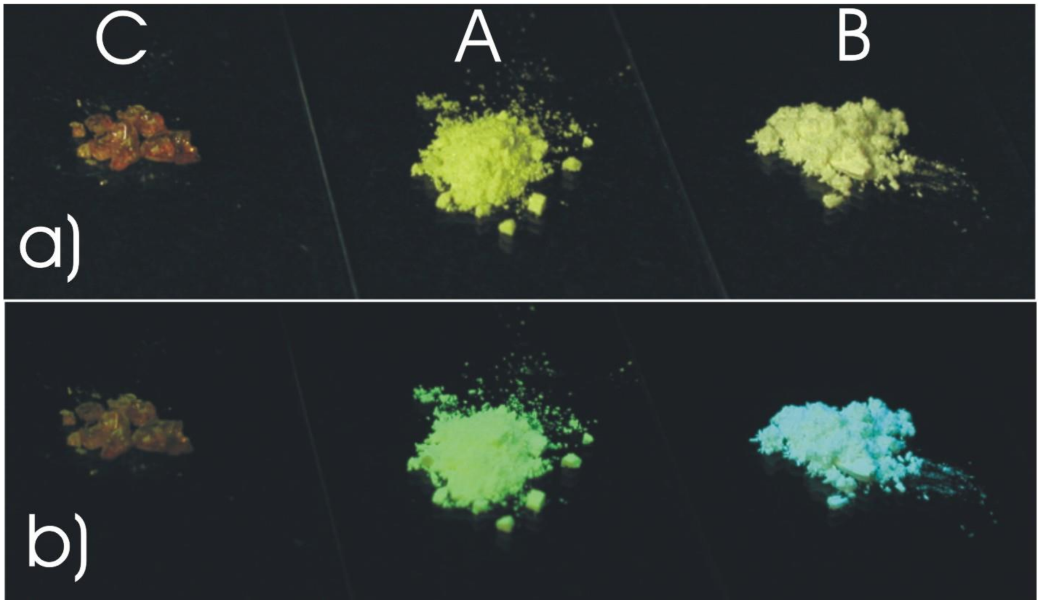

Figure 5: Photographs of Alq_3 samples taken from the regions A, B and C in Figure 3: a) at usual daylight and b) under UV-irradiation (excitation wavelength: 366nm), clearly showing the strong blue shift of the luminescence of annealed material.(CIE color coordinates for A: x=0.27, y=0.50; for B: x=0.16 , y=0.26).

evaporated film: 19% and quenched amorphous melt: 3%). This is, to our best knowledge, on the one hand the first report on blue luminescent Alq$_3$ obtained by a simple annealing process and on the other hand the first report on such a pronounced red shift for amorphous Alq$_3$. The dashed line in Figure 4 is the PL spectrum of an evaporated Alq$_3$-film as used in OLEDs. Although these films are commonly called "amorphous", one can clearly see that the PL maximum is located between amorphous and crystalline Alq$_3$. This is a hint for the nanocrystalline character of these films as reported already by Tang et al.[1] The observed red shift of the quenched melt as compared to the crystalline material seems to be related to the morphology and intermolecular interaction. This effect is still under investigation and will be discussed elsewhere.

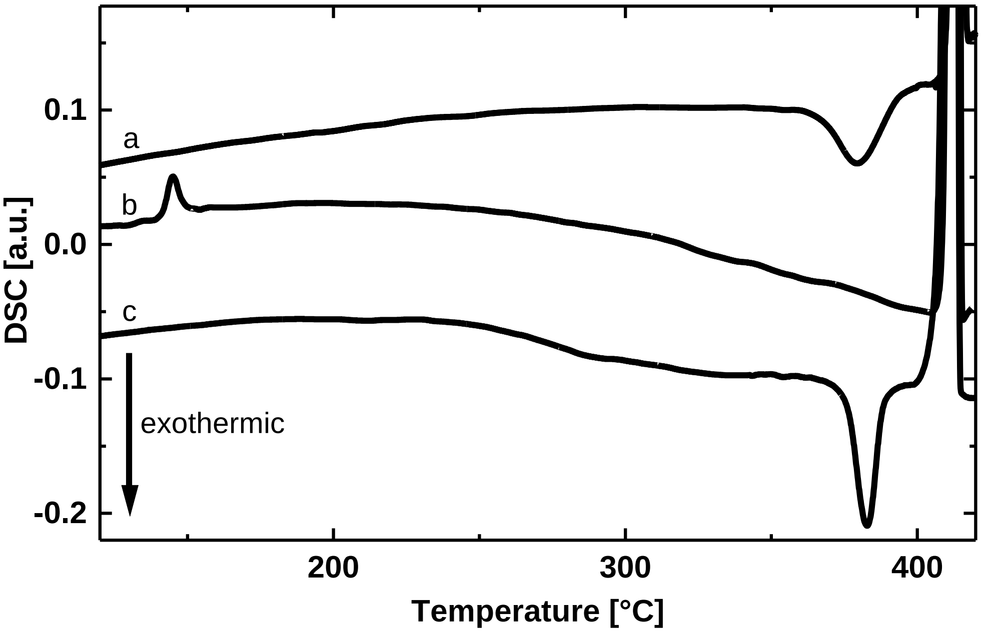

Figure 6: DSC traces of a: yellowish-green Alq$_3$ and b: blue Alq$_3$. Trace c shows a second heating cycle after cooling down the melt (b) again.

A comparison of the heating cycles of the yellowish-green Alq$_3$ and the blue Alq$_3$ is shown in Figure 6. Blue Alq$_3$ (trace b) has no phase transition in the region around 380°C. This confirms the fact, that the blue Alq_3 is formed in this exothermic process. In addition there is a small transition at 145°C observed only for the blue Alq_3. DSC measurements of amorphous samples (not shown) gave a glass temperature of 178°C and a pronounced recrystallization peak at 235°C, similar to the results reported by Sapochak et al.[8]

Another outcome of these DSC measurements is that all three phases can be easily converted into each other: Annealing yellowish-green Alq_3 at temperatures between 380°C and 400°C with subsequent slow cooling results in blue Alq_3. Melting blue Alq_3 and cooling down the melt slowly results in yellowish-green powder again as shown in trace c in Figure 6. The successful conversion from one phase into the other was confirmed by measurements of the PL spectra, FT-IR spectra, Raman spectra and X-Ray diffraction.

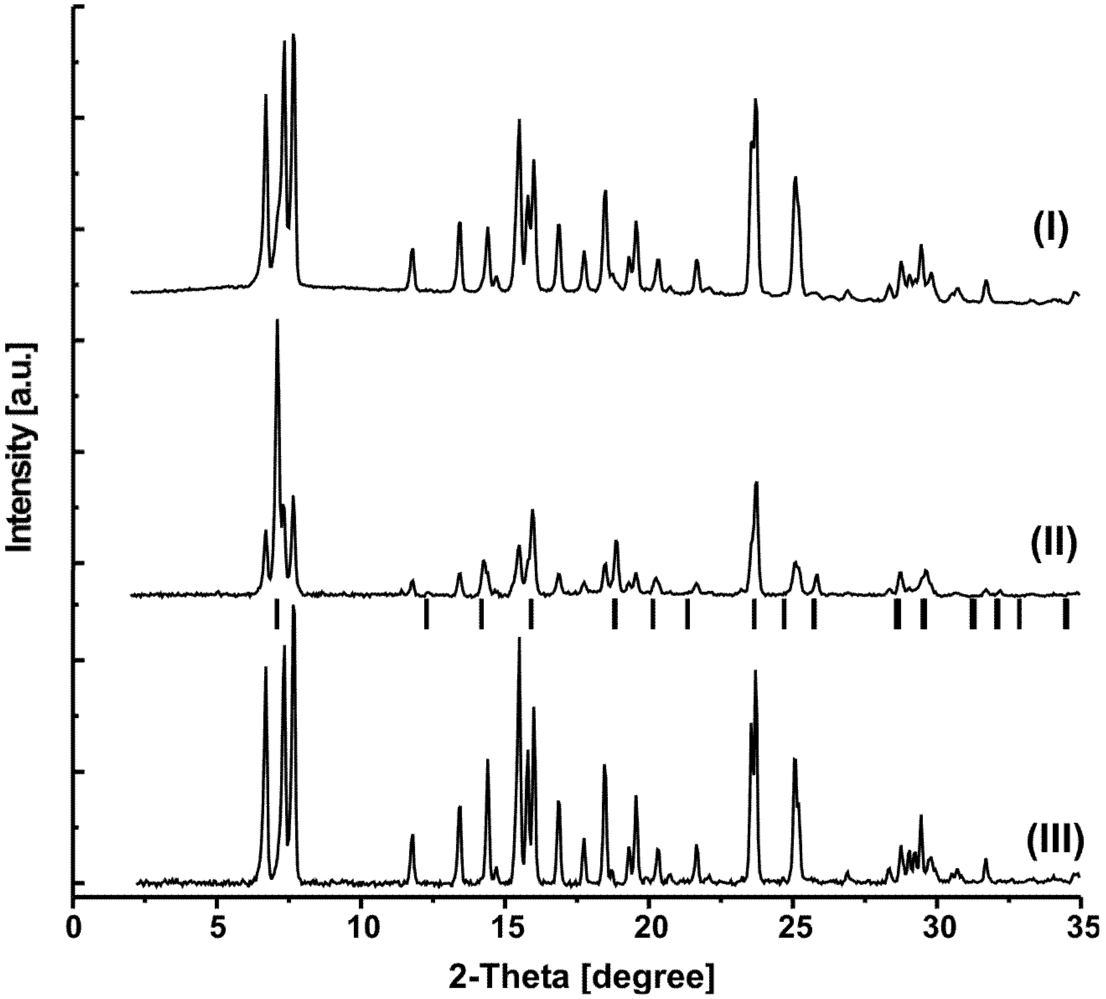

Figure 7: X-ray powder diffractograms of polycrystalline blue Alq_3 prepared under different conditions. For spectrum (I) yellowish-green Alq_3-powder (α-Alq_3) was annealed at 400°C for 2 hours. In Spectrum (II), the powder was annealed at 410°C (close to the melting point). For Spectrum (III) Alq_3 was annealed at 390°C for 6 hours. The additional lines and shoulders observed in spectrum (II) are not present in spectrum (III). Bars in spectrum (II) mark calculated positions for all possible x-ray peaks of γ-Alq_3.

From X-ray powder diffraction measurements the material in region A was confirmed to be the well known α-Alq_3 exhibiting yellowish-green fluorescence.[2,6] Figure 7 shows X-ray powder diffraction spectra of blue Alq_3 prepared under different conditions. For spectrum (I) yellowish-green Alq_3-powder (α-Alq_3) was annealed at 400°C for 2 hours. This spectrum is the same as reported in our first publication on blue luminescent Alq_3 (δ-Alq_3) obtained by using the train sublimation method.[6] The spectrum shows a small shoulder at $2\Theta=7.05°$ which causes considerable problems in the indexing procedure. Because of this uncertainty we supposed an additional phase, probably another high temperature phase, to be present in our samples. To test this, we annealed Alq_3 for several minutes at a higher temperature of 410°C (very close to the melting point) and we obtained a dark yellow substance, which exhibited only poor photoluminescence together with some blue luminescent material. Its x-ray spectrum (Figure 7

Table 1: Observed and calculated peaks from the x-ray powder diffractogram of blue Alq_3 (material B) in the 2Θ range 5-32° together with the indexing.

Peak No.	2Θ(°) (obs)	H	K	L	2Θ(°) (calc.)	Intensity (a.u.)
1	6.69	0	0	1	6.69	78
2	7.32	0	1	0	7.32	86
3	7.66	0	-1	1	7.65	100
4	11.76	0	1	1	11.77	18
5	13.41	0	0	2	13.42	28
6	14.40	1	0	0	14.40	45
7	14.70	0	2	0	14.68	6
8	15.49	-1	1	0	15.49	89
9	15.79	-1	0	1	15.79	48
10	16.00	1	0	1	16.01	63
11	16.86	-1	-1	1	16.88	30
12	17.74	0	1	2	17.75	16
13	18.46	0	-1	3	18.46	43
14	18.71	1	-2	1	18.70	5
15	19.31	1	1	1	19.31	13
16	19.55	-1	0	2	19.56	32
17	20.31	0	-3	1	20.30	12
18	20.73	-1	-2	1	20.73	3
19	21.65	1	2	0	21.66	14
20	22.09	0	3	0	22.10	3
21	23.58	1	1	2	23.56	58
22	23.69	1	-2	3	23.69	77
23	25.08	-1	-2	3	25.06	45
24	26.90	-1	2	2	26.89	4
25	28.33	-1	3	1	28.32	5
26	28.76	1	2	2	28.75	14
27	29.04	2	0	0	29.05	12
28	29.23	-2	1	0	29.24	11
29	29.45	2	-1	1	29.45	25
30	29.76	1	-4	1	29.80	10
31	30.70	-2	-1	1	30.70	5
32	31.70	-1	-3	4	31.69	9

(II)) has a number of new peaks, which becomes very obvious e.g. at 2Θ=7.05° and 25.85°. On the other hand, spectrum (III) shows Alq_3-powder annealed at 390°C for 6 hours. The additional lines observed in spectrum (II) are no longer present in spectrum (III). The 32 lowest 2Θ peaks of spectrum (III) in Figure 7 were used in the indexing routine STOE WinXPow. The best figure of merit belongs to a triclinic unit cell with a=6.177Å, b=13.241Å, c=14.425Å, α=95.924°, β =113.934°, γ=88.554° and V=1072.47Å^3. With the assumption of two molecules per unit cell a density of 1.42g/cm^3 is obtained. Table 1 gives the observed and calculated reflections in the range 5-32° (2Θ) together with the indexing.

Discussion

From x-ray spectra we can clearly identify the blue luminescent Alq_3 obtained by annealing yellowish-green Alq_3 (α-phase) above the phase transition at about 380°C as the δ-phase of Alq_3 with the above given unit cell. This material has recently been used for x-ray structural investigations at a synchrotron light source. The detailed results and their analysis by Rietveld refinement are described in a separate publication.[10] Of importance for the discussion here is that these measurements have proven that Alq_3 annealed at temperatures only a little above 380°C results in pure δ-phase material with no evidence for the presence of other phases. Furthermore, the above determined unit cell has been confirmed and the facial Alq_3 stereoisomer was identified to be the constituent of the δ-phase.

As compared to our previous work[6] we now have slightly different unit cell parameters, particularly the unit cell volume is only about half of the previously published value. The reason for this discrepancy is that in our previous analysis we have included the peak at 2Θ=7.05°. We note that the unit cell volume is with V=1072.47Å^3 nearly the same value as reported for the β-phase of Alq_3[2], however, lattice constants and angles are significantly different for the δ-phase. Niggli-reduction of the δ-phase shows that none of the cell parameters of the δ-phase are related to the β-phase.

As it became evident in Figures 7 (I) and (II), annealing Alq_3 at temperatures higher than 380° close to the melting point results in the appearance of new peaks in the x-ray spectra which can be ascribed to an additional high temperature phase. Brinkmann et al. already reported on such a high temperature phase, namely γ-Alq_3.[2] Using the given unit cell parameters from their work we calculated the position of all possible x-ray peaks for this phase as indicated by the vertical bars in Figure 7 (II). Obviously these calculated peaks are located at the positions where spectra (II) and (III) are different. Therefore it is suggestive that in sample (II) there is a high concentration of γ-Alq_3, whereas sample (III) is practically pure δ-Alq_3 as confirmed recently by Rietveld refinement.[10] From this we conclude that both, the δ- and γ-phase are high temperature phases of Alq_3.

In our previous work (Ref.[6]) the different phases were separated due to the temperature gradient within a sublimation tube. As δ-Alq_3 and the other high temperature phase (most likely γ -Alq_3) are formed in a relatively narrow temperature window, the separation of the two phases was difficult and a certain ratio of the other Alq_3-phase was still present in the samples of δ-Alq_3 using that method. Now, with the simple annealing process described here, it is possible to obtain large amounts (some grams) of pure δ-Alq_3 in a well-controlled process. Nevertheless, we emphasize that the blue luminescent Alq_3 obtained by train sublimation in our former work and now by annealing shows the same behavior concerning its solubility as well as its properties in PL, DSC, IR and Raman measurements.[6,11-13]

It is important to mention that the usual yellowish-green Alq_3 (α-phase) and the blue luminescent δ-Alq_3 can be easily converted into each other. Annealing yellowish-green Alq_3 at temperatures higher than 380°C results in blue Alq_3, while heating blue Alq_3 above the melting point and cooling down the melt slowly results in yellowish-green powder again. Another possibility to reconvert blue Alq_3 into yellowish-green Alq_3 is to evaporate the material or to solve it in any appropriate solvent (e.g. chloroform). The same holds for the glassy state of Alq_3 obtained from quenching the melt. It is readily solved in chloroform and films of good quality can be cast from such solutions. The PL spectrum of such cast films is the same as for evaporated films of Alq_3. By annealing material in the glassy state, it is possible to obtain both the yellowish-green α-Alq_3 and the blue δ-Alq_3 depending on the temperature. In all cases we obtained pure Alq_3 with no visible contaminating material. The possibility of transferring Alq_3 from one phase into the other allows us to conclude that even at these high temperatures there is no decomposition or chemical reaction of the material. So it is important to emphasize, that for all temperatures up to 425°C we are dealing with Alq_3. This is in agreement with ^{1}H NMR and FT-IR analysis of Alq_3 annealed at 422°C, where no decomposition products have been found.[8]

From DSC-measurements we can conclude that the blue luminescent δ-Alq_3 is the result of recrystallization into a more stable crystal structure above 380°C. However, for several samples we observed an additional small DSC peak at 145°C (see trace b in Figure 6). We are not sure about the origin of this transition, but after annealing at 350°C for 2 hours it almost disappears. This could be a hint for a small percentage of amorphous material in blue Alq_3 that crystalizes at temperatures above the glass temperature T_g. The temperature of this peak (145°C) is about 30°C lower than the T_g of α-Alq_3 (175°C)[9] and there is no comparable transition observed in the other phases investigated so far, excluding the possibility of an admixture e.g. of yellowish-green Alq_3.

A further circumstance is noteworthy: The transition from yellowish-green Alq_3 into blue δ-Alq_3 by a simple annealing process presented in this paper can be used to obtain thin films of blue luminescent Alq_3. In preliminary experiments we have used evaporated amorphous thin films with thicknesses from 300nm to 15µm, which were encapsulated (e.g. between two glass plates) to prevent the Alq_3 from volatilizing, and converted them at 390°C into homogeneous thin films showing blue luminescence. We also succeeded to evaporate blue luminescent thin films directly on heated glass substrates. This opens the way to fabricate OLEDs with blue luminescent δ-Alq_3. Further work to characterize such films and their application in OLEDs is in progress.

Conclusion

Using thermal, structural and optical measurements we have investigated the formation conditions of different phases of Alq_3. We identified the δ- and γ-phase to be high temperature phases of Alq_3 and reported an efficient method to obtain blue luminescent δ-Alq_3 by a simple annealing process. While the previously used train sublimation method resulted in only small amounts of δ-Alq_3 with admixtures of the γ-phase, it is now possible to prepare large amounts (several grams) of pure δ-Alq_3 choosing appropriate annealing conditions. This is the prerequisite for further characterization of this blue luminescent phase and for the preparation of blue OLEDs from this material.

Of course, there remain further issues to be investigated, a particularly interesting one is the isomerism of the Alq_3 molecule. As the facial isomer is predicted to have a larger energy gap than the meridional one, it is suggestive that δ-Alq_3 consists of the facial isomer.[6,11,14] We have recently resolved the structure of the blue luminescent δ-phase proving that it is indeed a pure phase composed of the facial Alq_3 stereoisomer.[10] Its presence in evaporated films as used for OLEDs is expected to have important implications for a better understanding of their charge transport and luminescence properties. Thus the possibility to prepare large amounts of pure δ-Alq_3 now opens the way for a further characterization of this material to address these issues.

Experimental

The aluminium tris-chelate complex (Alq_3) was synthesized by ourselves, following a slightly modified synthetic route from Ref. [15] and was purified by sublimation. Thermal analysis was performed by differential scanning calorimetry (DSC) using a Netzsch DSC 200. Samples (10-15mg) of polycrystalline powder were placed in aluminum pans under inert atmosphere and heated at a rate of 2°C/min if not marked otherwise. Indium and zinc metals were used as the temperature standard. Measurements of the photoluminescence (PL) have been performed under ambient atmosphere at room temperature in a Perkin Elmer Luminescence Spectrometer LS50B with an excitation wavelength of 350nm. The CIE color coordinates have been measured with a Minolta Chroma Meter CS-100. The photoluminescence quantum efficiency (PLQE) was measured by an integrating sphere and a spectrograph coupled with a CCD detector. The excitation was at 375 nm from an UV-LED with an interference filter.[16] X-ray powder diffractograms were obtained with Ge-monochromated Cu $K_{\alpha 1}$ radiation (λ=1.54056Å) on a STOE STADI P transmission powder diffractometer. Data were collected at room temperature in the 2Θ-range from 5 to 35°.

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