ORGANO-INORGANIC LUMINESCENT HYBRID MATERIALS BASED ON LEAD FLUORIDE AND ORGANIC PHOSPHORS

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***Abstract* — Hybrid organo-inorganic materials were prepared by solid-phase synthesis and by co-precipitation from aqueous solutions with phosphors — 8-hydroxyquinolates and diketonates of metals with hydrofluoric acid and ammonium fluoride. The photoluminescence spectra of the obtained hybrid materials were analyzed. A comparison was made with the spectral-luminescent properties of previously obtained hybrid materials by the melt technique using low-melting lead oxyfluoride glasses.**

Keywords— hybrid materials, lead fluoride, luminescence, co-precipitation

I. INTRODUCTION

Hybrid materials (HM) are widely used in new devices of passive, active and integrated optics and photonics [1-3]. Luminescent HM's based on organic phosphors the 8-hydroxyquinolates of metals of groups I, II and III of the Periodic Table [2] and β-diketonates of rare-earth metals [3], obtained as a result of a high-temperature exchange reaction in PbF_2-consist fluoroborate glass melt, have a wide smooth photoluminescence (PL) spectrum covering almost the entire visible range chromaticity coordinates close to white. The resistance of HM's to UV exposure, air, water vapor, heating [4] allows us to consider them as promising materials for light sources with high color reproduction. However, during melt synthesis, more than half of the introduced organic components have undergone thermal destruction, therefore, the actual task is the synthesis of HM's under "soft" conditions.

II. METHODOLOGY

As organic constituents, we used highly efficient phosphors: β-diketone complex of Eu, 8-hydroxyquinoline complexes with metals I II and III group of the Periodic Table, and individual organic ligand (Table 1).

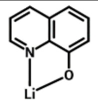
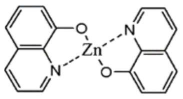
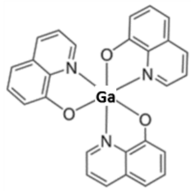
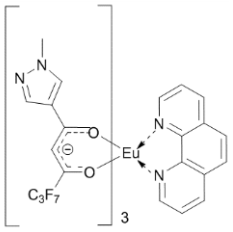
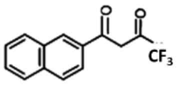
We synthesized HM's in the PbF_2 matrix both by the solid-phase technique (using high-pury PbF_2) and by co-precipitation from aqueous solutions (40 wt% aqueous hydrofluoric acid or 40 wt% ammonium fluoride solution and solutions of phosphors in ethanol). First of all, we prepared a solution of lead nitrates in bidistilled water and a solution of phosphors in ethanol (powders of phosphors, except for $Eu(L^1)_3Phen$, dissolved quite difficult), then mixed the solutions and dropwise added the mixture into a solution of hydrofluoric acid with continuous stirring by a magnetic stirrer [3-6].

In the process of synthesis by co-precipitation from aqueous solutions, an insoluble precipitate is formed by the following chemical reactions [5-7]:

$$Pb(NO_3)_2 + 2HF = PbF_2\downarrow + 2HNO_3 \quad (1),$$

$$Pb(NO_3)_2 + 2NH_4F = PbF_2\downarrow + 2NH_4NO_3 \quad (2).$$

TABLE I. ORGANIC COMPONENT OF HM

Name	Nomination	Chemical formula and Structure
8-hydroxyquinoline lithium	Liq	 $Li(C_9H_4ON)$
Bis (8-hydroxyquinoline) zinc	Znq_2	 $Zn(C_9H_4ON)_2$
Tris (8-hydroxyquinoline) gallium	Gaq_3	 $Ga(C_9H_4ON)_3$
4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-1-(1-methyl-1H-pyrazol-4-yl) nonane-1,3-dione -(1,10-phenanthroline) europium (III)	$Eu(L^1)_3Phen$	 $C_{54}H_{37}EuF_{39}N_2O_6$
4,4,4-trifluoro-1- (2-naphthyl) butane-1,3-dione	NTA	 $C_{14}H_8O_2F_3$

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The obtained precipitate was decanted, washed with bidistilled water to achieve a negative reaction of diphenylamine on nitrate ions, and dried in air at 40– 50°C.

To obtain HM's by the solid phase synthesis, Liq was used as the organic component and α-PbF_2 low-temperature modification formed the inorganic matrix. A mixture of powders, where 99 wt% PbF_2 and 1 wt% Liq were thoroughly milled in a mortar for at least 10 minutes until a homogeneous mixture of yellowish powders was obtained. Three samples were calcined at 200 °C, 300 °C, and 400 °C during 4 hours in a resistance furnace. Before annealing, fluoroplastic plates were placed in the furnace to create a fluorinating atmosphere. The annealed samples were white (grayish) powders. The absence of yellow color indicated that the powders were free from lead oxide and Liq.

Elemental analysis was performed on a JSM-5910- LV setup, which combined the functions of a scanning electron microscope and an X-ray spectral microanalyzer.

X-ray diffraction (XRD) analysis was performed with a D2 Phaser (Bruker AXS Ltd.) diffractometer (CuKα radiation, λ = 1.54060 Å) within the range of 2Θ angles from 10° to 70° with a scan step of 0.01° and an exposure of 2 s/step. The data were accumulated and processed with EVA and TOPAS (v. 4.2) software.

The luminescence spectra were measured at room temperature on a Fluorolog 3D (Horiba Jobin Yvon) spectrofluorimeter within a wavelength range of 550– 750 nm with a step of 0.1 nm under excitation by a pulsed diode laser (λ = 370 nm).

III. RESULTS AND DISCUSSION

When producing HM by the co-precipitation technique of hydrofluoric acid, powders of different phase composition and morphology were obtained depending on the organic component introduced (Fig. 2a).

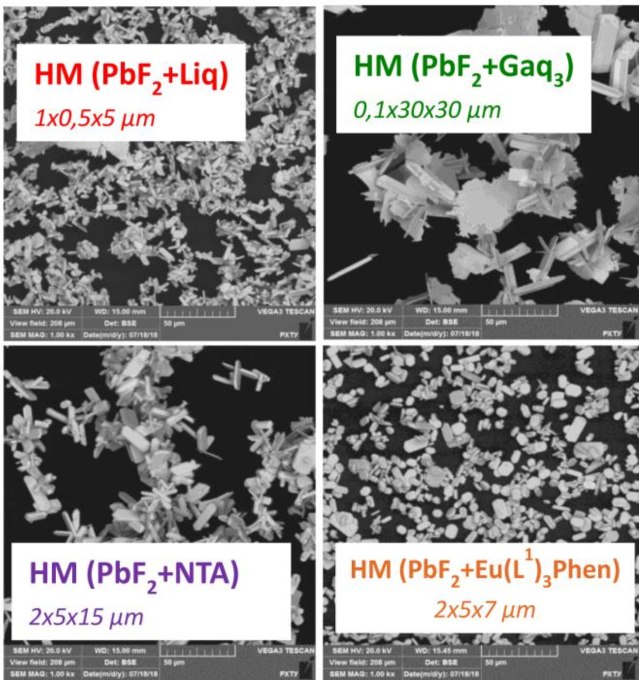

Fig. 1. SEM images of the HM based on PbF_2 powders obtained by coprecipitation with hydrofluoric acid.

In the case of poorly soluble in ethanol Liq, Gaq_3, NTA phosphors the formation of rhombic α-PbF_2 was observed similar to the deposition of nominally pure PbF_2 [7]. During the co-precipitation of the highly soluble compound $Eu(L^1)_3Phen$, an unknown phase was obtained, which is most likely a complex of lead oxohydrate. The crystallites had a size of several microns, their shape changed from plates to elongated flat scales (Fig. 1).

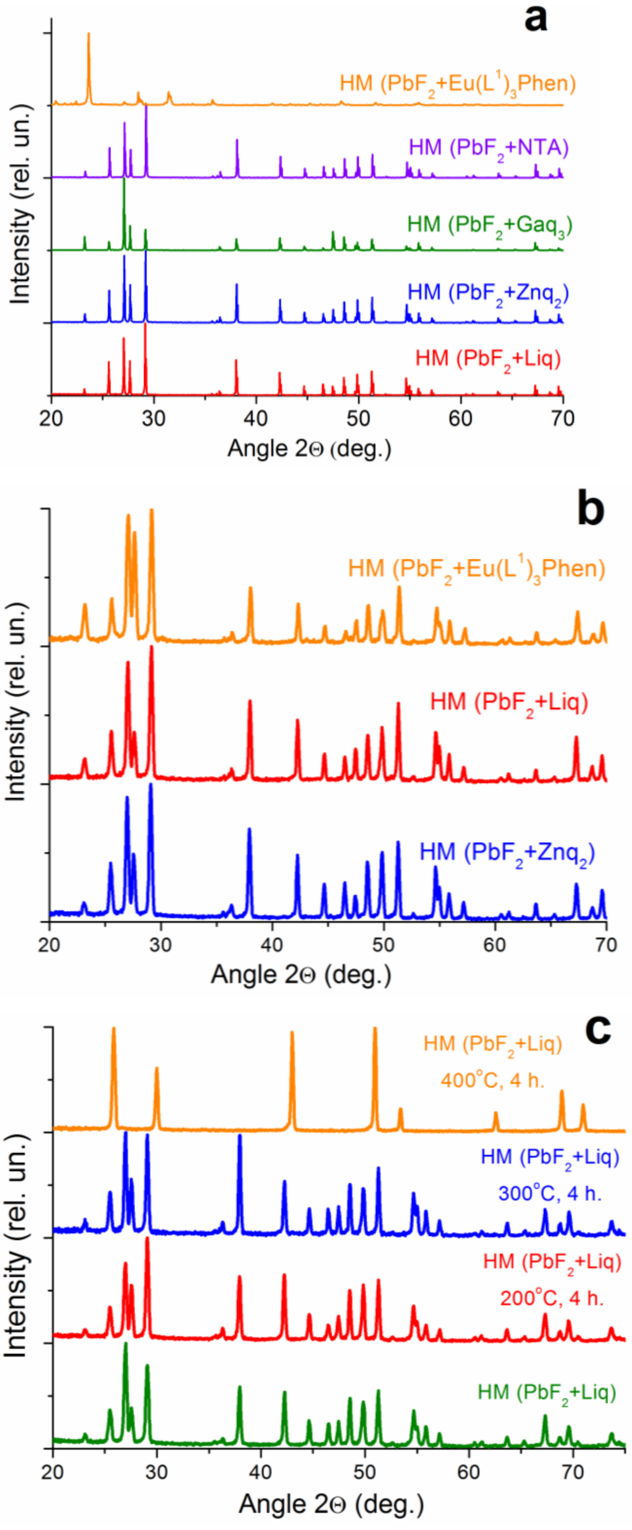

Fig. 2. X-ray diffraction patterns of HM's based on PbF_2-matrices:
a) coprecipitation from aqueous solutions by hydrofluoric acid;
b) coprecipitation from aqueous solutions by ammonium fluoride;
c) solid phase synthesis HM (PbF_2+Liq) at different temperatures.

The structure of HM powders obtained by co-precipitation of ammonium fluoride with all the phosphors correspond corresponded to the low-temperature α-PbF_2 phase (Fig. 2b). Particle size was more than few microns.

HM obtained by the solid-phase synthesis without calcination and after calcination at 200-300 °C corresponded to the α-PbF_2, and calcined at 400 °C corresponded high-temperature cubic phase β-PbF_2 (Fig. 2c), which was consistent with the data on the phase transition α-PbF_2→β-PbF_2 at 365 °C.

On the PL spectra of HM's (Fig. 3), it is seen that the synthesis from solutions (i.e. at low temperature) results to the same emitting centers as the high-temperature synthesis. The completeness of the synthesis for different phosphors differs. For Liq, the synthesis did not proceed completely, it is clear that the luminescence band is composite and contains two bands – close to the original phosphor (λ^{max} = 450 nm) and close to the high-temperature HM (λ^{max} = 500 nm). The difference we associate with the different solubility of organometallic phosphors and different kinetic parameters of exchange reactions resulting to the formation of Pb-complexes [8-9]:

in glass melt:

$$2\ \mathrm{Liq} + (PbF_2\text{-}B_2O_3)_{glass} \rightarrow (PbF_2\text{-}Li_2O\text{-}B_2O_3)_{glass} + [PbqF]_2 \qquad (3),$$

in solutions:

$$2\ \mathrm{Liq} + 3\ Pb(NO_3)_2 + 4\ HF \rightarrow PbF_2 + [PbqF]_2 + 2\ LiNO_3 + 4\ HNO_3 \qquad (4),$$

$$2\ \mathrm{Liq} + 3\ Pb(NO_3)_2 + 4\ NH_4F \rightarrow PbF_2 + [PbqF]_2 + 2\ LiNO_3 + 4\ NH_3\uparrow + 4\ HNO_3 \qquad (5),$$

$$Eu(L^1)_3Phen + 2\ Pb(NO_3)_2 + 5\ HF \rightarrow PbF_2 + EuF_3 + Pb(L^1)_2Phen + 4\ HNO_3 \qquad (6),$$

$$Eu(L^1)_3Phen + 2\ Pb(NO_3)_2 + 5\ NH_4F \rightarrow PbF_2 + EuF_3 + Pb(L^1)_2Phen + 5\ NH_3\uparrow + 4\ HNO_3 \qquad (7).$$

Investigation of the photoluminescence (PL) spectra showed that the luminescent properties of the HM's obtained by co-precipitation from aqueous solutions of NH_4F are more similar to that of the HM's obtained by the glass melt technique than those obtained by co-precipitation of HF (Fig. 3a, b). This can be explained by more complete proceeding of the exchange reactions under given pH.

In all spectra of HM's based on $Eu(L^1)_3Phen$, except for the broad luminescence band, one can see narrow lines corresponding to transitions in the Eu^{3+} ion (Fig. 3b). According to the characteristics of these lines, it can be argued that, in the HM's, the Eu^{3+} ion is located in the inorganic environment of fairly high symmetry, which confirms proceeding of the exchange reactions.

In solid-phase synthesis of HM's, the exchange reaction starts even with grinding of Liq and PbF_2 powders (Fig. 3c), however, a noticeable reaction occurs at 300 °C.

At 400 °C, the spectrum of the HM almost corresponds to the spectrum of HM produced by the glass-melt technique. Thus, it can be argued that the reaction

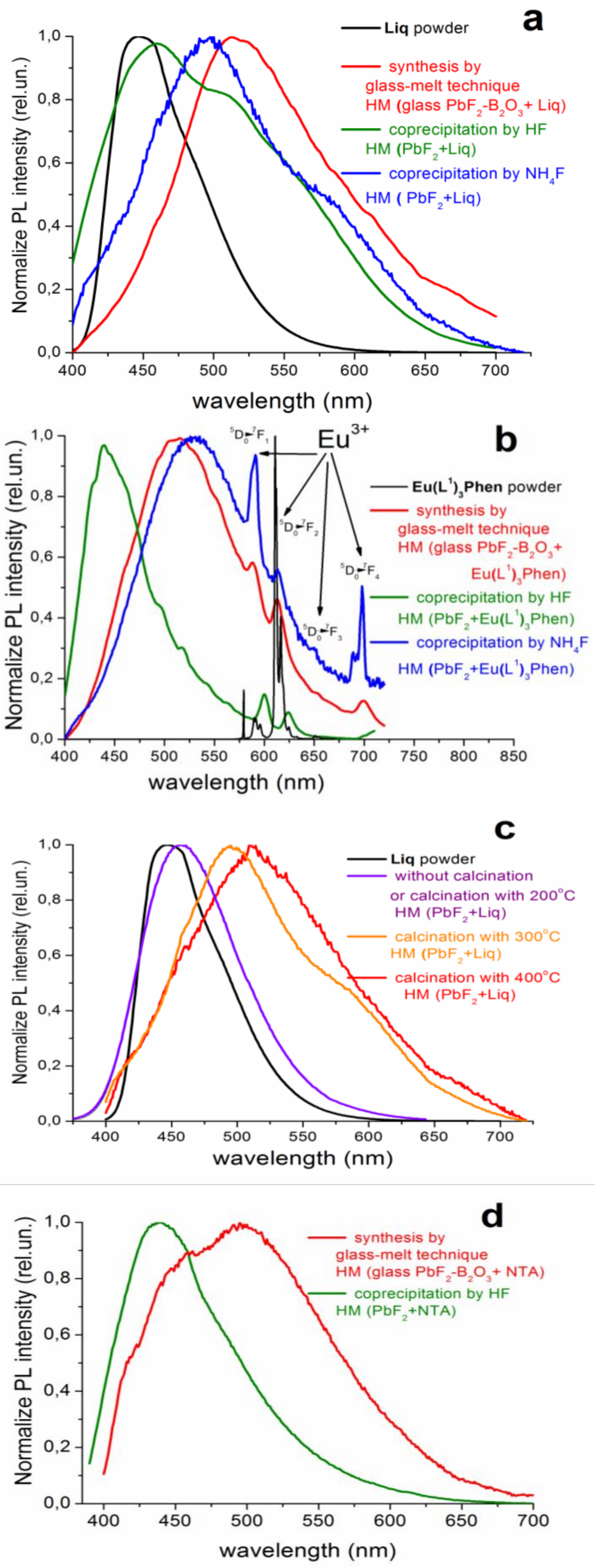

Fig. 3. The PL spectra of powdered phosphors and HM based on PbF_2-containing matrices (λ^{ex} = 370 nm): (a), (c) based Liq, (b) based $Eu(L^1)_3Phen$; (d) based NTA.

$$2\,\mathrm{Liq} + \mathrm{PbF_2} \rightarrow [\mathrm{PbqF}]_2 + 2\,\mathrm{LiF} \qquad (8).$$

can take place in the solid phase.

IV. CONCLUSIONS

New luminescent materials based on metal-organic and organic components and lead fluoride were obtained. It is shown that optical centers characteristics of lead luminescent complexes are formed both in glass melts and during the co-precipitation from solutions and during the solid-phase synthesis. When the co-precipitating from aqueous solutions with ammonium fluoride is used the reaction of formation of luminescent lead complexes proceeds more completely than during the co-precipitation with hydrofluoric acid.

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