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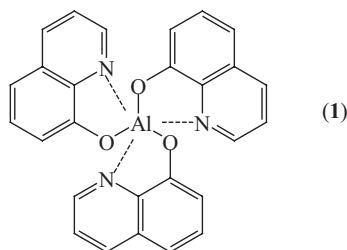
Preparation and Characterization of Blue-Luminescent Tris(8-hydroxyquinoline)aluminum (Alq₃)

By Michael Cölle,* Jürgen Gmeiner, Wolfgang Milius, Harald Hillebrecht, and Wolfgang Brütting*

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 (Alq₃). We have identified the δ -phase as a high-temperature phase of Alq₃ being composed of the facial stereoisomer, and report an efficient method to obtain blue luminescent Alq₃ by a simple annealing process. This allows the preparation of large amounts of pure δ -Alq₃ by choosing appropriate annealing conditions, which is necessary for further characterization of this blue-luminescent phase, and offers the possibility of fabricating blue organic light-emitting devices (OLEDs) from this material.

1. Introduction

Since the discovery of tris(8-hydroxyquinoline)aluminum (Alq₃)-based multilayer thin-film electroluminescent devices by Tang and co-workers in 1987,^[1] much progress has been made in the research field of organic light-emitting devices (OLEDs), which are of interest in various display applications. Alq₃ (**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, Alq₃ 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 electronic and optical properties of the material, in particular in the crystalline state. Recently, a systematic study of the optical properties

of solutions, amorphous films, and different polymorphic crystalline phases of Alq₃ was published.^[2] Three new crystalline phases (α -, β -, and γ -Alq₃) 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 nor investigation of this high-temperature phase have been published so far.

Another unresolved issue concerns the isomerism of the Alq₃ molecule.^[3–5] It is well-known that octahedral complexes of the type MN₃O₃, 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 Alq₃. Therefore, it is generally believed that the meridional isomer is predominant, both in amorphous films and crystals of Alq₃.

Recently, we have reported a new crystalline phase of Alq₃ (δ -Alq₃), which was obtained by thermal sublimation in a horizontal glass tube.^[6] 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 is characterized by a strong blue-shift of the photoluminescence maximum of about 0.2 eV.^[6] However, using the train sublimation method, only small amounts of blue luminescent δ -Alq₃ (some milligrams) 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 -Alq₃ 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 Alq₃. Therefore we have investigated the thermal properties of Alq₃ 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 -Alq₃, which is necessary for further characterization, and how to prepare blue luminescent thin films that might be used in OLEDs.

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[**] We thank M. Schwoerer, A. G. Mückl, and S. Forero Lenger for many stimulating discussions. Financial support by the Bayreuther Institut für Makromolekülforschung (BIMF) is gratefully acknowledged.

2. Results

Figure 1 shows the differential scanning calorimetry (DSC) measurement of polycrystalline Alq₃ powder taken with a heating rate of 20 °C min⁻¹. One observes a coupled endothermic and exothermic phase transition at about 395 °C prior to

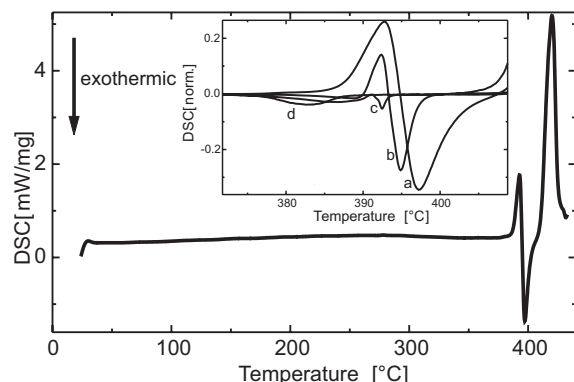


Fig. 1. DSC trace of Alq₃ with pronounced thermal transitions at 393 °C, 396 °C, and 419 °C measured with a heating rate of 20 °C min⁻¹. Inset: broadening and intermingling of the endothermic and exothermic transition around 395 °C in the DSC signal related to the sweep speed: a) 20 °C min⁻¹, b) 10 °C min⁻¹, c) 5 °C min⁻¹, d) 2 °C min⁻¹; normalized to the melting peak intensity. At low measuring speed only the more pronounced exothermic transition is visible.

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.^[2,7] It is very pronounced at fast heating rates (above 15 °C min⁻¹). For slow heating rates the endothermic and exothermic transitions become broader and less intense compared to the strong melting peak. They start to intermingle and are slightly shifted to lower temperature as shown in the inset of Figure 1 for heating rates of 20 °C, 10 °C, 5 °C, and 2 °C per minute. This behavior is similar to known irreversible monotropic solid–solid transitions.^[8] Typically, the monotropic transition is slow and is mostly observed at 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⁻¹) it is easy to “run over” the slow transition and so reach the melting temperature of the metastable low-temperature phase, giving an endothermic melting peak that merges directly into the exothermic crystallization peak that leads to the high-temperature phase. Although we did not investigate this process in detail, we think that the described scenario can explain the behavior shown in Figure 1.

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.^[7] was not observed in our samples. In the following we used a slow heating rate of 2 °C min⁻¹, where the shift of the peak temperatures is rather small (see Fig. 2) 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 Alq₃ phases by a controlled thermal annealing process.

We could distinguish three different phases of Alq₃ in these slow DSC measurements (see Fig. 2): first the usual yellowish–

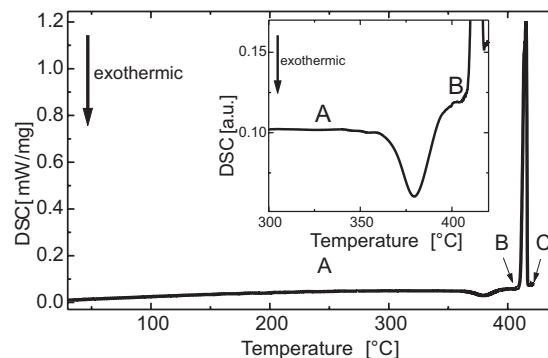


Fig. 2. DSC trace of Alq₃ measured with a heating rate of 2 °C min⁻¹. The clearly pronounced exothermic phase transition at 380 °C prior the melting point is zoomed out in the inset, as it becomes broad and less intense with respect to the melting peak for this slow heating rate. A, B, and C mark the regions of yellowish–green Alq₃, blue Alq₃, and melt, respectively.

green powder (A) before the exothermic phase transition, second a whitish powder (B) (hereafter denoted “blue Alq₃”) between this phase transition and the melting peak, and third the glassy state of Alq₃ (C). This glassy state of Alq₃ was obtained by quenching the melt in liquid nitrogen. Its highly amorphous character was verified using X-ray powder diffraction measurements and an image plate detection system (IPDS). Cooling down the liquid melt slowly again results in yellowish–green powder (A), as was previously reported.^[9] All of these phases are stable at room temperature.

Figure 3 shows the photoluminescence (PL) spectra of annealed polycrystalline Alq₃ powder from regions A and B, as well as of the quenched amorphous melt (C). For annealing

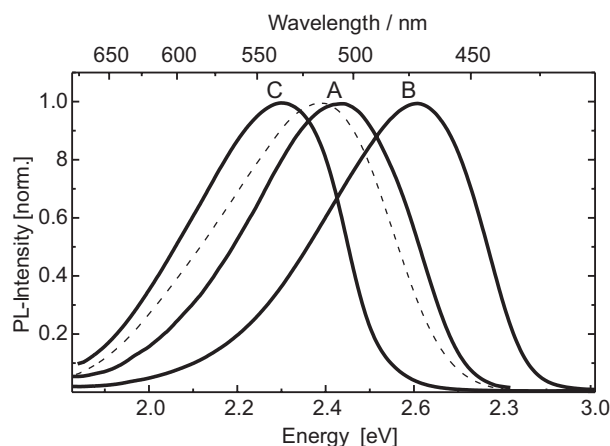


Fig. 3. PL spectra of Alq₃ samples taken from the regions A, B, and C in Figure 2, respectively, excited at 350 nm. For comparison the PL of an evaporated Alq₃ film is shown (dashed line).

temperatures up to 365 °C, Alq₃ is a yellowish–green powder with a PL maximum at 506 nm (curve A). After the exothermic transition at about 380 °C, there is a large blue-shift of 0.18 eV (37 nm), associated with a slight change in the shape of the PL spectrum (curve B), which is less symmetric for the blue Alq₃. 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 (0.14 eV) compared to the

yellowish-green Alq₃-powder (curve A). The strong difference in the emission color can be seen in Figure 4, where samples of the quenched melt, yellowish-green, and blue Alq₃ are shown at daylight (a) and under UV-irradiation (b). The emission col-

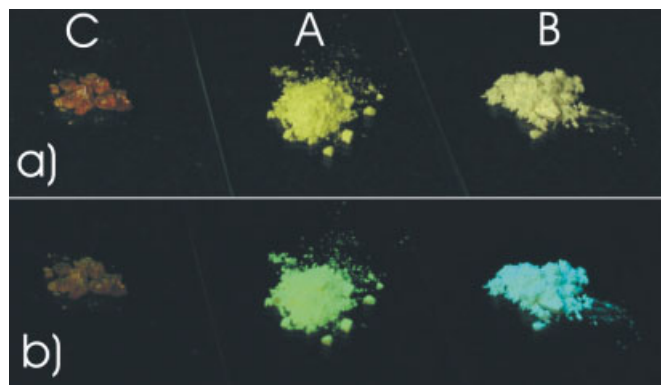


Fig. 4. Photographs of Alq₃ samples taken from the regions A, B, and C in Figure 2. a) under daylight. b) under UV-irradiation (excitation wavelength 366 nm). They clearly show the strong blue-shift of the luminescence of annealed material. (CIE color coordinates for A are $x=0.27$, $y=0.50$; for B $x=0.16$, $y=0.26$).

or is shifted from green (Commission Internationale de l'Eclairage (CIE) coordinates: $x=0.27$, $y=0.5$) to blue ($x=0.16$, $y=0.26$). From Figure 4 one can also see the relatively low PL intensity of the quenched melt compared to the very intense PL emission of blue Alq₃. This is due to the high PL quantum efficiency of crystalline Alq₃ (blue Alq₃: 51 %, yellowish-green powder: 40 %, evaporated film: 19 %, and quenched amorphous melt: 3 %). This is, to the best of our knowledge, on the one hand the first report on blue luminescent Alq₃ obtained by a simple annealing process, and on the other hand the first report on such a pronounced red-shift for amorphous Alq₃. The dashed line in Figure 3 is the PL spectrum of an evaporated Alq₃ 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 Alq₃. 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.

A comparison of the heating cycles of the yellowish-green Alq₃ and the blue Alq₃ is shown in Figure 5. Blue Alq₃ (trace b) has no phase transition in the region around 380 °C. This confirms the fact that the blue Alq₃ is formed in this exothermic process. In addition, there is a small transition at 145 °C observed only for the blue Alq₃. DSC measurements of amorphous samples (not shown) gave a glass-transition temperature of 178 °C and a pronounced recrystallization peak at 235 °C, similar to the results reported by Sapochak et al.^[7]

Another outcome of these DSC measurements is that all three phases can be easily converted into each other. Annealing yellowish-green Alq₃ at temperatures between 380 °C and 400 °C, with subsequent slow cooling results in blue Alq₃. Melting blue Alq₃ and cooling down the melt slowly results in yel-

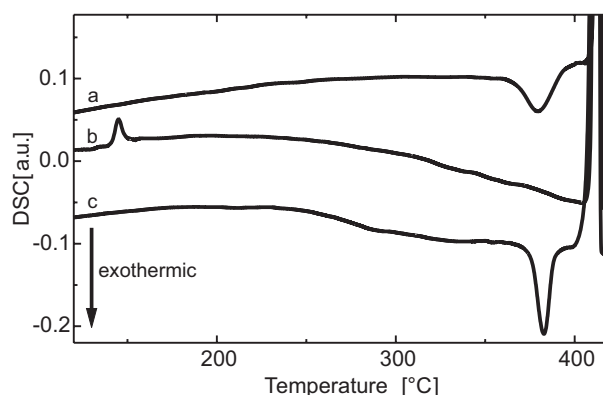


Fig. 5. DSC traces. a) yellowish-green Alq₃, b) blue Alq₃. Trace c shows a second heating cycle after cooling down the melt (b) again.

lowish-green powder again, as shown in trace c in Figure 5. 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.

From X-ray powder diffraction measurements the material in region A was confirmed to be the well known α -Alq₃ exhibiting yellowish-green fluorescence.^[2,6] Figure 6 shows X-ray powder diffraction spectra of blue Alq₃ prepared under different conditions. For spectrum (I) yellowish-green Alq₃ powder

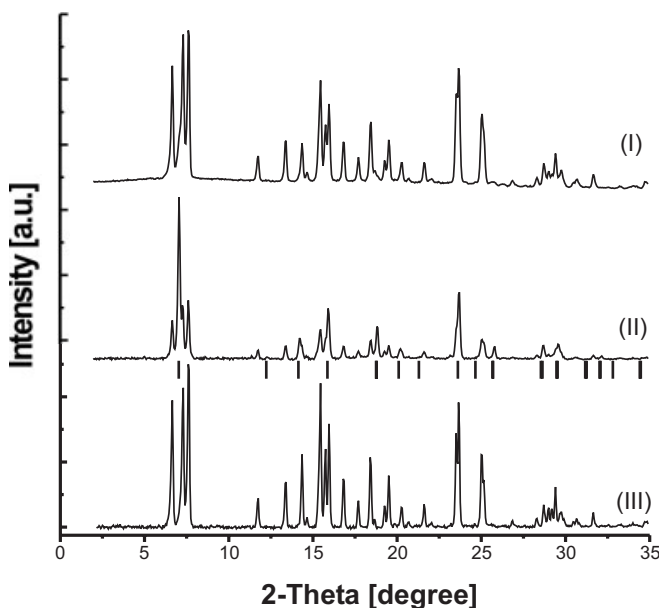


Fig. 6. X-ray powder diffractograms of polycrystalline blue Alq₃ prepared under different conditions. For spectrum (I) yellowish-green Alq₃ powder (α -Alq₃) was annealed at 400 °C for 2 h. In spectrum (II), the powder was annealed at 410 °C (close to the melting point). For spectrum (III) Alq₃ was annealed at 390 °C for 6 h. 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 -Alq₃.

(α -Alq₃) was annealed at 400 °C for 2 h. This spectrum is the same as reported in our first publication on blue-luminescent Alq₃ (δ -Alq₃) obtained by using the train sublimation method.^[6] The spectrum shows a small shoulder at $2\theta=7.05^\circ$, which causes considerable problems in the indexing procedure. Be-

cause of this uncertainty we supposed an additional phase, probably another high-temperature phase, to be present in our samples. To test this, we annealed Alq₃ 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 (Fig. 6(II)) has a number of new peaks that become very obvious, e.g., at $2\theta = 7.05^\circ$ and 25.85° . On the other hand, spectrum (III) shows Alq₃ powder annealed at 390 °C for 6 h. The additional lines observed in spectrum (II) are no longer present in spectrum (III). The 32 lowest 2θ peaks of spectrum (III) in Figure 6 were used in the indexing routine STOE WinXPow. The best figure of merit belongs to a triclinic unit cell with $a = 6.177 \text{ \AA}$, $b = 13.241 \text{ \AA}$, $c = 14.425 \text{ \AA}$, $\alpha = 95.924^\circ$, $\beta = 113.934^\circ$, $\gamma = 88.554^\circ$ and $V = 1072.47 \text{ \AA}^3$. With the assumption of two molecules per unit cell, a density of 1.42 g cm^{-3} is obtained. Table 1 gives the observed and calculated reflections in the range $5\text{--}32^\circ$ (2θ), together with the indexing.

Table 1. Observed and calculated peaks from the X-ray powder diffractogram of blue Alq₃ (material B) in the 2θ range $5\text{--}32^\circ$, 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

3. Discussion

From X-ray spectra we can clearly identify the blue-luminescent Alq₃ obtained by annealing yellowish-green Alq₃ (α -phase) above the phase transition at about 380 °C as the δ -phase of Alq₃ 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 Alq₃ annealed at temperatures only slightly larger than 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 Alq₃ 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 included the peak at $2\theta = 7.05^\circ$. We note that the unit cell volume ($V = 1072.47 \text{ \AA}^3$) is nearly the same value as reported for the β -phase of Alq₃,^[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 became evident in Figure 6, curve (I) and (II), annealing Alq₃ at temperatures higher than 380 °C, close to the melting point, results in the appearance of new peaks in the X-ray spectra that can be ascribed to an additional high-temperature phase. Brinkmann et al. already reported on such a high-temperature phase, namely γ -Alq₃.^[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 6, curve (II). Obviously these calculated peaks are located at the positions where spectrum (II) and (III) are different. Therefore it suggests that in sample (II) there is a high concentration of γ -Alq₃, whereas sample (III) is practically pure δ -Alq₃, as confirmed recently by Rietveld refinement.^[10] From this we conclude that both the δ - and γ -phase are high-temperature phases of Alq₃.

In our previous work,^[6] the different phases were separated due to the temperature gradient within a sublimation tube. As δ -Alq₃ and the other high-temperature phase (most likely γ -Alq₃) are formed in a relatively narrow temperature window, the separation of the two phases was difficult, and a certain amount of the other Alq₃-phase was still present in the samples of δ -Alq₃ made using that method. Now, with the simple annealing process described here it is possible to obtain large amounts (some grams) of pure δ -Alq₃ in a well-controlled process. Nevertheless, we emphasize that the blue-luminescent Alq₃ 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 Alq₃ (α -phase) and the blue-luminescent δ -Alq₃ can be easily converted into each other. Annealing yellowish-green Alq₃ at temperatures larger than 380 °C results in blue Alq₃, while heating blue Alq₃ above the melting point and cooling down the melt slowly results in yellowish-green powder again. Another possibility to reconvert blue Alq₃ into yellowish-green Alq₃ is to evaporate the material or to dissolve it in any appropriate solvent, e.g., chloroform. The same holds for the glassy

state of Alq₃ obtained from quenching the melt. It is readily dissolved 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 Alq₃. By annealing material in the glassy state, it is possible to obtain both the yellowish-green α -Alq₃ and the blue δ -Alq₃, depending on the temperature. In all cases we obtained pure Alq₃ with no visible contaminating material. The possibility of transferring Alq₃ from one phase into another 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 Alq₃. This is in agreement with ¹H NMR and FT-IR analysis of Alq₃ annealed at 422 °C, where no decomposition products have been found.^[7]

From DSC measurements we can conclude that the blue luminescent δ -Alq₃ 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 Fig. 5). We are not sure about the origin of this transition, but after annealing at 350 °C for 2 h it almost disappears. This could be a hint for a small percentage of amorphous material in blue Alq₃ that crystallizes 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 -Alq₃ (175 °C),^[9] and there is no comparable transition observed in the other phases investigated so far, excluding the possibility of an admixture of, e.g., yellowish-green Alq₃.

A further circumstance is noteworthy: The transition from yellowish-green Alq₃ into blue δ -Alq₃ by a simple annealing process presented in this paper can be used to obtain thin films of blue luminescent Alq₃. In preliminary experiments we have used evaporated amorphous thin films with thicknesses ranging from 300 nm to 15 μ m, which were encapsulated (e.g., between two glass plates) to prevent the Alq₃ from volatilizing, and converted at 390 °C into homogeneous thin films showing blue luminescence. We also succeeded in evaporating blue-luminescent thin films directly on heated glass substrates. This opens the way to fabricate OLEDs with blue-luminescent δ -Alq₃. Further work to characterize such films and their application in OLEDs is in progress.

4. Conclusion

Using thermal, structural, and optical measurements we have investigated the formation conditions of different phases of Alq₃. We identified the δ - and γ -phase to be high-temperature phases of Alq₃ and reported an efficient method to obtain blue luminescent δ -Alq₃ by a simple annealing process. While the previously used train sublimation method resulted in only small amounts of δ -Alq₃ with admixtures of the γ -phase, it is now possible to prepare large amounts (several grams) of pure δ -Alq₃ by choosing appropriate annealing conditions. This is the prerequisite for further characterization of this blue lumi-

nescent 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 Alq₃ molecule. As the facial isomer is predicted to have a larger energy gap than the meridional one, it is suggestive that δ -Alq₃ 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 Alq₃ 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 -Alq₃ now opens the way for a further characterization of this material to address these issues.

5. Experimental

The aluminum tris-chelate complex (Alq₃) was synthesized by us, following a slightly modified synthetic route from the literature [15] and was purified by sublimation. Thermal analysis was performed by differential scanning calorimetry (DSC) using a Netzsch DSC 200. Samples (10–15 mg) of polycrystalline powder were placed in aluminum pans under inert atmosphere and heated at a rate of 2 °C min⁻¹ if not marked otherwise. Indium and zinc metals were used as the temperature standard. Measurements of the photoluminescence (PL) were performed under ambient atmosphere at room temperature in a Perkin Elmer Luminescence Spectrometer LS50B with an excitation wavelength of 350 nm. 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-light-emitting diode (LED) with an interference filter [16]. X-ray powder diffractograms were obtained with Ge-monochromated Cu K α_1 radiation ($\lambda = 1.54056$ Å) on a STOE STADI P transmission powder diffractometer. Data were collected at room temperature in the 2θ range from 5° to 35°.

Received: July 4, 2002
Final version: October 24, 2002

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