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Luminescent hybrid materials based on (8-hydroxyquinoline)-substituted metal-organic complexes and lead-borate glasses

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ABSTRACT

Novel luminescent organic-inorganic hybrid materials based on 8-hydroxyquinoline metal complexes (Liq, Kq, Naq, Rbq, Mgq_2, Srq_2, Znq_2, Scq_3, Alq_3, Gaq_3, and Inq_3) have been synthesized by a high temperature exchange reaction with $80PbF_2–20B_2O_3$ inorganic low-melting glass. The mechanical and optical properties, transmission spectra, emission an excitation photoluminescence, and luminescence kinetic of hybrid materials were studied. All hybrid materials showed a wide luminescence band in the range 400–700 nm.

1. Introduction

The progress in organic photo- and electroluminescent phosphors opens up prospects for novel highly efficient light-emitting devices. Development organic-inorganic hybrid materials (HM's) with transparent inorganic matrices based on these new organic phosphors could solve the problem of degradation of the organic components under atmosphere and allows creating new materials with unique properties [1,2]. Along with the most common sol-gel method [3] one of the promising methods of HM's making is a heterophase high-temperature reaction using a low-melting glass. During the reaction we get a new hybrid material in which organic phosphor molecules homogeneously are distributed on a nanoscale level in a glassy matrix. The possibility of fluorescent HM's manufacturing by this method was demonstrated for 8-oxiquinoline metal complexes (Alq_3, Gaq_3, and Inq_3) in the B_2O_3 matrix [4] and various phenanthroline complexes Eu (III) in the B_2O_3, and oxyfluoride glass [5] and glass-ceramic material [6]. At that the advantages of HM's synthesis in oxyfluoride glass has been demonstrated.

PbF_2-B_2O_3 and PbF_2-PbO-B_2O_3 melts have long been used at crystal production by the melt solution growth technique due to low-melting fluxes having very low viscosity [7]. In the 600–700 °C temperature range the above mentioned melts have viscosity in 3 orders of magnitude lower than the for B_2O_3 melt, which facilitates the process of mass transfer during synthesis with stirring. The glasses of these compositions have sufficiently high values of mechanical and chemical resistances and can be used as laser materials when activated by Er^{3+} [8,9], Nd^{3+} [9], Sm^{3+} [10], Cr^{3+} [11] and other traditional luminescent doping ions.

The goal of the present research was the synthesis and study of luminescent properties of hybrid materials based on 8-hydroxyquinoline metal complexes for metals of I, II, and III groups of the Periodic Table having general formula Mq_n (Liq, Kq, Naq, Rbq, Mgq_2, Srq_2, Znq_2, Scq_3, Alq_3, Gaq_3, and Inq_3. Herein and below "**q**" is referred to the 8-hydroxyqionoline ligand). These complexes in the form of powders exhibit photoluminescence [14]. Some of them are used in OLED technology. For example Liq is used as an emission (blue

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emitter), and electronic-transport material [13], Alq_3 is also an emission (green emitter and an electron-transport material [14].

2. Experimental

2.1. Synthesis of phosphors

8-Quinolinol was purchased from Sigma–Aldrich and additionally purified by vacuum sublimation. All solvents were procured from Merck.

The synthesis was conducted in 2-propanol solution at pH = 9–10 (depending on the metal ion) at 25 °C and continuous mixing for 1 h by the reaction of 8-hydroxyquinoline with metal ions (Fig. 1). We obtained precipitates of Mq_n, which were filtered, dried under vacuum and finally purified by vacuum sublimation ($p = 10^{-5}$ Torr).

2.2. Purity measurements

Powder preparations were consequently dissolved in H_2O_2 (1 mL), then HNO_3 (1 mL, 1%) and fully decomposed by means of a microwave decomposition procedure (Berghof Speedwave Four Microwave Digestion System) in DAC-100 TFM-PTFE autoclaves. Impurity measurements were carried out by NexION 300D ICP-MS (Perkin–Elmer Inc.) in the KED mode. The powder preparations purity (trace metals) is presented in Table 1. All preparations were at least as pure as 99.95%. And their purity corresponds to the purity of inorganic reagents (PbF_2 – 99.99 wt%, B_2O_3 – 99.99 wt%). The certain impurity concentrations are presented in Tables S2 and S3 (see Supplementary).

2.3. Synthesis of glass matrix

The 80(mol.%)PbF_2–20(mol.%)B_2O_3 glasses were synthesized using PbF_2 and B_2O_3 preparations. The batches were 50 g in weight. Glasses were synthesized at 850–900 °C during 0.25–0.5 h in closed corundum crucibles. The melt was poured into a steel mold heated to 200°C.

2.4. Synthesis of HM's

Synthesis of HM's was also carried out in corundum crucibles. Pre-synthesized glass (5 g) was melted at 800 °C then cooled up to 600 °C and powdered organometallic phosphor Mq_n (0.10–0.15 wt %) was dropped into the melt. Then the mixture was stirring during 30 s. The samples were obtained by rapid casting into a steel mold.

2.5. Elemental analysis

Scanning Electron microscopy (VEGA-3-LMU, Tescan) equipped with an energy-dispersive spectroscopy (EDS Inca Energy X-MAX-50, Oxford Instruments) supported by AZTec software was used for data gathering and processing. The glass composition was controlled by SEM-EDX analysis after carbonization, the beam energy was 30 KeV for glasses.

Table 1
Total purity of 8-oxiquinolin metal complexes determined by ICP-MS.

Compound	Notation	Purity [wt%]
$Li(C_9H_4ON)$	Liq	99.9991
$Na(C_9H_4ON)$	Naq	99.9990
$K(C_9H_4ON)$	Kq	99.9386
$Rb(C_9H_4ON)$	Rbq	99.9663
$Mg(C_9H_4ON)_2$	Mgq_2	99.9860
$Sr(C_9H_4ON)_2$	Srq_2	99.9979
$Zn(C_9H_4ON)_2$	Znq_2	99.9501
$Al(C_9H_4ON)_3$	Alq_3	99.9982
$Ga(C_9H_4ON)_3$	Gaq_3	99.9906
$In(C_9H_4ON)_3$	Inq_3	99.9928
$Sc(C_9H_4ON)_3$	Scq_3	99.9886

2.6. Absorption spectra

The absorption spectra of glasses and HM were recorded on a Varian Cary 5000 (UV/VIS/IR) spectrophotometer in 400–3000 nm wavelength range with 1 nm step.

2.7. Luminescence measurements

All luminescence measurements were carried out at room temperature. A Fluorolog FL3-22 spectrofluorimeter (Horiba Jobin Yvon) with double grating excitation and emission monochromators was used for luminescent measurements in a wavelength range of 400–700 nm with a 0.1 nm step. The emission and excitation spectra, luminescence decay kinetics were studied at excitation by the pulsed diode laser ($\lambda = 377$ nm, $\Delta\tau = 1.5$ ns) and Xenon 450 W Ushio UXL-450S/O lamp. Processing of luminescence decay curves was carried out with OriginPro 8 SR4 software using the Fit Exponential procedure. All decay curves were described by two exponentials (criterion Adj. R-Square> 0.98).

2.8. Microhardness measurements

The microhardness was determined by the Vickers method using a PMT-3 microhardness tester. Measurements were carried out on both sides of a tested plate at 6 different loads. The each load was measured for at least 4 prints. A minimum load was chosen based on the size of the print and it was 25 g. The maximum load was chosen based on the appearance of cracks in the corners of the print and it was 100 g.

The refractive index was determined by the Lodochnikov technique for $\lambda = 488$, 540, 582, and 619 nm.

2.9. X-ray crystallography

Yellow crystals of $Sc(q)_2(OH)$ were obtained from slow evaporated of saturated acetone solution at room temperature. Crystals of $Sc(q)_2(OH)$, a crystallosolvate with acetone ($C_{81}H_{70}N_8O_{15}Sc_4$, M = 1575.29), are monoclinic, space group $P2_1/n$, at 120 K: a = 13.8135(10), b = 31.892(2), c = 18.4130(13) Å, β = 105.527(2) °, V = 7815.5(10) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.339 g cm^{-3}, μ(MoKα) = 4.02 cm^{-1}, F(000) = 3264. Intensities of 136160

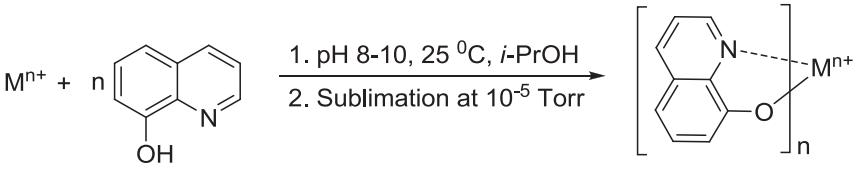

Fig. 1. Scheme of the reaction for producing of n(8-hydroxyquinoline)metal complexes.