FAC AND MER- AlQ₃ ISOMERS OBTAINED BY DIRECT SOLID STATE REACTION

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A new route for AlQ₃ synthesis was developed starting from Al(OH)₃ and 8-hydroxyquinoline compounds, by solid state reaction. At 95°C the bayerite and/or gippsite of Al(OH)₃ is decomposed in AlO(OH) boemite which react with 8-hydroxyquinoline, leading to a new crystalline phase containing both meridional and facial Alq₃ isomers. Vibrational spectroscopy gives useful details for identification of fac and mer isomers. X-ray diffraction patterns confirm the presence of a triclinic structure with low symmetry. Scanning Electron Microscopy and cathodoluminescence measurements confirm the presence of an unstable compound under the electron beam and characteristic X-ray with lower emission efficiency.

Keywords: Tris (8-hydroxyquinoline) aluminum, OLED, solid state reaction

1. Introduction

Tris (8-hydroxyquinoline) aluminum is an organometallic molecule widely used in different areas, especially in the light emitting layer for the Organic Light Emitting Diodes (OLED’s) [1-5] but also as an electron transport layer [6,7], host for fluorescent and phosphorescent dyes [8,9].

Alq₃ is an octahedrally coordinated chelate complex M(N^O)₃, where M is a trivalent metal, N and O are the nitrogen and oxygen atoms in the bidentate quinolinolate ligand. The Alq₃ complex can occur in two isomeric forms (facial and meridional), depending on the orientations of the ligands [10].

Beside of these two isomers, the thermal annealing processes induces different crystalline structures called α, β, γ and even δ phase [11]. These phases can be determined from Differential Scanning Calorimetry (DSC) starting with 290°C up to 420°C where the melting point is [12].

Several efforts have been made to prepare both isomers and for tuning the emission wavelength of Alq₃ through modulation of HOMO levels, by synthesizing differently substituted 8-hydroxyquinolines in which the

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substitutions are introduced to the phenoxide ring [13]. Various other aspects, such as doping electroluminescent materials into Alq₃ [14], or by embedding Alq₃ into mesoporous materials [15] have been studied. In parallel, different types of Alq₃ with variety of field-emission properties were investigated and reported as nanoparticle [16], wirelike [17] and blue luminescent δ crystal phase Alq₃ [18–20].

The common way to prepare the Alq₃ compounds is the wet synthesis in which 8-hydroxyquinoline is mixed with different aluminum salts like AlCl₃, Al(NO₃)₃·9H₂O or Al₃(SO₄)₂·nH₂O, which provide mainly meridional isomer or α-phase [21]. Comparing the luminescence of δ-phase and α-phase, there is a blue shift of about 0.2 eV [19]. It is generally agreed that the meridional form of Alq₃ is predominant in the both amorphous and crystalline structures. Another route to obtain different crystalline phases, except the α-phase, is thermal sublimation of the α-Alq₃.

The aim of this paper is to develop a new route for synthesis of Alq₃ by pure solid state reaction (further called solid state reaction compound or ssr) between 8-hydroxyquinoline and Al(OH)₃. Previous attempts have been made by using the solid state reaction between aluminum oxide-hydroxide AlO(OH) with 8-hydroxyquinoline but in a different way [21]. Due the water insolubility of the AlO(OH), the synthesis with 8-hydroxyquinoline was done by mixing the compound in the demineralized water and stirred under reflux in an oil bath maintained at 110°C.

Several measurement techniques have been involved in characterization of the mer-Alq₃ and the new compound like Differential Scanning Calorimetry (DSC), X-ray diffraction (XRD), photoluminescence, Raman and FT-IR vibrational spectroscopy, SEM and cathodoluminescence measurements.

2. Materials and methods

Solid state reaction was done by mixing 8-hydroxyquinoline and Al(OH)₃ in quartz crucible, in the ratio 2:1 in order to compare the final compound with the most common mer-Alq₃. The mixture was then slowly milled until the homogeneity was reached. The quartz crucible was moved in the Nabertherm programmable furnace and heated up to 95°C with a 10°C/min and kept for 36 hours in air. The cooling was done in air by slow quenching of the obtained compound. The final powder is pale yellowish colored.

Meridional tris (8-hydroxyquinoline) aluminum (Alq₃) was synthesized by mixing 8-hydroxyquinoline and Al(OH)₃ at about 95°C. In a typical synthesis, 0.39 g (0.005 mol) of Al(OH)₃ was gradually dropped into 80 ml distilled water which contains 1.45 g (0.01 mol) of 8-hydroxyquinoline. The ratio between 8-hydroxyquinoline and Al(OH)₃ was chosen as 2:1, which in the fast reaction
conditions (up to 24 h), results in the mer-Alq₃ formation. When this ratio is 3:1, the synthesis leads to the formation of needle-shape of 8-quinolinol crystals [22]. The pH was adjusted by using acetic acid in order to dissolve the 8-hydroxyquinoline powder. The reaction time of 6 h led to the production of yellowish Alq₃ powder. In the final stage, the pH was adjusted to the neutral value by adding NH₃ (precipitating agent) drop by drop with continuous stirring to get the maximum yield. The synthesized Alq₃ is obtained as a form of precipitate.

This precipitate was filtered and washed with double distilled water until the filtered became colorless and dried at 110 °C for 10 days. From the synthesis, the raw powder has partially crystalline structure. The powder consists of a very large number of randomly oriented micro-size crystals or particles.

2.1. Advanced characterization

For the Differential Scanning Calorimetry (DSC), we have used a SETARAM Setsys Evolution 18 in TG-DSC mode Thermal Analyzer in the 25 to 400 °C temperature range.

The XRD measurements have been performed on a BRUKER D8 ADVANCE type X-ray diffractometer, in focusing geometry, equipped with copper target X-ray tube and LynxEye one-dimensional detector, using CuKα₁ radiation (λ = 1.54056 Å ), at 40 kV and 40 mA. The 2θ scan range was 5–20°, with a step size of 0.02° and 0.01° resolution. The XRD patterns were obtained after subtraction of Kα₂ lines from the Kα₁-Kα₂ doublet, by the Rachinger algorithm, using the Bruker Difracplus Basic Evaluation program package [23].

We employed a Zeiss EVO 50 SEM with LaB₆ cathode with Bruker EDX system. Based on the SEM images, the equipment can generate secondary electrons, back scattered electrons, characteristic X-ray and cathodoluminescence.

Raman spectra have been recorded on bulk glass samples with a Jasco NRS-3100 spectrometer, from 50 to 1000 cm⁻¹, using 632 nm lasers. Infrared spectra have been recorded at room temperature with a Jasco FT-IR FT/IR-6200 type A spectrometer with a TGS detector, between 7000-350 cm⁻¹. The scan speed was set at 2 mm/s and the resolution at 2 cm⁻¹. Photoluminescence (PL) spectra have been recorded at room temperature, in the UV-VIS region 200-800 nm, using Edinburgh F900 spectrophotometer.

Molecular geometry of mer-Alq₃ and fac-Alq₃ were optimized using Kohn-Sharm Density Functional Theory (DFT) [24] and computational calculations with Gaussian 03W software.

We have used the B3LYP hybrid exchange correlation functional of Becke three-parameter theory and 6-31g basic sets, including geometry connectivity. After initial geometry optimization, the next steps of calculation were dedicated to Raman and infrared computational spectra for the both isomers.
3. Results and discussion.

3.1. Differential Scanning Calorimetry Analysis

Thermal decomposition of Al(OH)$_3$ can be evaluated by DSC measurements from 20 to 400°C. Figure 1 shows the results of DSC curves of the initial Al(OH)$_3$ and the compound obtained by solid state reaction.

On the initial DSC curve, a large endothermic peak centered at 170°C, is observed between 50 to 350°C. This decomposition peak of aluminum hydroxide involves the following evolution of phases [25]:

\[ \text{Al(OH)}_3 \rightarrow \text{AlO(OH)} \]

In other words, the bayerite and/or gippsite structure of Al(OH)$_3$ suffer a partial water loss and is transformed in boehmite. The small endothermic peak from 40°C can be assigned to the loss of water surface from the Al(OH)$_3$ crystals.

When the solid state reaction between Al(OH)$_3$ and 8-hydroxyquinoline take place, the endothermic peak from 170°C strongly decreases and an exothermic peak centered at 380°C with a long tail up to 390°C appears. The solid state reaction process was made at fixed temperature (95°C) in order to compare the powder with the wet chemical synthesis of mer-Alq$_3$, made at the same temperature.

![DSC curve](image)

Fig. 1. Differential Scanning Calorimetry before and after solid state reaction

3.2. X-Ray Diffraction Analysis

Rajeswaran et al. [26] have studied the phase changing of $\alpha$-Alq$_3$ from 20 to 440, and found two exothermic peak centered at 389°C, and 405°C, but with 50°C/min. which were attributed to $\gamma$ and $\delta$ Alq$_3$ phases. In our case, using a scan
speed of 10°C/min., these two peaks appear at 380°C and 395°C (see the inlet). In the mer-Alq3, the second peak is not so prominent, suggesting a lower δ-phase concentration, compared with the new compound obtained by solid state reaction.

A comparison between the XRD patterns of mer-Alq3 and the solid state reaction product reveals some significant differences (figure 2). Firstly is the presence of a new peak at 2θ=7.05°. Similar behavior was observed by M. Cölle et al. and was assigned to the blue Alq3, obtained from the yellowish-green Alq3 powder (α-Alq3) which was annealed at 400°C for 2 h and at 410°C for a few minutes [10]. Secondly, in the solid state reaction product, some additional peaks between 22° and 26° appears, especially the one at 25.8°. Similar behaviors were observed by M. Cölle et al. when the annealing has been done at 390°C, besides the peak from 7.05°. All of these characteristics were attributed to the δ-Alq3 which has a blue emission as we will see in the photoluminescence measurements. However, the presence of one peak at 9.35°, which is due to the un-reacted 8-hydroxyquinoline, denote an incomplete reaction.

3.3. Raman Spectroscopy

Vibrational spectroscopy allow us to show the formation of the Alq3 powder (mer and/or fac isomers) and gives useful details about the structure of the Alq3 in order to indentify each isomer contribution.

In the figure 3, it is a comparison between the Raman behaviors of the pale yellowish powder obtained by solid state reaction, the mer-Alq3 compound and the 8-hydroxyquinoline.

This figure and the inlet, shows only the main differences which appears at low frequencies (below 150 cm⁻¹) and at 525-550 cm⁻¹. Both zones give useful
details about the Al-O and Al-N vibrations. At low frequencies, mer-Alq₃ shows three peaks centered at 70 cm⁻¹ and 99 cm⁻¹ which were attributed to the Al-O vibrations, called Al-oxine deformations [26].

Another broad peak at 118 cm⁻¹ and 124 cm⁻¹ shoulder was reasonably assigned to the coupled vibrations Al–O deformation + Al-N stretching and C-O-Al bending. In the case of the compound obtained by solid state reaction, the C-O-Al bending seems to be in the same position, around 124 cm⁻¹, but the main peak is shifted from 118 cm⁻¹ to 113 cm⁻¹. It means that the above coupled vibrations have slightly different Al-O and Al-N bonding lengths.

In the second vibrational zone, from 525 cm⁻¹ and 550 cm⁻¹, there are three predicted peaks in mer-Alq₃ at 525 cm⁻¹, 534 cm⁻¹ and 541 cm⁻¹. The first peak was assigned to the coupled vibrational modes Al-O stretching and ring deformation [26]. The other two peaks comes from another coupled modes formed by Al-O and Al-N stretching, and ring deformation. In our case, a broad peak centered at 539 cm⁻¹ with a shoulder at 545 cm⁻¹ can be seen. It is supposed that in the case of the compound obtained by solid state reaction, some Al-O and Al-N vibrations are altered probably due to the configurationally changes between compounds. The last vibrational peak from 549 cm⁻¹ comes from the 8-hydroxyquinoline vibrations.

3.4. FT-IR Analysis

Figure 4 shows the IR spectra of mer-Alq₃ in comparison with the compound obtained by solid state reaction, both powders being spread on the KRS glass to ensure the transparency in the whole IR range. The inlet shows the
peak shift assigned to the coupled vibrations between Al-O and Al-N stretching and ring deformation. Although both spectra have almost the same peak positions, some differences can be evidenced between powders. The \textit{mer}-Alq$_3$ compound reveals two peaks centered at 648 cm$^{-1}$ and 547 cm$^{-1}$ that corresponds to the Al-O stretching modes [28].

![FT-IR spectra](image)

Figure 4 shows the IR spectra of \textit{mer}-Alq$_3$ and the solid state reaction compound together with DFT results. The infrared spectra of the \textit{mer}-Alq$_3$ and the solid state reaction compound show the presence of two peaks centered at 648 cm$^{-1}$ and 547 cm$^{-1}$, respectively. These peaks are assigned to the Al-O stretching modes. The \textit{mer}-Alq$_3$ compound shows two additional peaks at 542 cm$^{-1}$ and 642 cm$^{-1}$, which are attributed to the coupled modes between Al-O stretching and the ring deformation and Al-O and Al-N stretching and ring deformation, respectively. These observations support the conclusion that the \textit{mer}-isomer is the predominant species in both powders. However, in the simulated IR spectra for \textit{mer} and \textit{fac} Alq$_3$, the strong vibration peak assigned to the coupled vibrations between Al-O and Al-N stretching, and ring deformation seems to be slightly shifted from 572 cm$^{-1}$ to 567 cm$^{-1}$. This is consistent with the experimental observations.
shift in the simulated spectra between mer and fac Alq₃ is bigger, between 650 cm⁻¹ to 680 cm⁻¹. DFT simulations allow us to identify the molecular vibrations for the calculated peak positions. For example, the vibration from 572 cm⁻¹ in mer Alq₃ and 567 cm⁻¹ in fac Alq₃ are assigned to the in-phase vibrations of the O-Al-N structure and those from 648 cm⁻¹ and 642 cm⁻¹ are assigned to the out-phase vibrations of the same structure.

### 3.5. Photoluminescence Analysis (PL)

The green photoluminescence (PL) of Alq₃ has been measured at room temperature using the same excitation, by means at 397 nm for the both compounds. In the case of mer-Alq₃, the green PL is peaked at 525 nm, while in the case of the pale green-yellowish compound, a blue shift up to 502 nm (0.1 eV) can be seen (figure 5). Similar behaviors concerning the blue shift photoluminescence of the Alq₃ in δ phase, was observed by M. Colle et. al [19].

Investigations of the photoluminescence excitation spectra (PLE) for our Alq₃ compound show that any excitation energy in the range of 390-425 nm contributes to the broad green photoluminescence, even if the PL is shifted between the two compounds. This behavior is due to fast non-radiative relaxations from the ¹B₉ to the ¹Lₐ state, with subsequent radiative recombination to the ground state [27].

![Fig. 5. Photoluminescence spectra of mer-Alq₃ excited at 397 nm](image)

The PLE spectra, measured at room temperature, at different wavelengths between 488-525 nm, can be seen in the inlet. The location of the PLE peaks is the same in the range of 275 to 450 nm. It is concluded that the PLE spectra allow better isolation and identification of different spectral contributions to the observed photo-luminescence, giving quantitative information about their ratio. From the positions of the PLE peaks, we can conclude that the broad green
phosphorescence comes from the same electronic transition contributions. The blue shift of the photoluminescence in the case of our compound comes from different configurations of the atoms in the Alq₃.

3.6. Cathodoluminescence Analysis

Fig. 6. Cathodoluminescence and SEM images of the solid state reaction compound.

The cathodoluminescence patterns (right side) were obtained under 20 keV electrons beams and gives useful details of the mechanism of luminescence excitation by electrons. Figure 6 shows a detailed view of cathodoluminescence image for Alq₃ obtained by solid state reaction and in the left side, a secondary electron image structure of the same compound. Some white spots can be seen in the secondary electron imaging suggesting a slightly charging of the Alq₃ surface.

It is important to note that the structure of the obtained compound is unstable under the electron beam or the X-ray generated by the LaB₆ cathode, even at low energy electrons, up to 5 keV. This fact can be seen during cathodoluminescence measurements.

The cathodoluminescence spectrum (CL) can be obtained by passing the emitted light under X-ray excitation through a classical monochromator and compared with the photoluminescence (PL) excited at 397 nm. Both spectra were rescaled for comparison (figure 7).
Fig. 7. Cathodoluminescence spectra of mer-Alq3 and solid state reaction compound.

In the inlet, is shown the original cathodoluminescence spectra recorded at the same electron beam energy (20keV). It can be seen that the cathodoluminescence of our compound, is lower compared with mer-Alq3 for the same excitation energy. For comparison with PL spectrum, the cathodoluminescence spectrum was recorded at low energy electron beam (5keV). This fact was explained with low efficiency of triplet state emission of 2% in the case of fac-Alq3 compared with 25% in the case of mer-Alq3 [29].

DFT calculations give a significant theoretical energy differences between the two Alq3 isomers. In our case, the mer-Alq3 structure is more stable, with 6.27 kcal/mol compared with fac-Alq3, and has also different dipole lengths, 4.37 Debye and 8.9 Debye. Similar high value of 9.369 Debye for the fac-Alq3 was also calculated [26].

Several theoretical details were obtained by Curioni, but using different functionals BYLP [30]. The energy differences between the two Alq3 isomers was estimated at 4 kcal/mol, but other authors gives an energy differences between the two Alq3 isomers from 4 to 8 kcal/mol [31-33].

A possible interaction between dipole moments could induce this lower energetic stability between fac-Alq3 molecules.

4. Conclusions

A new route for Alq3 synthesis by pure solid state reaction between Al(OH)3 and 8-hydroxyquinoline was developed, the final product being a mixture between mer and fac isomers.

At 95°C, Al(OH)3 is decomposed from bayerite and/or gippsite structure to boemite structure of AlO(OH) which reacts with the 8-hydroxyquinoline, leading to the Alq3 compound.
From the XRD patterns, the crystal structure of the new compound is of low symmetry (triclinic), similar with the Alq$_3$ $\alpha$-phase but with slightly differences concerning the angles and the $a$-axis which is slightly longer.

The obtained compound has lower stability suggested by the DSC and CL measurements. The cathodoluminescence is weaker than in the case of mer-Alq$_3$ for the same energy of the electron beam. This fact was explained with low efficiency of triplet state emission of 2% in the case of fac-Alq$_3$ compared with 25% in the case of mer-Alq$_3$. The photoluminescence of the new compound is blue shifted compared with the mer-Alq$_3$ with about 0.1 eV.

Vibrational spectroscopy shows some differences for those peaks which involve Al-O and Al-N bonds. This fact was evidenced by DFT calculations in which two bonds between Al-O are longest and one shorter in the case of mer-Alq$_3$ and have the same bond in the case of fac-Alq$_3$ [34].

The secondary electron images show some white spots, suggesting a slightly charging of the Alq$_3$ surface.

In particular, we examine the two molecular isomers of Alq$_3$ and argue that they could coexist in the real amorphous material, obtained by direct solid state reaction.

According to the markedly different properties we suppose that the new crystalline phase contains the facial isomer of Alq$_3$.

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