

## CONDENSED-MATTER SPECTROSCOPY

# The Influence of Synthesis Conditions on the Stability of Tris(8-Hydroxyquinoline) Aluminum Organometallic Luminophore

A. A. Akkuzina\*, A. V. Khomyakov, R. I. Avetisov, and I. Ch. Avetissov

Mendeleev Russian University of Chemical Technology, Moscow, 125047 Russia

\*e-mail: akkuzina@yandex.ru

Received September 28, 2016; in final form, November 10, 2016

**Abstract**—Single-phase crystalline luminophore tris(8-hydroxyquinoline) aluminum ( $\text{Alq}_3$ ) has been synthesized at  $T = 483$  K and a partial pressure of 8-hydroxyquinoline vapor from 0.15 to 6.12 Torr. The influence of  $P_{8\text{-Hq}}$  on the luminescent characteristics of crystalline  $\text{Alq}_3$  samples has been studied. It has been found that an increase in  $P_{8\text{-Hq}}$  led to a shift of the photoluminescence-band maximum and to a change in the photoluminescence-decay kinetics. It has been shown that  $\text{Alq}_3$  synthesized at  $T = 483$  K and  $P_{8\text{-Hq}} = 6.12$  Torr had the most stable spectral-luminescent characteristics. The results obtained are discussed taking into account defect formation in crystalline  $\text{Alq}_3$ .

DOI: 10.1134/S0030400X17040026

## INTRODUCTION

The use of organic compounds in light-emitting devices was started by studies of electroluminescent properties of crystals of dibenzopyridine and anthracene representatives [1]. Despite the fact that the first light-emitting structures based on these compounds had some drawbacks, the search for new highly efficient semiconductor organic materials with luminescent properties made it possible to solve many problems restricting their practical application. The first organic light-emitting diode (OLED) structures [2], which are today actively incorporated into various displays and light sources, beginning from microdisplays and ending with large flat video panels, were developed in the 1980s.

One urgent problem related to the materials of organic semiconductor electronics is increase of their life time with preset output parameters. Degradation of the characteristics of organic functional materials in the composition of an OLED structure is to a large extent determined by the phase purity and the concentration of impurity point defects in these materials. However, the possibility of formation of not only impurity, but also intrinsic (nonstoichiometry), point defects [3, 4] in crystalline organic materials in the process of their synthesis has not yet been considered. Nonstoichiometry of different degrees takes place in all crystalline phases of chemical compounds at temperatures above 0 K [3] and should be observed to a greater or lesser extent in organometallic crystalline materials.

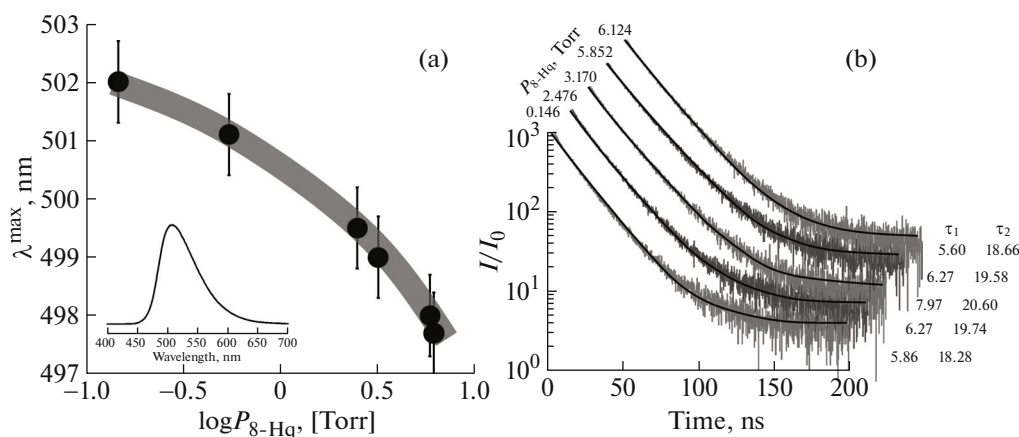
The properties that most strongly depend on defects of the real crystalline-phase structure are called “structure-sensitive” [4]. First of all, these are

structural or electrophysical properties. Finding the relation between the synthesis conditions of organic semiconductor materials, their properties, and the electroluminescent characteristics of light-emitting structures based on these materials will allow one to formulate requirements for new highly efficient organic functional materials for OLEDs and for electronics and photonics in general [5].

We studied in [6] the effect of the synthesis temperature and the partial pressure of 8-hydroxyquinoline vapor ( $P_{8\text{-Hq}}$ ) on the structural and luminescent characteristics of tris(8-hydroxyquinoline) aluminum ( $\text{Alq}_3$ ) organometallic electroluminophore. The dependences obtained were interpreted within the theory of defect formation at the  $\text{Alq}_3$  crystal-lattice level. The present research continues these investigations. We studied the influence of the synthesis condition on the stability of  $\text{Alq}_3$  photoluminescence characteristics taking into account changes in the crystal structure.

## EXPERIMENTAL TECHNIQUE

To study the nonstoichiometry of an  $AB$  binary compound, one synthesizes the single-phase nonstoichiometric inorganic semiconductor crystal under monovariant ( $S_{AB}LV$ ) or bivariate ( $S_{AB}V$ ) conditions fixing one or two intense thermodynamic parameters, respectively [4]. This approach can also be used in the case of the well-studied  $\text{Alq}_3$  organometallic complex [7], considering it as a quasi-binary compound consisting of two components, i.e., of the  $\text{Al}^{3+}$  coordination ion as the first component and the 8-hydroxy-



**Fig. 1.** (a) PL-peak position and (b) PL-decay kinetics of Alq<sub>3</sub> powders synthesized at  $T = 483$  K at different  $P_{8\text{-Hq}}$ . The inset shows a typical PL spectrum of  $\alpha$ -Alq<sub>3</sub>.

quinoline ligand ( $\text{C}_9\text{H}_6\text{ON}$ )<sup>−</sup> as the second component. In this case, the thermodynamic state of the quasi-binary Alq<sub>3</sub> crystal can be fixed by annealing it at a given temperature and partial pressure of the vapor of the 8-hydroxyquinoline (8-Hq) ligand-forming compound.

The purity of compounds with respect to inorganic impurities was controlled by inductively coupled plasma-mass spectrometry (ICP-MS) using a NexION 300D (PerkinElmer, United States) mass spectrometer. The detection limit of impurities in analyzed specimens was from  $10^{-6}$  to  $10^{-12}$  g/mL with allowance for the initial purity of solvents used.

The structural characteristics of crystalline Alq<sub>3</sub> were determined by X-ray powder diffraction on a Bruker ADVANCE diffractometer, Cu- $K_\alpha$  ( $\lambda = 0.154184$  nm), in the  $2\Theta$  range of  $5^\circ$ – $35^\circ$  with a scan step of  $0.05^\circ$  and in the pulse-accumulation regime (2.5 s per point). Data processing was performed using the TOPAS (ver. 2.4) software package.

The photoluminescence (PL) spectra of synthesized Alq<sub>3</sub> powder specimens were measured at room temperature using a Fluorolog FL3-22 (Horiba Jobin Yvon S.A.S) spectrofluorimeter with double monochromatization of exciting and generated radiation within the wavelength range of 400–700 nm with a step of 0.1 nm. Luminescence was excited by a Xenon 450W Ushio UXL-450S/O lamp. The luminescence-decay kinetics was studied using the same spectrofluorimeter under excitation by a pulsed-laser diode ( $\lambda = 370$  nm,  $\Delta\tau = 1.5$  ns) at a wavelength corresponding to the PL maximum of the sample. The luminescence kinetics was analyzed using the OriginPro 8 SR4 software package according to the nonlinear curve-fit procedure.

The Alq<sub>3</sub> crystalline powder was synthesized and purified by sublimation using the technique described in detail in [8].

The sublimated Alq<sub>3</sub> powder was annealed for 60 h in an evacuated ( $10^{-5}$  Torr) fused-quartz ampoule in a two-zone furnace. The Alq<sub>3</sub> specimen was placed into the hot zone at  $T = 483$  K, while 8-Hq was in the cold zone, the temperature of which determined the partial pressure of 8-hydroxyquinoline within the range from 0.15 to 6.12 Torr according to the equations

$\log P_{8\text{-Hq}} [\text{Torr}] = 13.251 - 4666.1/T$  for sublimation,  $298 < T < 351$  K [9],

$\log P_{8\text{-Hq}} [\text{Torr}] = 8.4249 - 2963.5/T$  for evaporation,  $351 < T < 402$  K [6].

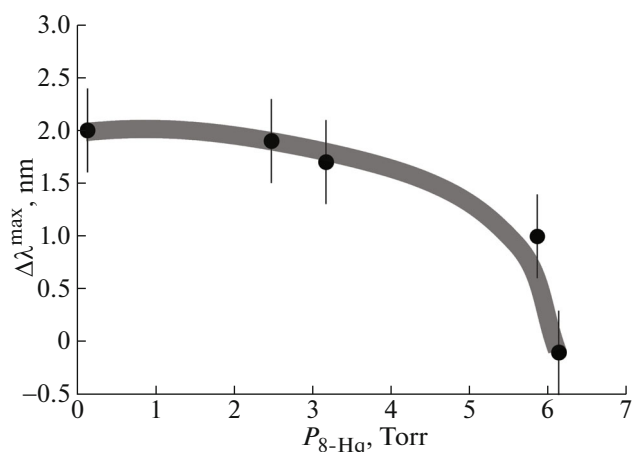
At the temperatures used, we noted no resublimation of Alq<sub>3</sub> from the hot to the cold part of the ampoule and no thermal dissociation of 8-Hq in the vapor phase. The crystal-structure defects formed in the process of synthesis were “frozen” in the crystal lattice by quenching the ampoule with the specimen in water with ice from the annealing temperature.

## RESULTS AND DISCUSSION

According to ICP-MS analysis, the inorganic purity of sublimated Alq<sub>3</sub> and 8-Hq specimens was 99.9987 and 99.9991 wt %, respectively. These values satisfy well the requirements imposed on the concentration of foreign impurities for high-purity inorganic substances [10]. Point defects in the crystal structure (nonstoichiometry defects) of such compounds can be detected if their concentration exceeds  $10^{-3}$  wt %.

According to X-ray-diffraction analysis, all the specimens annealed in 8-Hq vapors corresponded to the polymorphous modification  $\alpha$ -Alq<sub>3</sub>. However, the crystal-lattice parameters for Alq<sub>3</sub> samples synthesized at  $T = 483$  K at different  $P_{8\text{-Hq}}$  within the range of 0.15–6.12 Torr were found to be considerably different [6].

The PL spectrum of  $\alpha$ -Alq<sub>3</sub> is characterized by a single band with a maximum in the region of 500 nm (Fig. 1a, inset). It has been found that an increase in



**Fig. 2.** Absolute shift of the PL peak of Alq<sub>3</sub> powders synthesized at  $T = 483$  K at different  $P_{8\text{-Hq}}$  and excited by a xenon lamp ( $\lambda_{\text{exc}} = 370$  nm) for 5 min.

the 8-Hq vapor pressure in the process of synthesis led to a hypsochromic shift of the PL peak (Fig. 1a) of quenched specimens, as well as to a change in the PL-decay kinetics (Fig. 1b). All the luminescence-decay curves for Alq<sub>3</sub> specimens annealed at different  $P_{8\text{-Hq}}$  were successfully described by two exponents. This result indicates the existence of two types of centers, i.e., centers with short ( $\sim 6$  ns) and long ( $\sim 20$  ns) lifetimes. Simultaneously, it was shown that the PL peak of Alq<sub>3</sub> samples shifts in the process of measurements in air under the action of the xenon lamp (Fig. 2). It has been found that the sample synthesized at  $P_{8\text{-Hq}} = 6.12$  Torr was most stable with respect to degradation of the spectral-luminescent characteristics. The degradation was estimated from the long-wavelength shift of the PL-band maximum as

$$\Delta\lambda = (\lambda_{\text{max}})_{t=5\text{ min}} - (\lambda_{\text{max}})_{t=0\text{ min}}.$$

The results obtained can be explained from the point of view of formation of point defects in crystalline Alq<sub>3</sub> at a given temperature and 8-hydroxyquinoline vapor pressure [6]. The behavior of dependences of the spectral characteristics on  $P_{8\text{-Hq}}$  can be explained by a monotonic change in the concentration of point structural defects with increasing partial pressure of 8-Hg vapor in the studied range of pressures. Since we are dealing with a thermodynamically stable phase, the change in the concentration of point defects should be symbatic to the change in the partial pressure of 8-Hg. In other words, the concentration of defects should increase with  $P_{8\text{-Hq}}$  increasing. Most probably, these defects are aluminum vacancies ( $V_{\text{Al}}$ ).

In this case, we may suggest that the following process occur in the presence of gaseous oxygen. Aluminum, which plays the role of the central atom in the Alq<sub>3</sub> coordination compound, is in the form of the positive ion  $\text{Al}^{3+}$  and is bound to oxygen and nitrogen

of the 8-hydroxyquinoline ligand [11]. The Al–O bond in the Alq<sub>3</sub> molecule has a lower energy than the Al–O bond in Al<sub>2</sub>O<sub>3</sub>. The latter easily forms upon interaction of  $\text{Al}^{3+}$  with atmospheric oxygen. This process occurs even more efficiently in the presence of water vapor [12], which is a generally accepted fact in OLED technology. A long-term period of contact of Alq<sub>3</sub> with air can lead to the formation of Al<sub>2</sub>O<sub>3</sub> and, as a result, to destruction of the Alq<sub>3</sub> crystal structure. The presence of  $V_{\text{Al}}$ , especially in the surface layers of the crystal structure, decreases the probability of Al<sub>2</sub>O<sub>3</sub> formation, because the appearance of sites without Al makes it difficult for oxygen to form the Al–O bond. This hypothesis explains why an increase in the concentration of vacancies decreases the degradation of spectral-luminescent properties.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 16-32-60035.

## REFERENCES

1. A. Bernanose, *J. Chem. Phys.* **52**, 396 (1955).
2. C. W. Tang and S. A. van Slyke, *Appl. Phys. Lett.* **51**, 913 (1987). doi 10.1063/1.98799
3. P. V. Kovtunenkov, *Physical Chemistry of Solid-State Materials. Defect Crystals* (Vyssh. Shkola, Moscow, 1998) [in Russian].
4. F. A. Kroger, *Chemistry of Imperfect Crystals* (North-Holland, Amsterdam, 1964).
5. T. Tsujimura, *OLED Display Fundamentals and Applications*, Vol. 25 of *Wiley Series in Display Technology* (Wiley, New York, 2012).
6. I. Ch. Avetissov, A. A. Akkuzina, R. I. Avetisov, A. V. Khomyakov, and R. R. Saifutyanov, *Cryst. Eng. Commun.* **18**, 2182 (2016). doi 10.1039/C6CE00011H
7. M. Brinkmann, G. Gadret, and M. Muccini, *J. Am. Chem. Soc.* **122**, 5147 (2000). doi 10.1021/ja993608k
8. R. Avetisov, O. Petrova, A. Khomyakov, O. Mushkalo, A. Akkuzina, A. Cherednichenko, and I. Avetissov, *J. Cryst. Growth* **401**, 449 (2014). doi 10.1016/j.jcrysgro.2014.02.018
9. M. A. V. da Silva, M. J. S. Monte, and M. A. R. Matos, *J. Chem. Thermodyn.* **21**, 159 (1989). doi 10.1016/0021-9614(89)90127-4
10. M. F. Churbanov and A. P. Vel'muzhov, *Chemistry of Very Pure Inorganic Substances* (Nizhegor. Gos. Univ., Nizhnii Novgorod, 2015) [in Russian].
11. M. Rajeswaran, T. N. Blanton, R. H. Young, and W. Brennessel, *J. Chem. Crystallogr.* **40**, 195 (2010). doi 10.1007/s10870-009-9633-x
12. F. Papadimitrakopoulos, X. M. Zhang, and K. A. Higginson, *IEEE J. Sel. Top. Quantum Electron.* **4**, 49 (1998). doi 10.1109/2944.669465

Translated by M. Basieva