



Charge carrier traps in tris-(8-hydroxyquinoline) aluminum



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ARTICLE INFO

Keywords:

Organometallic compound
Thermoluminescence
Photoluminescence
Charge carrier traps

ABSTRACT

Thermoluminescent measurements between 40 and 300 C revealed two traps in the irradiated Alq₃ powder synthesized from Al(OH)₃, at 0.8 and 1.1 eV below the conduction band. These two traps have been assigned with the Alq₃ facial and meridional isomers and the trapping process stand for a long time after the switching off the irradiation source. The spectra recorded an hour after switching recover 60% from the photoluminescence and also decreasing the TL signals. A theoretical model was proposed in order to explain the trapping and de-trapping processes in both meridional and facial Alq₃ isomers based on the XPS measurements for the HOMO, LUMO, ionization potential and optical bandgap, completed with the DFT calculated parameters and similar experimental results concerning the evidences of the triplet states in Alq₃ compound.

1. Introduction

Tris-(8-hydroxyquinoline) aluminum (Alq₃) has become the pioneer of the organometallic compounds applied to electroluminescence devices since Tang and Van Slyke use this material for the first OLED structure [1]. However, the electroluminescence of this material remain a debating subject in the field of the OLEDs, mainly concerning the energy levels involved in the charge transport and emissive properties of Alq₃. For example, T. Mori et al. measured the thermal stimulated currents in Alq₃ thin films and proves the existent of electron trap at 0.8 eV below the conduction band, on the assumption of the conduction band and a single set of carrier traps [2]. More than that, the authors discuss the electrical conduction and electroluminescence of Alq₃ thin films using the band conduction mechanism because the electroluminescence emission peak from 520 nm (2.40 eV) does not correspond with the gap between the conduction and the valence band estimated at 475 nm (2.61 eV). Assuming the valence band as being the ground state level, the state responsible for the electroluminescence at 2.40 eV must be a trap state with a trap depth of 0.23 eV below the conduction band. Because the electroluminescence of Alq₃ thin films is extended to over 700 nm (1.77 eV), the estimated electroluminescence from the 0.8 eV trap situated below the conduction band at 685 nm (1.81 eV) cannot be observed.

By using current-voltage (I-V) and electroluminescence (EL) characteristics, P.E. Burrows et al. [3] explain the injection of charges in thin film into a large density of traps distributed in energy below the lowest unoccupied molecular orbital (LUMO), suggesting a trapped-charge-limited conduction mechanism in OLEDs at high injection

currents. This mechanism was further extended to a few Mq₃ metal chelate complexes (where M = Al, In, Ga and Sc) where the analysis of current-voltage characteristics at different temperatures proves the existence of an exponential distribution of traps with a characteristic energy $E_t = 0.15$ eV below the LUMO of Alq₃, quite close to the one determined by T. Mori et al. at 0.23 eV. This trap level energy was explained as difference between the lowest-energy transitions for mer-Alq₃ in neutral and anion states, leading to a theoretical difference of 0.21 eV. When an electron is localized on an Alq₃, the molecule structurally relaxes in response to populating the antibonding orbitals and this relaxation serve to “self-trap” the electron since this relaxation energy must be provided to promote the electron to an adjacent Alq₃ molecule. This theory seems to be a good one because the previous attempts to interpret the trap centers include the interface between a crystalline region and the amorphous one [2] or the adsorption (doping) of oxygen molecules. Concluding, in order to explain the electroluminescence behaviors of Alq₃, at least two traps were identified in the band gap, one at 0.23 eV below the conduction band and one at 0.8 eV both of them measured by using thermal stimulated currents in Alq₃.

There are many experimental and theoretical studies on Alq₃ energy states which determine the Highest Occupied Molecular Orbitals (HOMO) state and the Lowest Unoccupied Molecular Orbitals (LUMO) state [4–7]. From the theoretical point of view, again the calculated HOMO and LUMO states depends on the Density Functional Theory and the additional software used, being significant difference between ZINDO, Amsterdam Density Functional and Gaussian one. As experimental methods, the more used two are the Ultraviolet Photoelectron

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Spectroscopy (UPS) which allows the determining of the HOMO level and the Ionization potential (Ip) while the second used method is the cyclic voltammetry (CV) which takes into account the oxidation potential of the metal in the chelate complexes.

Regarding the trapping levels, thermoluminescence (TL) measurements below room temperature has been used by E.W. Forsythe et al. [8] to identify these ones and to explain the trapping and de-trapping processes. The method is useful for the study of the thermally activated luminescent recombination of the charge carriers (electrons and holes, produced by irradiation) trapped by the energy levels within the band gap. TL measurements have evidenced three traps in AlQ₃ thin films irradiated with 363 nm UV-light irradiation argon laser (100 mW) at 156 K and only one 67 K, with different activation energies from 0.07 eV up to 0.25 eV [8]; the trapping mechanism involved a combination of first and second order emission.

The aim of this paper is an extension of the studies of AlQ₃ energy states and trapping states associated by using thermoluminescence (TL) measurements correlated to the DFT calculations. For this purpose, the AlQ₃ powder was synthesized, but also was compared with the one obtained from Sigma Aldrich.

2. Materials and methods

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) [9].

Irradiation time for all samples was set to 90 min and the photoluminescence of the AlQ₃ powder excited to 405 nm (3.06 eV) was recorded before and after irradiation. X-ray diffraction measurements were performed with a BRUKER D8 ADVANCE type X-ray diffractometer, in focusing geometry, with a vertical theta-theta goniometer and horizontal sample carrier, in order to check if the crystalline structure of AlQ₃ is affected or not by the irradiation procedures (see [Supplementary information](#)).

Thermoluminescence (TL) measurements were performed on synthesized and commercial AlQ₃ powder samples, by using a Harshaw 3500 TL reader, in the 50–300 °C temperature by using a band-pass (450–600 nm) glass filter and heating rate 2 °C/s. Prior to the TL measurements, the samples were irradiated at room temperature (RT) by using either UV-laser light source (405 nm/10 mW), close to the main absorption peak of AlQ₃ powder situated at 390 nm (3.17 eV) and X-rays with 40 kV and 40 mA or γ-ray (Co 661 MeV), all for 90 min.

Density Functional calculations were performed with Gaussian 3 W by using B3LYP functional for the ground state and the 6–31 g basis sets. The combination B3LYP/ 6–31 g allows prediction of the excited states with more accuracy. The molecular geometry was optimized using the Kohn-Sham DFT. The calculations were done in order to determine not the HOMO and LUMO states with more accuracy but the band gap and the lowest energy transitions (singlets and triplet) to complete the missing experimental information (see [Supplementary information](#)).

3. Theoretical background

Thermoluminescence (TL) is the light emitted by a solid sample when it is heated after being irradiated at “low temperatures” by ionizing radiation such as UV light, X-rays, gamma-rays, etc. [10]. The basic TL model assumes that some of the charge carriers (electrons and holes) produced by irradiation are trapped in local energy levels (such as vacancies, interstitials, or impurities) within the band gap; during the heating, they are thermally released and recombine with carriers of the opposite sign, giving rise to TL [11].

The properties of the trap are reflected by the TL peak temperature

maximum and its shape, the activation energy corresponding to the peak being equal to the trap depth; “shallow” traps will empty at low temperatures (for example around 150 °C) and “deeper” traps will empty at higher temperatures (for example around 300 °C).

According to the general order kinetic model a TL peak can be described by the equation [11]:

$$I(T) = sn_0 \exp\left(-\frac{E}{kT}\right) \{1+(b-1)\frac{s}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'\}^{-\frac{b}{(b-1)}}$$

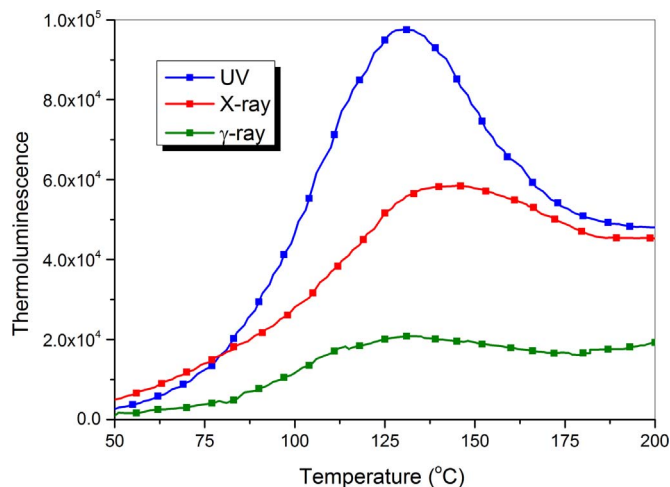
where E is the activation energy of the trap, b is the kinetic order and s is the frequency factor.

Regarding the nature of the recombination centers valuable information are provided by the TL spectra or glow curves recorded in different spectral domains corresponding to various recombination processes. In order to establish a detailed model for trapping and recombination processes, complementary information from TL spectra, thermal or optical bleaching and TL dose dependence have to be carefully analyzed [11].

4. Results and discussions

Thermoluminescence curves recorded on synthesized AlQ₃ powder after irradiation with different sources are depicted in the [Fig. 1](#). As the TL signals observed after X-ray and γ-ray exposure are smaller compared with the ultraviolet irradiation this suggests a highly efficient better band-to-band excitation in the last case in agreement with the photoluminescence measurements (see below). Therefore, for the following measurements and discussion of the trapping centers and recombination we will use UV irradiation on both synthesized and commercial AlQ₃ powder.

[Fig. 2](#) shows the photoluminescence spectra of synthesized AlQ₃ powder before and after UV-light irradiation at 405 nm (3.06 eV) for 90 min. The photoluminescence intensity decreases down to about 20% after irradiation. This fact indicates a decrease of the number of photoluminescent centers after irradiation accompanied by their trapping of the charge carriers produced during UV-light irradiation (i.e. HOMO-LUMO excitation)-see the TL curves ([Fig. 1](#)). However, measuring the photoluminescence spectra after storage (in the dark) one hour after UV irradiation it can be observed a partially recovering up to about to 60% from the initial photoluminescence signal. This fact indicates a strong instability of the charge carries on the trapping levels during a long time after irradiation. Similar photoluminescence decreasing can be induced by irradiation with X-ray and γ-ray obtained from the Co (661 MeV) sources ([Fig. 2](#), inlet). As can be seen, the UV-light



[Fig. 1](#). Thermoluminescence curves recorded on synthesized AlQ₃ powder sample after irradiation with different sources.

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