

## MICROSTRUCTURAL CHARACTERIZATION OF POLYCRYSTALLINE Alq<sub>3</sub> GROWN BY SUBLIMATION

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A microstructural investigation on polycrystalline electroluminescent Alq<sub>3</sub> obtained by train sublimation method is reported in the paper. The morphology and crystalline structure of the obtained Alq<sub>3</sub> phases have been analyzed by transmission electron microscopy performed on samples collected from 3 different regions along the sublimation tube.

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### 1. Introduction

Aluminum tris(quinoline-8-olate) (Alq<sub>3</sub>) is an organometallic chelate complex that has become one of the most used materials in organic light emitting devices (OLEDs) [1] thanks to its electroluminescent properties discovered in 1987 [2]. Substantial effort has been devoted to the properties, structure, and dynamics of the Alq<sub>3</sub> complex to improve its light emission quantum efficiency and time stability. The results obtained by several experimental physical techniques (x-ray powder diffraction [3-5], optical spectroscopy and luminescence [6-8], Raman and infrared spectroscopy [9-11], NMR [12-14], ESR [15,16]) and theoretical methods of bonding analysis and reactivity [17, 18] have been directed towards the crystalline structure and properties of the Alq<sub>3</sub> molecule, as well as their dependence on thermal and annealing treatments. Very recently, the existence of different paramagnetic defect centers has been observed and analysed by EPR [19]. It may increase further the technological interest in this material.

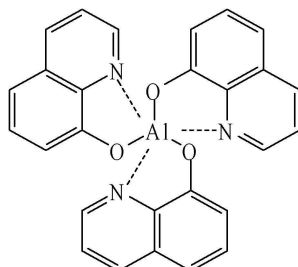


Fig. 1. Chemical structure of the Alq<sub>3</sub> (C<sub>27</sub>H<sub>18</sub>AlN<sub>3</sub>O<sub>3</sub>) molecule.

The chemical structure of the Alq<sub>3</sub> molecule is shown in Fig. 1. It is a metal octahedral coordinated chelate, with the aluminum ion surrounded by three 8-hydroxyquinoline molecule. Two geometric isomers exist - meridional (mer-Alq<sub>3</sub>) with the oxygen atoms forming a meridian of the distorted coordination octahedron and facial (fac-Alq<sub>3</sub>) with the oxygen forming a face of the

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octahedron - having  $C_1$  and  $C_3$  symmetry, respectively [17, 20]. In principle, both isomers are stable and could coexist. Until recently, only the meridional isomer was clearly identified in the  $\alpha$ - and  $\beta$ - $Alq_3$  phases [3]. Newly X-ray structural analysis [5] and NMR investigations [12] have proved that the discovered high temperature  $\delta$ - $Alq_3$  phase [4] consists of the facial isomer of the  $Alq_3$  molecule. An in depth analysis of the point defects identified in  $Alq_3$  samples from the three fractions and a correlation with the TEM results is presented in Ref. [19].

In the present paper we report on structural and morphological characterization of sublimated  $Alq_3$  powder, both as obtained and after a thermal treatment in an inert atmosphere.

## 2. Experimental

Polycrystalline powders of different phases of  $Alq_3$  have obtained by sublimation in a horizontal glass tube with a temperature gradient (320°-380°C) or by direct annealing of the powder at a defined temperature, in inert atmosphere as described in Refs. [4, 21]. The formation of various crystalline phases is temperature-dependent. In the glass tube three main fractions (1, 2, and 3) of  $Alq_3$  have been distinguished. Fraction 1 (a whitish microcrystalline powder with blue fluorescence), is the smallest amount formed at the hottest end of the tube. Fraction 2, composed of yellowish acicular microcrystalline grains with green-yellow fluorescence, is the main fraction in the middle zone of the tube. Fraction 3, formed in the coldest zone, contains small green crystals of different morphologies with green fluorescence.

Given the large crystalline variety in a relatively narrow temperature range, we have performed microstructural studies on sublimated  $Alq_3$  powder submitted to additional thermal treatments. Hence, powder samples from fractions 2 and 3 have been heated at 390 – 400 °C in inert atmosphere for different time intervals followed by slow cooling or rapid quenching in liquid nitrogen in order to reveal the various crystalline phases of this compound.

The transmission electron microscopy (TEM) measurements were performed with a JEOL 200CX electron microscope operated at 200 kV. TEM specimens were prepared by fine grinding of the powder product and collecting crystal grains on TEM copper grids covered with carbon membranes.

## 3. Results

Several crystalline phases have been identified for  $Alq_3$  [4, 5] and some other unknown phases may still exist. We summarize hereafter the crystallographic data concerning the known phases of  $Alq_3$ :

$\alpha$ - $Alq_3$  – triclinic (S.G. P-1),  $a = 0.627$  nm,  $b = 1.292$  nm,  $c = 1.473$  nm,  $\alpha = 109.6^\circ$ ,  $\beta = 89.7^\circ$ ,  $\gamma = 97.7^\circ$ ;  
 $\beta$ - $Alq_3$  – triclinic (S.G. P-1),  $a = 0.844$  nm,  $b = 1.025$  nm,  $c = 1.317$  nm,  $\alpha = 108.58^\circ$ ,  $\beta = 97.06^\circ$ ,  $\gamma = 89.74^\circ$ ;  
 $\gamma$ - $Alq_3$  (high temperature) – trigonal (S.G. P-31c),  $a = b = 1.441$  nm,  $c = 0.622$  nm,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ ;  
 $\delta$ - $Alq_3$  – triclinic (S.G. P-1),  $a = 1.324$  nm,  $b = 1.442$  nm,  $c = 0.617$  nm,  $\alpha = 88.55^\circ$ ,  $\beta = 95.92^\circ$ ,  $\gamma = 113.93^\circ$ .

$Alq_3$  samples examined in this work by TEM proved to be electron beam sensitive and their observation in the TEM was possible at low beam intensity only. Grains observed at high electron beam intensities undergone a rapid (within a few seconds) amorphization process. This fact imposed low limits to the image magnification (around 10 000 x) in order to keep sufficient illumination on screen and to use reasonable exposure times (less than 15 seconds) to record the image on plan films. Images recorded at longer exposure times were subject to specimen drift in the TEM and became blurred. We mention that no crystalline phase transitions were noticed during the samples observation in the TEM operated at low beam intensity.

In general terms, all the samples examined by TEM consisted in mixed crystalline phases, as revealed by the selected area electron diffraction (SAED) patterns recorded on agglomerated or individual crystal grains. However, we could not derive precise quantitative information about the predominance of one or the other of the crystalline phases formed along the sublimation tube. We present hereafter the TEM results on  $Alq_3$  samples collected from 3 regions in the sublimation tube, in descending order of the deposition temperature and two samples treated at high temperatures.

### *Fraction 1*

Powder sample showing blue fluorescence and referred as fraction 1 was collected from the hottest end of the sublimation tube. Diffraction patterns from individual grains oriented along

different zone axis have been recorded. The diffraction patterns have been indexed and attributed to known crystalline Alq<sub>3</sub> phases. However, some diffraction patterns could not be indexed and assigned to any of the known crystalline Alq<sub>3</sub> phases. In Fig. 2 we show a series of TEM images and associated SAED patterns of Alq<sub>3</sub> crystal grains belonging to different phases and in various crystallographic orientations. Hence, the formation of the  $\gamma$  and  $\delta$  phases has been detected. In Fig. 2e the interplanar distances 0.538 nm and 1.336 nm corresponding to the indicated diffraction spots are not characteristic to any of the known Alq<sub>3</sub> crystalline phases and the diffraction pattern could not be indexed. We conclude that the powder collected from the hot end of the sublimation tube consists in a complex mixture of several known crystalline phases such as  $\gamma$ ,  $\delta$  and one or even more unknown phases that could not be indexed.

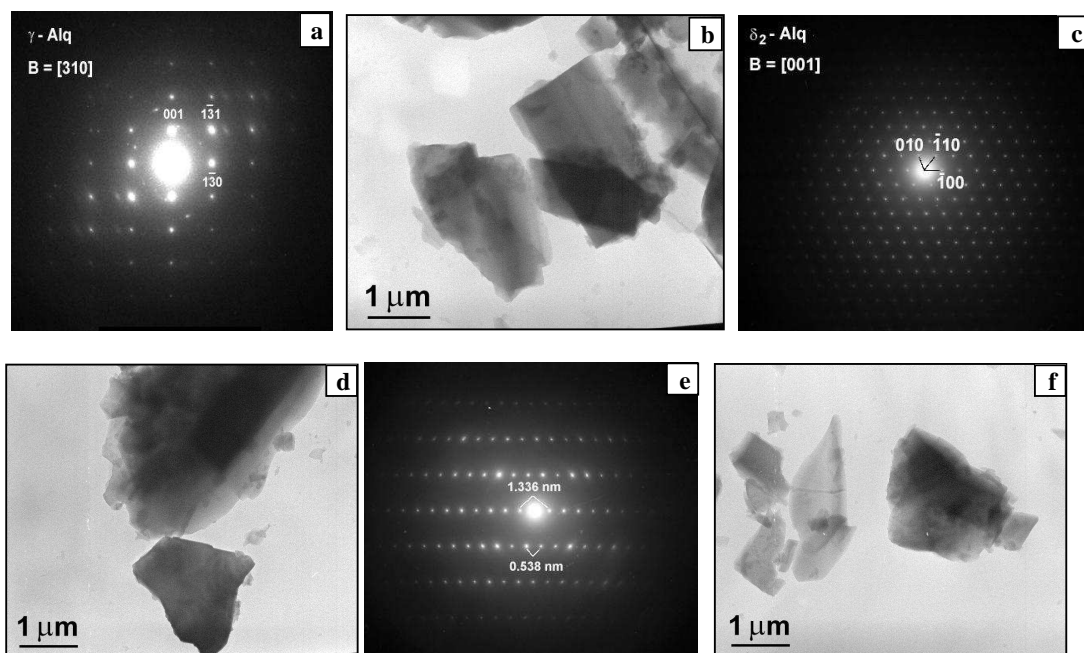


Fig. 2. TEM images and associated SAED patterns of oriented grains belonging to the  $\gamma$  (a, b),  $\delta$  phase (c, d) and a supplementary unknown phase (e, f).

#### Fraction 2

The yellow powder collected from the fraction 2 consists in acicular crystalline grains with lengths between 1.5–2  $\mu\text{m}$  and a width around 0.3  $\mu\text{m}$ . Unfortunately, none of the SAED patterns recorded on individual oriented grains could be indexed according to any Alq<sub>3</sub> crystalline structure listed above. The typical acicular morphology of the powder is presented in Fig. 3a. The associated SAED pattern (Fig. 3b) corresponding to a selected oriented crystal grain reveals interplanar distances that are not characteristic to any of the known Alq<sub>3</sub> phases. The  $2mm$  symmetry of the diffraction pattern implies that the overall symmetry class of the crystallographic system corresponding to this phase is superior to triclinic.

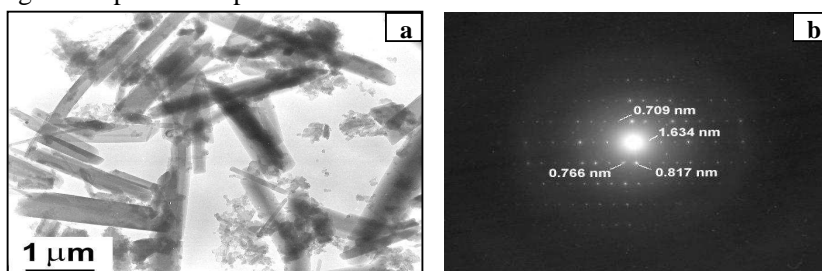


Fig. 3. (a) Typical TEM image of a sample from fraction 2 (yellow powder) showing acicular grain morphology; (b) example of a SAED pattern from an oriented grain.

### Fraction 3

The powder sample of fraction 3 proves to be a mixture of  $\alpha$ -Alq<sub>3</sub> and a new, not yet identified, crystalline phase. The two phases show different morphologies: grains with irregular shape for the  $\alpha$  phase and acicular grains for the unidentified phase, as presented in Fig. 4. The 1.673 nm interplanar distance is not characteristic to any of the known Alq<sub>3</sub> phases. The 1.336 nm interplanar distance presented in the pattern in Fig. 4f was evidenced in the case of the unidentified phase in fraction 1. The 90° angle between the reciprocal vectors marked on the micrograph (Fig. 4f) confers a  $2mm$  symmetry to the SAED pattern indicating a crystallographic system with symmetry higher than triclinic. The new phase evidenced in fraction 3 shows the same acicular morphology as the unidentified phase from fraction 2.

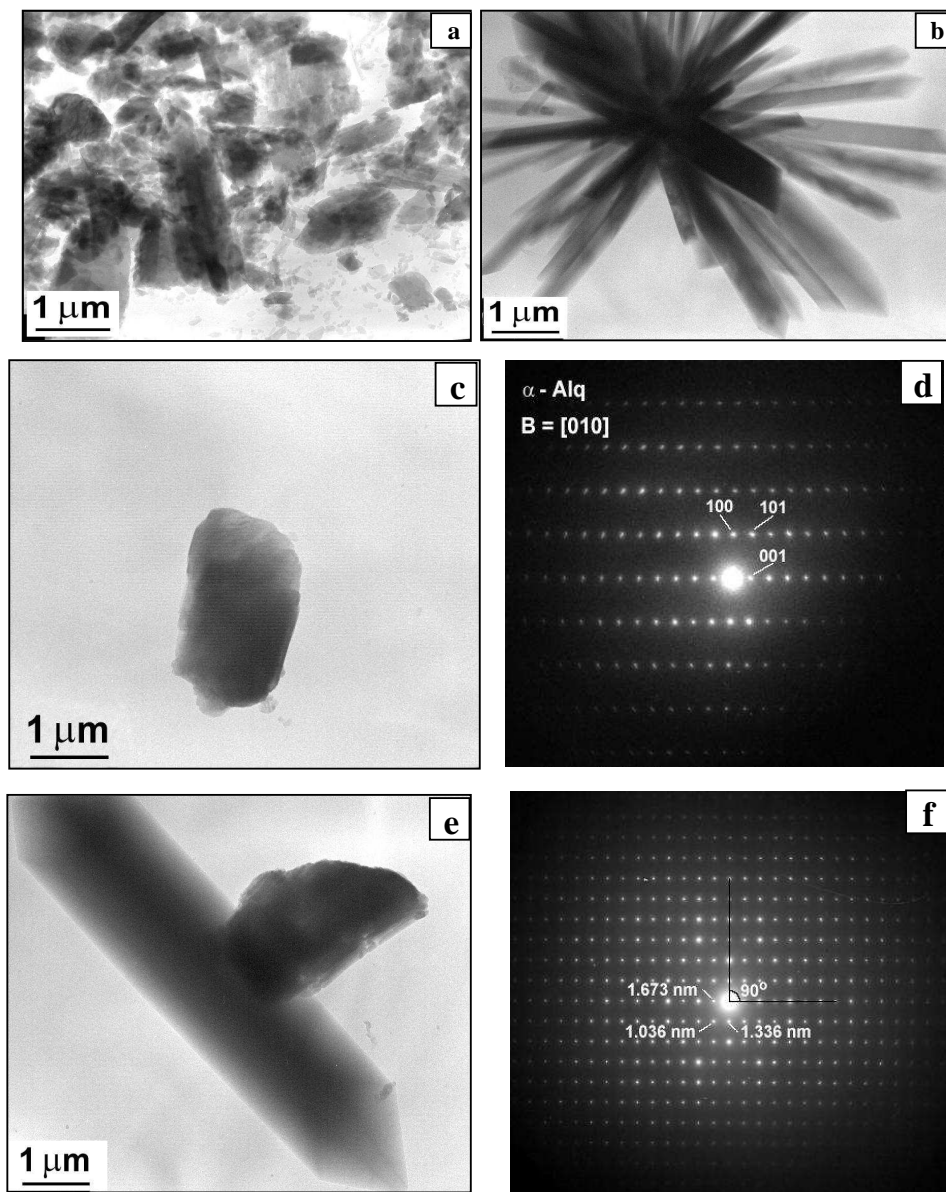


Fig. 4. Crystal grains with two different morphologies present in fraction 3 (a, b); Typical crystal grain belonging to the  $\alpha$  phase (c) and the corresponding electron diffraction pattern along the [010] zone axis (d); Needle-like crystal grain and the corresponding SAED pattern (e) revealing the presence of the new unknown crystallographic phase (f).

*Thermally treated samples*

Alq<sub>3</sub> powder samples from fraction 2 and 3 have been heated at 390 – 400 °C in an inert atmosphere. After annealing for two hours, the powder consists in a mixture of  $\alpha$ -,  $\gamma$ -Alq<sub>3</sub> phases and the new unidentified crystalline phase.

By increasing the time of annealing up to six hours only, the  $\gamma$ - and  $\delta$ -Alq<sub>3</sub> phases were identified by SAED. Morphologically, the TEM images (Fig. 5a) present two classes of grains: on one hand, crystallites of various irregular shapes with sizes from tens of nanometers to a few micrometers long, as resulted from TEM specimen preparation. Besides these small crystal grains, one can also notice the presence of long needle-like grains, about 0.5  $\mu\text{m}$  wide and up to a few micrometers long. A polycrystalline SAED pattern taken on a cluster of small crystal grains is presented in Fig. 5b. Measuring and indexing the diffraction rings reveals the formation of the trigonal  $\gamma$ -Alq<sub>3</sub> phase. A SAED pattern recorded on one of the long needle-like grains is shown in Fig. 5c. The pattern was indexed and it also proves to belong to the trigonal  $\gamma$ -Alq<sub>3</sub> phase. The crystal grain was oriented close to the [210] zone axis. However, the presence of crystal grains belonging to the  $\delta$ -Alq<sub>3</sub> phase was also noticed on this specimen, as proved for instance by the indexed SAED pattern shown in Fig. 5d coming from a crystal grain oriented close to the [100] triclinic zone axis. A volume ratio of the two crystalline phases contained in this specimen cannot be estimated from the TEM observations, but considering the higher rate at which identified SAED patterns correspond to the  $\gamma$  phase compared to the  $\delta$  phase, we may say that  $\gamma$ -Alq<sub>3</sub> is the predominant phase in this sample.

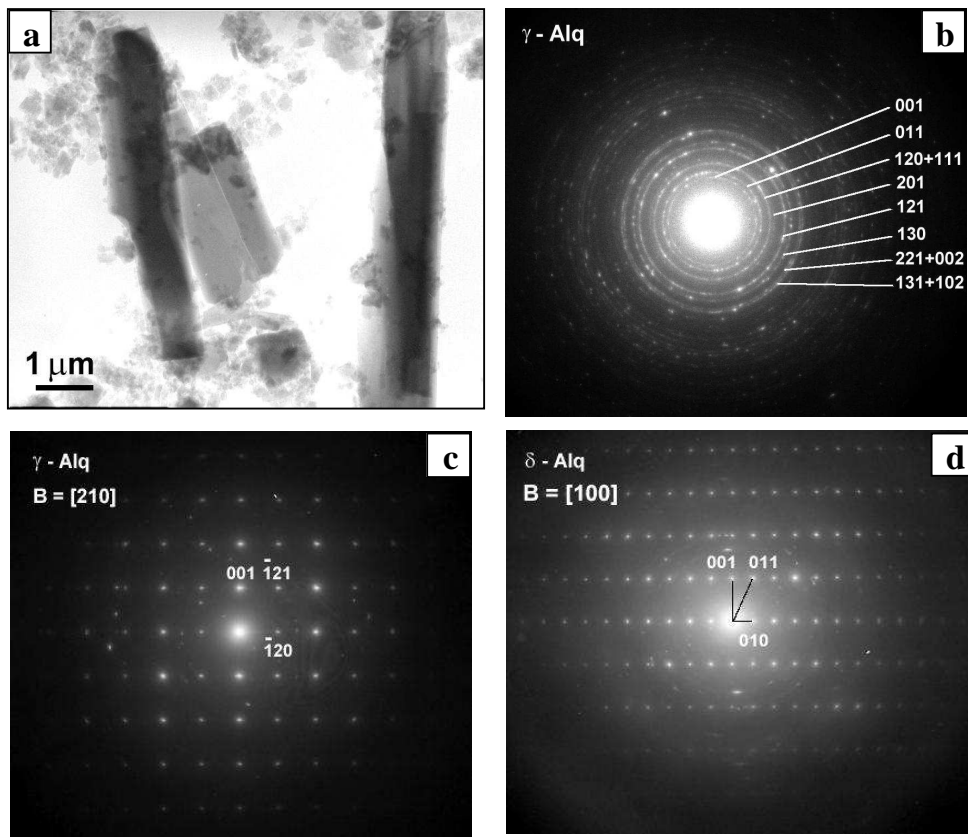


Fig. 5. TEM images of the sample annealed at 390 °C for 6 hours; two classes of grains are noticed: grains with various shapes and sizes and long needle-like grains; (b) Indexed polycrystalline SAED pattern showing the presence of the  $\gamma$ -Alq<sub>3</sub> phase; (c) SAED pattern along the trigonal [210] zone axis of a needle-like grain belonging to the  $\gamma$  phase; (d) SAED pattern along the [100] zone axis of a grain belonging to the  $\delta$ -Alq<sub>3</sub> phase.

Another interesting result was obtained for annealed powder from fraction 2 suddenly quenched at 77 K. In this case, all the SAED patterns recorded on individual grains were indexed according to the  $\gamma$ -Alq<sub>3</sub> phase only. In Fig. 6 we present a typical TEM image of large micrometric crystal grains showing cleavage steps (Fig. 6a) and single crystal SAED patterns corresponding to different such grains oriented along three main zone axes:  $[-111]$ ,  $[010]$  and  $[-110]$  (Fig. 6b-d). It has been shown that the ratio between  $\delta$ - and  $\gamma$ -Alq<sub>3</sub> is strongly dependent on the preparation conditions [23]. Since all the recorded SAED patterns were indexable according to the  $\gamma$ -Alq<sub>3</sub> phase, we consider that the sample of fraction 2, annealed at 400°C and quenched at 77 K, mainly consists of the trigonal  $\gamma$  phase. This result is not surprising since  $\gamma$  is the high-temperature phase of Alq<sub>3</sub>.

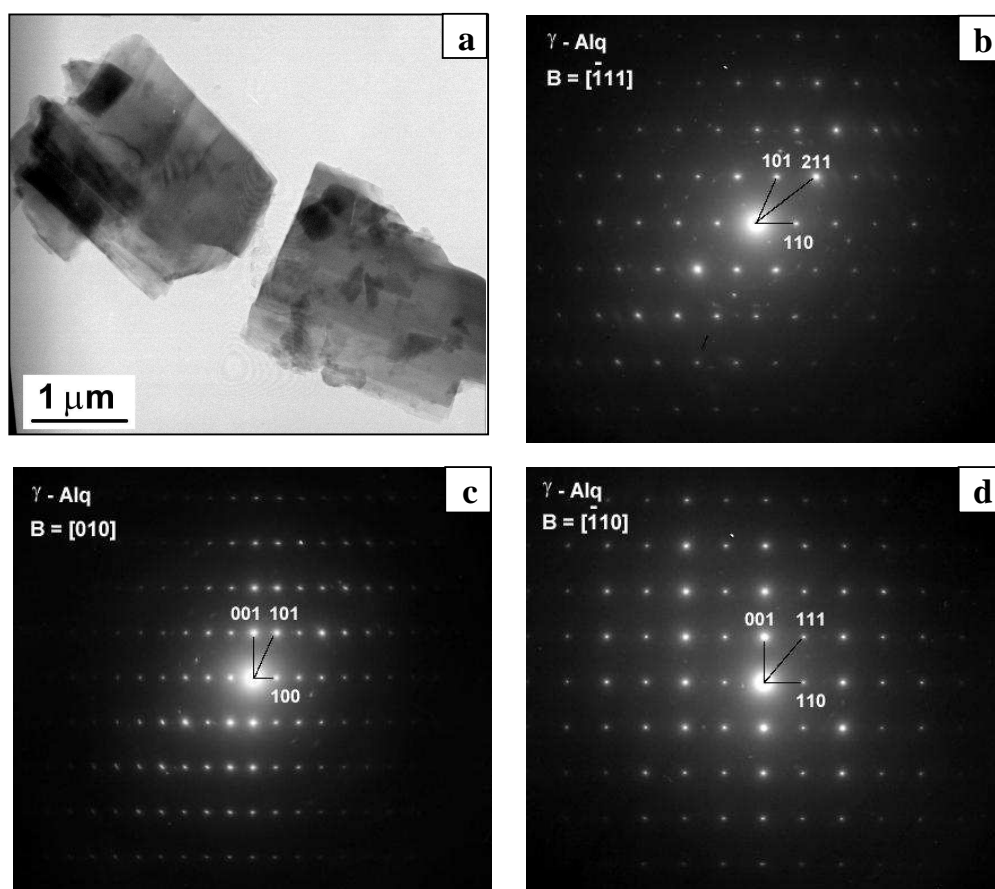


Fig. 6. (a) TEM image of typical micrometric grains from the quenched powder showing cleavage steps. (b) Single crystal SAED pattern of a grain oriented close to the trigonal  $[-111]$  zone axis. (c) Single-crystal SAED pattern of a grain oriented close to the trigonal  $[010]$  zone axis. (d) Single-crystal SAED pattern of a grain oriented close to the trigonal  $[-110]$  zone axis.

We remark that none of the SAED patterns recorded on individual oriented grains from all analyzed fractions could be indexed according to the  $\beta$ -Alq<sub>3</sub> crystalline phase.

#### 4. Conclusions

Alq<sub>3</sub> (aluminum tris(quinoline-8-olate)) is an organic compound with electroluminescent properties showing a wide structural variety in a rather narrow temperature range (tens of degrees). In this paper polycrystalline Alq<sub>3</sub> has been obtained by sublimation inside a horizontal tube. The

local deposition temperature varied from 380 °C to 320 °C along the tube. According to the visual aspect (color, grain shape and size), three different regions have been defined along the synthesis tube (fractions 1 to 3) and powder samples from each region have been characterized by electron microscopy. Microstructural investigations by electron diffraction have shown that all the analyzed fractions consist in mixtures of different Alq<sub>3</sub> phases ( $\alpha$ ,  $\gamma$ ,  $\delta$ ), according to the local deposition temperature along the tube. Hence, a structural gradient along the tube has been evidenced, starting from a phase mixture where the high-temperature phase  $\gamma$  is present (at the hottest end of the tube) and ending with a mixture where  $\alpha$  represents the preponderant phase. None of the analyzed fractions contained the  $\beta$  phase. On the other hand, the formation of at least supplementary unknown phase has been indicated by some of the SAED patterns. The crystallites belonging to the unknown phases generally show an acicular morphology. Some of the corresponding SAED patterns suggest a structural symmetry higher than triclinic one. We are currently performing further investigations in order to identify the unknown phases evidenced by the SAED patterns.

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