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Organic luminophor metal complex in inorganic glass matrix—A new hybrid material



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ABSTRACT

Hybrid materials were synthesized on the base of borate glass matrix and the tris(8-hydroxyquinoline) aluminum, gallium and indium ($Mq_3 = Alq_3, Gaq_3, \text{ and } Inq_3$) organic complexes, which are used as phosphors in OLED devices. The luminescence properties of hybrid materials containing 0.02–0.1 wt% of Mq_3 in B_2O_3 glass matrix were studied. It was found that the luminescence peaks of hybrid materials were significantly shifted to shorter wavelengths. The measured luminescence lifetimes of Mq_3 based hybrid materials fitted by two exponents were found to be several times less for the shorter components and nearly the same for the long components when compared with pure Mq_3 .

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1. Introduction

Hybrid materials (HM) based on organic–inorganic substances are of a great interest due to specific properties of nanosize particles disordered or ordered into a matrix [1]. Organic luminescent materials demonstrate high efficiency both at optical and electric current excitations [2]. But, in general, most of organic phosphors are unstable at room atmosphere and need to be protected. An incorporation of organic materials into transparent inorganic matrix could solve a problem of degradation and give an opportunity to get new materials with unique properties.

In the recent 15 years a lot of studies of HMs with an inorganic matrix based on glasses [3,4], silicon oxide nanospheres [1,5,6], thin amorphous films [7,8], xerogels [9,10], layered double hydroxides and [11], single crystals [12,13] have been carried out. HMs were synthesized by variations of sol–gel technique [3–11]. Thin HM films have been produced by a vapor-deposited mixed layers technique [14] but there were difficulties with organic component temperature control and a partial decay of an organic component. HM single crystals have been grown from solutions [12,13]. An application of solution techniques results in incorporation of OH-groups in HMs and correspondingly to luminescence quenching at the OH-group oscillations.

A synthesis of new efficient phosphors based on organic metal–complex compounds with a high decay temperature ($> 300^\circ\text{C}$) allows obtaining hybrid optic materials using a glass melt technology. In this case one could decrease the energy dispersion on residual anion groups.

Attempts to use low-melting borate glasses ($B_2O_3, Li_2O-B_2O_3, Na_2O-B_2O_3, Li_2O-Na_2O-B_2O_3, PbF_2-B_2O_3$) as a glass matrix showed that only the pure B_2O_3 matrix resulted in production of a luminescent hybrid material [17] in which organic metal complexes of M^{3+} with 8-quinolinol (C_9H_7NO)– Mq_3 ($M=Al, Ga, \text{ and } In$) were responsible for luminescence.

Mq_3 molecules exist as two geometrical isomers: meridional and facial (*mer*- and *fac*-), and crystallized in some polymorphous modifications (*mer*- in α -, β - and ϵ -phases and *fac*- in γ - and δ -phases) [11,14–16]. Mq_3 luminescence properties strongly depend on preparation purity, a central ion, a polymorph, and an isomer. In [16] we presented the general scheme of polymorphous transitions for high-pure Alq_3, Gaq_3 and Inq_3 preparations resulted from *in situ* measurements of luminescence and Raman spectra vs. temperature in the range from RT to the full melting both in vacuum and under Ar pressure (Fig. 1) correlated with XRD measurements of quenched samples.

The present study is the extension of our investigation on Alq_3 -based hybrid materials previously reported in [17]. It was found that $Alq_3-B_2O_3$ HM demonstrated a strong shift of luminescence maximum towards the short wavelength. To clarify the observed phenomenon we tried to investigate a row of HM based on Alq_3 analogs, namely, Gaq_3 and Inq_3 , which are also applied as electroluminescent materials in OLED structures.

2. Experimental technique

Metal complexes were synthesized by the reaction:



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The synthesis was conducted in isopropanol (pH=10) at 25 °C and continuously mixed for 1 h. We obtained precipitates of Mq_3 which were purified by vacuum sublimation ($p < 10^{-5}$ Torr). The powdered preparations were as pure as 99.997% by ICP-MS analysis (NexION 300D, PerkinElmer Inc.) and α -phases were dominant according to XRD measurements (Bruker Advance) (Fig. 2a).

HMs were synthesized by melting of dried B_2O_3 powder and 0.02–0.1 wt% Mq_3 mixture for 8–60 min in glassy carbon crucibles at 380–420 °C temperatures, which were below the Mq_3 decay temperatures (Table 1). Samples were obtained by melt freezing or by pulling of thick fibers.

The absorption spectra were measured on a VARIAN 5000 Cary UV–VIS–NIR spectrophotometer. A Fluorolog FL3-22 spectrofluorometer (Horiba Jobin Yvon) with double-grating excitation and emission monochromators was used for luminescence

measurements in 350–800 nm wavelength range. The luminescence decay kinetics were studied at excitation by the pulsed diode laser ($\lambda = 370$ nm, $\Delta\tau = 1.5$ ns).

3. Results and discussion

Hybrid samples were transparent in 250–2700 nm range. The samples had an amorphous structure (glass samples) according to XRD analysis (Fig. 2b) and they did not contain visible inclusions nor bubbles. Small dark inclusions resulted from partial organic decay rejected to peripheral parts of the glass plates, or fibers.

The influence of glass melting parameters on HM's spectral properties showed that the synthesis duration increase results in the luminescence maximum shift to shorter wave lengths in comparison with the pure crystalline phosphors (Table 1).

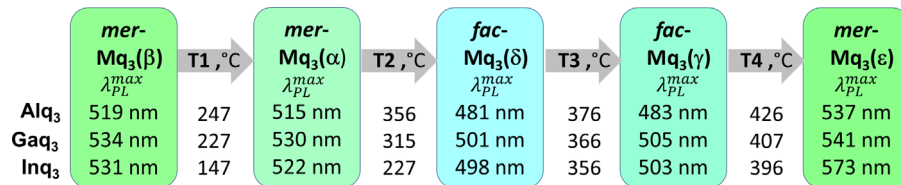


Fig. 1. The scheme of polymorphous transitions in organic phosphor Alq₃, Gaq₃ and Inq₃ [16].

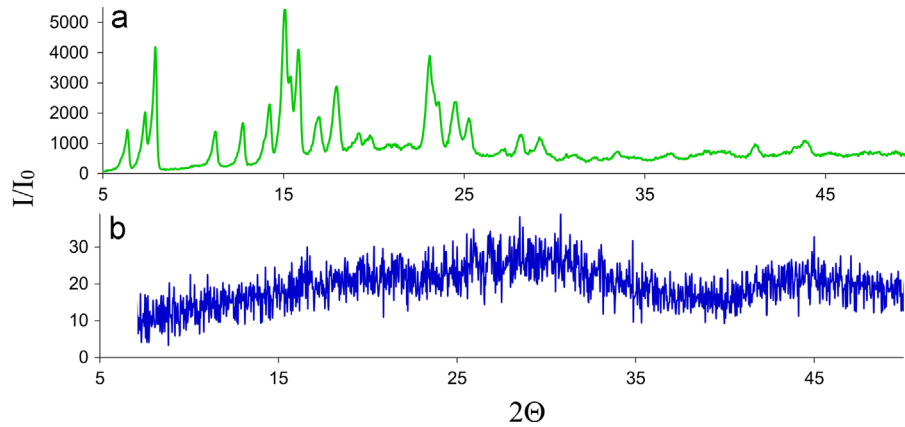


Fig. 2. XRD patterns for powdered Alq₃ (a) and glassy hybrid material (b).

Table 1
Synthesis conditions and luminescence properties of hybrid materials.

Composition	Synthesis conditions		Wavelength of maximum λ_{PL}^{max} (maxima component; nm)	FWHM (nm)	Color coordinates (X, Y)	Lifetimes (ns)	
	Temperature (°C)	Time (min)				τ_1	τ_2
Alq ₃	as synthesized		518 (510, 554)	82	0.3007, 0.5364	21.3	28.7
Alq ₃	396	60	489 (478, 502)	100	0.2140, 0.3565		
Alq ₃ /B ₂ O ₃ (1)	400–420	8	493 (463, 501)	110	0.2098, 0.3490	8.95	37.6
Alq ₃ /B ₂ O ₃ (2)	400	10	490 (477, 492)	104	0.1923, 0.3021	6.07	38.7
Alq ₃ /B ₂ O ₃ (3)	390	30	485 (450, 487)	108	0.1908, 0.3114	3.14	31.6
Alq ₃ /B ₂ O ₃ (4)	400	60	443 (429, 474)	99	0.1526, 0.1455		
Gaq ₃	as synthesized		534 (562, 519)	106	0.3617, 0.5600	6.14	14.6
Gaq ₃	396	60	511 (503, 541)	104	0.2735, 0.4815		
Gaq ₃ /B ₂ O ₃ (1)	380	2	503 (496, 550)	108	0.2359, 0.4117		
Gaq ₃ /B ₂ O ₃ (2)	380	5	502 (488, 524)	106	0.2287, 0.4065		
Gaq ₃ /B ₂ O ₃ (3)	390	60	499 (505, 428, 406)	118	0.2321, 0.3779	1.62	15.0
Inq ₃	as synthesized		531 (530, 594)	94	0.3571, 0.5542	5.98	11.8
Inq ₃	386	60	504 (498, 553)	100	0.2568, 0.4655		
Inq ₃ /B ₂ O ₃ (1)	400	8	490 (452, 490)	111	0.2037, 0.3257		
Inq ₃ /B ₂ O ₃ (2)	400	15	490 (450, 501)	122	0.2034, 0.3138		
Inq ₃ /B ₂ O ₃ (3)	390	60	488 (450, 488)	101	0.1694, 0.3089	1.29	13.3

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