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Luminescent Stability of Hybrids Based on Different Borate Glass Matrix's and Organic Metal Complexes

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Abstract: The stability of the luminescent properties of new hybrid materials based on 8-oxyquinoline metal (Li, Rb, Sr) complexes and Eu complex with phenanthroline and low-melting Pb-based inorganic glass matrixes under conditions of prolonged exposure under ambient conditions and heating above the glass transition temperature of the matrix's has been investigated.

Keywords: fluoroborate glass, hybrid material, luminescence, metalorganic.

I. INTRODUCTION

Hybrid materials (HM) are widely used in photonics as active and passive elements as well as integral optics components [1]. One of the problems which can be solved by the creation of HM is protection of organic phosphors from environmental conditions (oxygen, water vapor, UV light, etc.) which lead to the destruction of metal-organic complexes and their loss of luminescence properties [2]. The possibility of synthesis of photoluminescent HM based on 8-hydroxyquinoline [3]-[6] and phenantroline [7]-[8] metal organic phosphors and inorganic low melting glasses as a matrix using a non-aqueous technique has been demonstrated. Glassy boron oxide, borate and borosilicate glasses were used as boron-based matrix. For preparation of a volume HM a glass matrix should have both a low melting temperature and low melt viscosity. In the present research we have synthesized the HM using the melt of fluoroborate and lead borosilicate glasses.

One of the main requirements to HM's is their stability to adverse environmental conditions. We have found out that the B₂O₃-based HM's have not been sufficiently stable at prolonged exposure [7], while the HM's based on the glass matrix with the composition of 80PbF₂ - 20B₂O₃ have been stable enough not only at prolonged exposure [7], but also when heated to the glass transition temperatures of the matrix [8].

In the present research we have analyzed two different low melting glass matrixes for HM' in respect of improvement of their stability towards air, humidity and heating.



The first glass matrix with the composition of 80(mol.%)PbF₂-20(mol.%)B₂O₃ (matrix **M1**) have the lowest operating temperatures in PbF₂-B₂O₃ system. These glasses are stable and widely applied in photonics [9]-[10]. The second matrix with the composition of 62(mol.%)PbO-26(mol.%)B₂O₃-12(mol.%)SiO₂ (matrix **M2**) is a eutectic composition in the PbO-B₂O₃-SiO₂ quazi ternary system with the lowest-melting temperature of 484°C [11].

As an organic part of HM we used 8-hydroxyquinoline complexes (Mq_n) of metals (M), and metal-phenanthroline complexes of REE. These complexes are successfully used in OLED technology as emitting materials [12].

II. EXPERIMENTAL

Synthesis of hybrid materials

Metal organic complexes synthesis. 8-Hydroxyquinolinol was purchased from Sigma–Aldrich and additionally purified by high vacuum sublimation. All solvents were procured from Merck.

The syntheses have been conducted in 2-propanol solution at pH = 9-10 and 25-27°C (depending on the metal ion) and continuous mixing for 1 h by the reaction of 8-hydroxyquinoline with metal ions as described in [13]. We obtained precipitates of Mq_n, which were filtered, dried under vacuum and finally purified by high vacuum sublimation ($p = 10^{-5}$ Torr).

Synthesis of complex - Europium (III) tris-(4,4,4-trifluoro-1-(2-naphthyl)butane-1,3-dionato) (1,10-phenantroline) - Eu(NTA)₃(Phen) has been conduction as described in [7].

Synthesis of glass matrices. The glasses have been synthesized using PbF₂, PbO, SiO₂ and H₃BO₃ preparations. All reagents were purchased from Sigma–Aldrich and were as pure as 99.99 wt%. B₂O₃ has been produced by vacuum dehydrolization of H₃BO₃ with further melting in a Pt crucible. The final B₂O₃ had 99.999 wt% purity according to ICP-MS analysis (Fig. 1a). The batches were 50 g in weight. Glasses have been synthesized at 850–900°C during 0.25–0.5 h in closed corundum crucibles. The melt has been poured into a steel mold heated to 200°C.

Synthesis of HM's. Synthesis of HM's has also been carried out in corundum crucibles. Pre-synthesized glass (5 g) has been melted at 800°C then cooled up to 600°C and powdered organometallic phosphors (0.10 – 0.15 wt%) was dropped into the melt. Then the mixture has been stirring during 10-20 seconds. The samples have been obtained by rapid casting into a steel mold.

Measurement techniques

Purity Measurements. Powder preparations were consequently dissolved in H₂O₂ (1 mL), then HNO₃ (1 mL, 1%) using microwave decomposition procedure (Speedwave Four, Berghof GmbH) in DAC-100 TFM-PTFE autoclaves. Impurity measurements were carried out by an inductively coupled plasma mass-spectrometer NexION 300D (Perkin–Elmer Inc.) in the KED mode. The powder preparations purity (trace metals) is presented in Fig.1. All metal-organic complexes were at least as pure as 99.96%. And their purity corresponds to the purity of inorganic reagents.

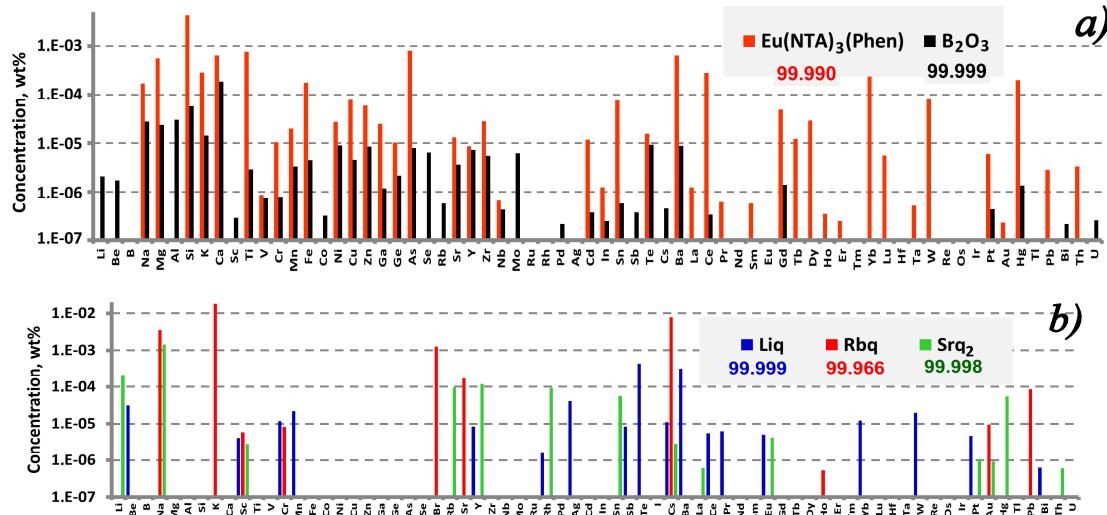


Fig.1. Concentration of impurity elements in and $\text{Eu(NTA)}_3(\text{Phen})$ and B_2O_3 (a), and Meqn (b) determined by ICP-MS technique.

Stability measurements. The stability testing of HM's have been carried out by their exposure during 3-6 months at RT, UV natural lighting and natural humidity. We have also heated HM's to temperatures higher the glass transition temperatures (T_g) of the corresponding glass matrixes at the exposure during 2 hours (350°C for **M1** and 270°C for **M2**).

Luminescence measurements. All luminescence measurements have been carried out at room temperature. A Fluorolog FL3-22 spectrofluorimeter (Horiba Jobin Yvon, USA) with double grating excitation and emission monochromators has been used for luminescent measurements in a wavelength range of 390–700 nm with a 0.1 nm step. The emission were studied at excitation by the pulsed diode laser ($\lambda = 377$ nm, $\Delta\tau = 1.5$ ns).

III. RESULTS AND DISCUSSION

Analysis of resistance of HM's based on 8-oxyquinoline with **M1** towards the room humidity has demonstrated high performance of luminescent properties after 3-6 months exposure (Fig. 2 a, b). The difference in PL spectra of as-synthesized and annealed HM's could be explained by a chemical exchange reaction proceeding between metal complex and the matrix. As a result of the reaction a spatial glass net is forming. In the net the organic ligands form the new complexes with matrix cations (Pb, Al, B).

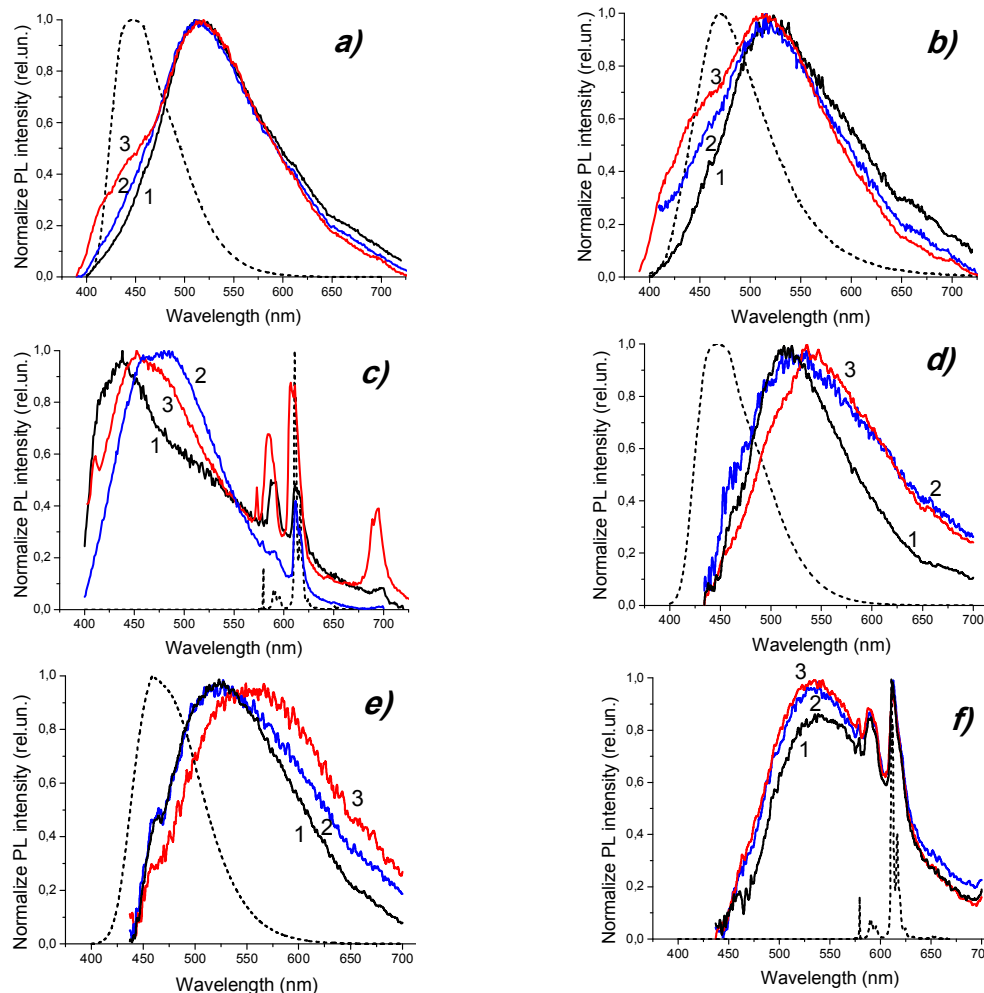


Fig. 2. PL spectra of as-synthesized HM's (1, solid black line) based on Liq+**M1** (a), Rbq+**M1** (b), Eu(NTA)₃(Phen)+**M1** (c), Liq+**M2** (d), Srq₂+**M2** (e), Eu(NTA)₃(Phen)+**M2** (f), compared with the PL spectra of the initial metal organic complexes (dash lines) and HM's exposed at RT during 6 months (2, blue line) and HM's annealed over glassy temperatures (3, red line).

In the case of HM's based on Eu(NTA)₃(Phen) in PL spectra besides a wide band shifted towards a short wave region comparing to Meq_n spectra we observed narrow lines attributed to f-f transitions on the Eu³⁺ ion (Fig. 2 c).

Formation of complexes of Pb with organic ligands which demonstrate a wide PL band with 520-530 nm maximum has been described in [14].

The HM's based on the **M2** matrix have performed less stability. It should be noted that the absolute values of luminescence intensities of HM in the **M1** matrix are higher comparing to the **M2** matrix with the same amount of the phosphor added into the matrix at HM's synthesis. At heating and air exposure in the case of HM based on **M1** we fixed not only the PL spectrum outline preservation, but also the constancy of the absolute values of intensities. The PL intensities increased just when an appreciable crystallization of the matrix took place

In the case of the HMs based on M2 matrix absolute intensity markedly increased with exposure under air and at heating. Probably, in the case of more reactive **M1** matrix, in which

Pb^{2+} is surrounded by a movable F^- ions, the Pb-based stable complexes were formed directly during HM's synthesis. Inside the more inert M2 matrix the Pb^{2+} ion is surrounded by the O^{2-} ions forming a stable PbO_4 pyramid, whose structure is specific for the glasses containing PbO at concentrations higher than 50 mol% [15]. The organic ligands are not completely reacted with Pb^{2+} ions in the matrix and remain as nonluminescent fragments. During prolonged exposure or heating the HM's based on the **M2** matrix the reaction of lead-organic complex formation starts to proceed at a significant rate. It results to an increase in luminescence intensity with luminescence maximum near 530 nm. Such an increase in intensity suggests that HM's based on the **M2** matrix may be promising materials for laser-stimulated luminescence [5]. The color of luminescence of HM's varied from blue to yellow-green (Table 1).

Table I. PL maximum and CIE 1939 color coordinate (X,Y) of hybrid materials

Complex Matrix	Liq		Rbq		Sr _{q2}		Eu(NTA) ₃ Phen	
	$\lambda_{\text{PL max}}$, nm	X Y	$\lambda_{\text{PL max}}$, nm	X Y	$\lambda_{\text{PL max}}$, nm	X Y	$\lambda_{\text{PL max}}$, nm	X Y
—	446	0.1484 0.0569	469	0.1767 0.2538	459	0.1413 0.0851	611	0.6613 0.3385
M1	514	0.3102 0.4478	523	0.3272 0.4395	-	-	438	0.2054 0.2769
M1 After 6 months	514	0.3203 0.4546	516	0.2950 0.4036	-	-	480	0.2547 0.2567
M1 after heating	515	0.3091 0.4271	512	0.2918 0.3968	-	-	452	0.2708 0.2872
M2	513	0.3098 0.4905	-	-	523	0.3293 0.4758	612	0.3986 0.4976
M2 After 6 months	512	0.3430 0.4461	-	-	527	0.3500 0.4638	539, 612	0.3850 0.4916
M2 after heating	536	0.3715 0.4876	-	-	549	0.3924 0.4778	540, 612	0.3776 0.4913

IV. CONCLUSION

New fluorescent hybrid materials based on 8-hydroxyquinoline and phenantroline metal organic phosphors and inorganic low melting lead glasses have been synthesized. It has been shown that HM's based on the $\text{PbF}_2\text{-B}_2\text{O}_3$ matrix exhibited high stability of luminescent properties both in prolonged exposure at ambient conditions and at heating, resulting from the formation of stable lead-metal complexes. HM's based on $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ matrix demonstrated less stability because in this case the reaction of formation of lead organic complex proceeded slowly and there was a need in heating or prolonged exposure under air.

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