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# Subgap absorption in tris (8-hydroxyquinoline) aluminium

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## Abstract

Photothermal deflection spectroscopy was performed on films of tris (8-hydroxyquinoline) aluminium. The presence of an exponential part of the absorption spectrum was found followed by a broad defect absorption. The former is ascribed to HOMO and LUMO tail states and their relevance to the photoluminescence is discussed. The intensity of the defect absorption depends on the used source material. The optically detected defect states are correlated with trap states seen in transport measurements.

**Keywords:** Photothermal deflection spectroscopy, photoluminescence, tris (8-hydroxyquinoline) aluminium.

## 1. Introduction

Thin films of thermally evaporated tris (8-hydroxyquinoline) aluminium ( $\text{Alq}_3$ ) have been successfully applied as electron transporting and emitting layers in organic light emitting diodes (LED) [1]. The investigations of the transport [2] and the recombination kinetics [3] of this material led to the identification of trapping sites with energetic position within the optical gap. An attempt to detect them by direct absorption measurement was performed in [4]. In the present paper, we clearly show the existence of well-defined subgap absorption.

## 2. Experimental

Films with a thickness between 0.5 and 5  $\mu\text{m}$  were prepared by vacuum sublimation on quartz substrates at room temperature. Photothermal deflection spectroscopy (PDS) setup with a measurement range  $10^{-4} < \alpha d < 3$  was used as described in [5]. The photoluminescence quantum efficiency was measured using excitation at 374 nm from an GaN-LED with an interference filter as described in [5]. The transmission measurements were performed on spectrophotometer Perkin Elmer Lambda 2.

## 3. Results and Discussion

The optical absorption of  $\text{Alq}_3$  films is characterized by two well pronounced bands at 3.15 eV and 4.67 eV [2]. A typical absorption coefficient spectrum is shown in Fig. 1. The data above 4.3 eV were obtained for a 50 nm film by transmission measurement. Below the absorption edge at about 2.7 eV [2] the spectrum can be described by an exponential law extending more than three orders of magnitude followed by a broad subgap absorption. The sharp bands at 1.09, 0.89 and 0.74 eV are due to

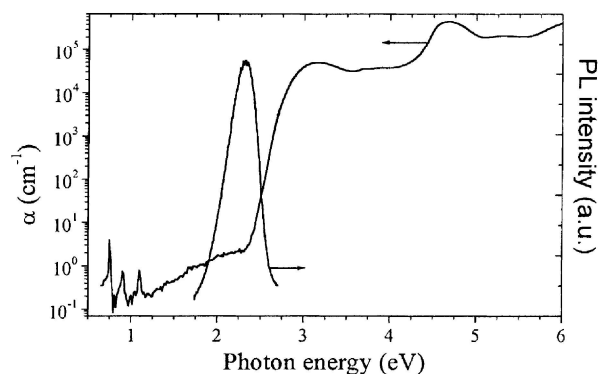


Figure 1. Typical absorption coefficient and photoluminescence spectra of  $\text{Alq}_3$  film.

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multiphonon absorption. A signal originating from the quartz substrate contributes also to the band at 0.89 eV. Our discussion will be focused on the results below 2.7 eV. The observed exponential region is characteristic for amorphous as well as for crystalline materials [6]. Because of existing potential fluctuations of diverse origin states originating from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) move into the HOMO-LUMO gap with a density decreasing exponentially to the center of the gap. Such tail states can act as shallow traps for charge carriers. Burrows et al. [2] have already introduced the presence of exponential trap distribution below the LUMO in order to explain the current-voltage characteristics. However the traps were identified as states arising as a consequence of structural relaxation upon the presence of injected electrons on individual molecules. Also the characteristic energy of 150 meV is much higher than the value of the Urbach energy  $E_U=40$  meV which we obtained describing the exponential part of the absorption in Fig. 1 using the expression [6]

$$\alpha = \alpha_0 \exp(E/E_U)$$

Additionally one has to consider that the optical measurements probe the joint density of states whereas the transport measurements probe the density of states near the transport level. Assuming that the tails near the LUMO and the HOMO are nearly equal we can roughly estimate the characteristic energy for each individual tail as 20 meV.

Humbs et al. [3] have introduced shallow and deep traps in Alq<sub>3</sub> films in order to explain the time resolved photoluminescence measurements. The average gap between the shallow traps and the exciton band was estimated as 20 meV which is consistent with the absorption data in Fig.1. The processes of trapping of the excited carriers on the tail states, their thermally activated release and re-trapping govern the recombination processes in the Alq<sub>3</sub> films and at the end determine the position of the photoluminescence maximum. A typical photoluminescence spectrum is also shown in Fig.1. The intensity of the photoluminescence at 2.7 eV is about an order of magnitude lower than at the maximum because the

charge carriers trapped at these shallow levels are thermally activated at high rates. If the carriers thermalize to low energy states the phonon-assisted transitions are suppressed because of the low density of states. As a result the photoluminescence maximum appears at energies where the density of states is low enough. In the case in Fig. 1 the maximum of the photoluminescence is at 2.32 eV and at this energy the density of states is more than three orders of magnitude lower than the density of the more extended states above 2.7 eV.

PDS were applied on films deposited from different source materials. The corresponding absorption spectra do not show differences in the exponential part of the absorption spectrum and in the position of the photoluminescence band. Also the photoluminescence quantum efficiency was always 17-20 %.

Differences between the different samples were observed in the subgap absorption below 2.3 eV which is caused by the presence of defect states. Because of the localization of the electronic excitations on the individual quinoline complexes and due to the low level of the defect absorption ( $\alpha < 10$  cm<sup>-1</sup>) it does not influence significantly the photoluminescence.

Figure 2 shows the absorption coefficient spectra for samples deposited from a material purified by sublimation (crosses) and from non-purified material (solid line). The latter sample shows about an order of magnitude higher subgap absorption. The defect states responsible for this subgap absorption may act as deep traps for charge carriers and it is expected to have influence on the transport properties of the films. In order to verify the correlation between the optically detected defect states and the transport properties single layer structures were deposited by using purified and non-purified source materials. The current-voltage characteristics of the Al/Alq<sub>3</sub>/Ca structures made from non-purified material showed systematically lower current density at 0.8 MVcm<sup>-1</sup>. From the analysis of the double- logarithmic plot we can draw the conclusion that the trap density and depth in the films deposited from non-purified material is higher. Hence the defect states detected in the optical absorption are electrical active and act as traps.

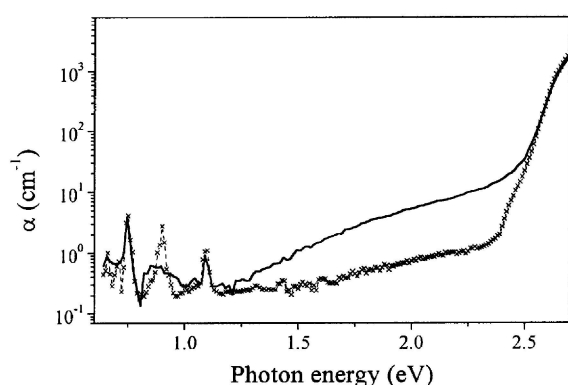


Figure 2. Absorption coefficient spectra of Alq<sub>3</sub> films deposited from different source materials.

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