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Luminescent hybrid materials based on organic phosphors and fluorides in the PbF₂-LaF₃ system

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Abstract. Powder hybrid materials based on 8-hydroxyquinolate lithium organic phosphor and - LaF₃ inorganic fluoride matrix PbF₂ have been synthesized. Hybrid materials were obtained by co-precipitation from aqueous-alcoholic solutions with ammonium fluoride under various conditions - different concentrations of precursor solutions, Pb/La ratio, and the siquensy of reagents' mixing. All obtained hybrid materials showed effective broadband luminescence in the region of 390-500 nm. The photoluminescence intensity during reverse deposition was found to be higher than during direct deposition for different concentrations of reagents.

1. Introduction

Hybrid materials (HM) combine organic and inorganic components at the molecular level [1]. When classifying HM according to the «host-guest» type [2], two main classes of hybrid systems are distinguished: inorgano-organic (inorganic clusters or nanoparticles embedded in the organic matrix of a macromolecular polymer), and organo-inorganic (organic molecules or macromolecules are embedded in an inorganic matrix).

Organo-inorganic HMs have a number of advantages as materials for photonics [3], including luminescent materials, namely, the ability to include a large number of emitting centers; uniform distribution of optical centers in the material; transferring energy from a matrix to emitting centers due to the formation of new chemical bonds; variation of optical and mechanical properties; creation of different shapes and textures in the HM depending on the intended application.

Analysis of HMs luminescence properties showed that the solution synthesis (i.e., at temperatures no higher than 50 °C) produced the same emitting centers as the high-temperature synthesis (solidphase synthsis and low-melting glass synthesis). The formation of optical centers occurs as a result of an exchange reaction and formation of new bonds between lead and organic ligands. However, the degree of decay of organic components in solution synthesis is 1.5-2 times lower comparing with a solid-phase synthesis, and 5-7 times lower than in a melt synthesis. A low-temperature synthesis follows by two mechanisms - by capture of whole molecules of organic phosphor from solution and by an exchange reaction.

It is well known that fluorides are more stable than oxides. So, in the research we used a complex fluoride system of PbF₂-REF₃ as an inorganic matrix for HMs. HMs based on PbF₂-containing matrices were synthesized by various methods: melting synthsis in low-melting glasses [4-6], solid-

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phase synthesis [7], vacuum deposition of films with laser activation [8] and co-precipitation technique [9].

The metal complex of 8-hydroxyquinoline lithium (Liq) was chosen as an organic luminescent component. This phosphor has an intense blue luminescence with a maximum at λ =447-450 nm. During HM sysnthesis bis-(8-hydroxyquinoline) lead (Pbq₂), halogen-substituted dimer complexes [PbqF]₂, [PbqI]₂, Laq₃, and halogen-substituted complexes La(Clq)₃ could be formed. But their green luminescence with maxima about λ =500-505 nm for Pbq₂ [10], 520 nm for Laq₃ [11] and 515 nm for La(Clq)₃ [12] is far away form Liq luminescence. Thus, we can use luminescence analysis to separate the optical centers of trapped Liq molecules and lead and lanthanum complexes and to estimate the completeness of the exchange reaction at HM synthesis.

The crystal structure of HMs obtained by co-precipitation corresponds to the low-temperature rhombic modification of α -PbF₂ (space group *Pnma*, contunite type), which is similar to the case with the deposition of nominally pure PbF₂ from solution [13]. Solid-phase synthesis allows obtaining both a low-temperature α -PbF₂ and a high-temperature cubic β -PbF₂ (space group *Fm3m*, fluorite type). The stabilization of the cubic phase during the low-temperature synthesis is possible by doping PbF₂ with a rare-earth dopant [14] with the formation of Pb_{1-x}RE_xF_{2+x}. solid solution of the cubic fluorite type. This resulted to the formation of luminescent materials [15]. So, in the present study we tried to understand the influence of PbF₂ crystal structure on luminescent properties of HMs in the PbF₂-REF₃-Liq system. In order the REs luminescence did not interfere with the HMs luminescence we used La which had not have intrinsic *f*-*f* transitions and did not generate luminescence.

2. Materials and experiments

The synthesis was carried out by co-precipitation from aqueous solutions [6, 9, 13, 16]. The starting materials were lead nitrate $Pb(NO_3)_2$ (99.99 wt%, Khimmed Group), lanthanum nitrate $La(NO)_3 \times 6H_2O$ (99.99 wt%, LANHIT Ltd.), ammonium fluoride NH₄F (TECH System Ltd.). Ethanol and lithium 8-hydroxyquinolate were addinionally purified to 99.999 wt%.

8-hydroxyquinolate lithium (Liq) was dissolved in ethanol to obtain a saturated solution and then mixed with an aqueous solution of lead and lanthanum nitrates ($C_1 = 1.43$ M or $C_2 = 0.8$ M). The nominal content of lanthanum in the nitrate solution corresponded to 10, 15, 20, and 25 mol%. An aqueous solution of nitrates was added to Liq solution in such proportions as to provide the 99:1 ratio (by weight) of the mixed fluoride $Pb_{1-x}La_xF_{2+x}$ to Liq. Then, precipitation of the final product was carried out using a tenfold excess of 15% aqueous solution of ammonium fluoride as a fluorinating agent. The precipitation was conducted in a polypropylene reactor with constant stirring by a magnetic stirrer for one hour. The deposition rate was 10 ml/min. To provide a local excess of nitrate or fluorinating agent during the synthesis we used various orders of mixing of the reagents, namely, a «direct precipitation» (dropwise addition of ammonium fluoride solution to the solution obtained at the first stage of synthesis with constant stirring) and a «reverse precipitation» (dropwise addition solution obtained in the first stage of the synthesis to a solution of ammonium fluoride with constant stirring).

The precipitation of an insoluble precipitate proceeded according to the following reaction (1):

$$\begin{array}{c} (2-x)Pb(NO_3)_2 + xLa(NO_3)_3 + (2+x)NH_4F + 2Liq \rightarrow \\ Pb_{1-x}La_xF_{2+x}\downarrow + Pbq_2\downarrow + (2+x)NH_4NO_3 + 2LiNO_3 \ (1) \end{array}$$

A produced suspension was separated from the liquid phase and washed with 3% solution of ammonium fluoride until a negative reaction with diphenylamine for nitrate ions was occurred. Then the powder was dried at 40-50 °C. For the synthesis procedure we used polypropylene reactors, separating funnels and beakers. Combinations of synthesis conditions and concentrations are presented in Table. 1.

The crystal structure of the obtained samples was analyzed by the X-ray diffraction technique (XRD) using an Equinox 2000 X-ray diffractometer (CuK_{α} radiation, $\lambda = 1.54060$ Å).

The photoluminescence (PL) spectra were studied in 400-700 nm spectral range using a Fluorolog FL-22 spectrofluorimeter (Horiba Jobin Yvon) with double monochromatores for emission and excitation. A a wavelength of 370 nm was used for PL excitation (Xenon 450W Ushio UXL-450S/O lamp). The measuremets were carried out at room temperature.

Notation	Nominal concentration	Precipitation	Nitrates solution	
	$La^{3+}(x)$ in $Pb_{1-x}La_xF_{2+x}$	order	concentration	
	mol.%			
Pb-10La-1Liq_0.8_Dir	10	Direct	0.8M	
Pb-10La-1Liq_0.8_Rev	10	Reverse	0.8M	
Pb-10La-1Liq_1.43_Dir	10	Direct	1.43M	
Pb-10La-1Liq_1.43_Rev	10	Reverse	1.43M	
Pb-15La-1Liq_0.8_Dir	15	Direct	0.8M	
Pb-15La-1Liq_0.8_Rev	15	Reverse	0.8M	
Pb-15La-1Liq_1.43_Dir	15	Direct	1.43M	
Pb-15La-1Liq_1.43_Rev	15	Reverse	1.43M	
Pb-20La-1Liq_0.8_Dir	20	Direct	0.8M	
Pb-20La-1Liq_0.8_Rev	20	Reverse	0.8M	
Pb-20La-1Liq_1.43_Dir	20	Direct	1.43M	
Pb-20La-1Liq_1.43_Rev	20	Reverse	1.43M	
Pb-25La-1Liq_0.8_Dir	25	Direct	0.8M	
Pb-25La-1Liq_0.8_Rev	25	Reverse	0.8M	
Pb-25La-1Liq_1.43_Dir	25	Direct	1.43M	
Pb-25La-1Liq_1.43_Rev	25	Reverse	1.43M	

Table 1. Notations and synthesis parameters for the samples in (PbF₂+LaF₃+Liq) system.

3. Results and discussions

In the (PbF_2+LaF_3+Liq) system, samples with a nominal relative La content of 15, 20, and 25 mol.% were synthesized by co-precipitation. The resulting powders were analyzed by XRD (Fig. 1).

It is important to note that when powders are obtained by the co-precipitation, the process is far from equilibrium, and the order in which the reagents are fed can affect the phase composition. Direct deposition promotes the formation of a cubic solid solution $Pb_{1-x}La_xF_{2+x}$. At a high concentration of nitrate solution (1.43 M), even at a nominal LaF₃ content of 10 mol%, the phase of a cubic solid solution crystallizes mainly. During the direct co-precipitation only the $Pb_{1-x}La_xF_{2+x}$ phase crystallizes at the nominal LaF₃ content of 15 mol%. During the reverse co-precipitation a mixture of two phases of α -PbF₂ and a phase of a cubic solid solution crystallize. The rhombic phase α -PbF₂ remains during the reverse co-precipitation at the nominal LaF₃ content of 20 and 25 mol%.

In the case of the reverse co-precipitation we obtained the higher yield of α -PbF₂, due to a significant excess of NH₄F during the entire process, which reduces the solubility of lead fluoride. In the case of the direct co-precipitation, a high concentration of metal cations is formed at the beginning of the process, which contributes to the formation of the Pb_{1-x}La_xF_{2+x} cubic solid solution.

The calculated parameters of the crystal lattices of α -PbF₂ for all samples were close to the literature data. For the Pb_{1-x}La_xF_{2+x} cubic solid solutions *a* ranged from 5.894 to 5.95 Å (Table 2), while the reference lattice parameter for pure β -PbF₂ is *a* = 5.94 Å [17].

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Figure 1. X-ray diffractograms of HM (Pb-La-Liq) system: $\blacksquare -\beta$ -PbF₂(*Fm*3*m*), $\blacklozenge -\alpha$ -PbF₂ (*Pnma*).

Table 2	The detected p	hases and	their lattic	e parameters	for HMs	obtained by	different	variants	of the
co-preci	pitation technic	jue.							

Direct co-precipitation		Reverse co-precipitation		
Sample	Detected phases and their lattice parameters, Å	Sample	Detected phases and their lattice parameters, Å	
Pb-10La-1Liq_0.8_Dir	α-PbF ₂ <i>a</i> =6.440, <i>b</i> =3.899, <i>c</i> =7.651 β-PbF ₂ <i>a</i> =5.935	Pb-10La-1Liq_0.8_Rev	α-PbF ₂ <i>a</i> =6.440, <i>b</i> =3.899, <i>c</i> =7.651 β-PbF ₂ <i>a</i> =5.947	
Pb-10La- 1Liq_1.43_Dir	a-PbF ₂ <i>a</i> =6.440. <i>b</i> =3.899, <i>c</i> =7.651 β-PbF ₂ <i>a</i> =5.950	Pb-10La-1Liq_1.43_Rev	α-PbF₂ <i>a</i> =6.440, <i>b</i> =3.899, <i>c</i> =7.651 β-PbF₂ <i>a</i> =5.942	
Pb-15La-1Liq_0.8_Dir	β-PbF ₂ <i>a</i> =5.914	Pb-15La-1Liq_0.8_Rev	α-PbF ₂ <i>a</i> =6.442, <i>b</i> =3.899, <i>c</i> =7.650 β-PbF ₂ <i>a</i> =5.930	
Pb-15La- 1Liq_1.43_Dir	β-PbF ₂ <i>a</i> =5.932	Pb-15La-1Liq_1.43_Rev	α-PbF ₂ <i>a</i> =6.442, <i>b</i> =3.899, <i>c</i> =7.650 β-PbF ₂ <i>a</i> =5.925	
Pb-20La-1Liq_0.8_Dir	β-PbF ₂ <i>a</i> =5.928	Pb-20La-1Liq_0.8_Rev	β-PbF ₂ <i>a</i> =5.933	
Pb-20La- 1Liq_1.43_Dir	β-PbF ₂ <i>a</i> =5.933	Pb-20La-1Liq_1.43_Rev	β-PbF ₂ <i>a</i> =5.932	
Pb-25La-1Liq_0.8_Dir	β-PbF ₂ <i>a</i> =5.899	Pb-25La-1Liq_0.8_Rev	β-PbF ₂ <i>a</i> =5.931	
Pb-25La- 1Liq_1.43_Dir	β-PbF ₂ <i>a</i> =5.910	Pb-25La-1Liq_1.43_Rev	β-PbF ₂ <i>a</i> =5.894	

Nonstoichiometric $Pb_{1-x}R_xF_{2+x}$ cubic fluoride phases were based on the high-temperature β -PbF₂ phase. The lattice parameter for these solid solutions obeys a linear equation (Vegard's law):

$$a = 5.940 + kx,$$
 (2)

where 5.940 Å is a lattice parameter of β -PbF₂, x is the molar percentage of RE, k is the coefficient.

For La, the *k* according to the data of different authors, can be both positive k = +0.000031 [17], and negative k = -0.00025 [18]. In any case *kx* value is smaller the experimental error of determination of the lattice parameter in our experiments. So, we failed to determine the La content in the solid solution by XRD technique. In this case the difference in the experimental values of *a* might be associated with the nonequilibrium of the obtained samples.

Investigations of the HM photoluminescence (PL) showed that all samples demonstrated intense blue PL with a maximum of 420-440 nm. The PL intensity increases with an increase in the nominal lanthanum content, at equal concentrations during the reverse deposition (Fig. 2).



Figure 2. Luminescence spectra HM (PbF₂-25LaF₃-1Liq). $\lambda^{exc} = 370$ nm.

We estimated Liq content in HMs by the measurement of Li concentration by ICP-MS (see Ref.[19] for details). In the case of the reverse co-precipitation Li content was a little higher comparing to the direct co-precipitation. But we failed to find the correlation between Li concentration in HMs and PL intensity. It means that the formation of HM for the system under study is more complex than a simple exchange reaction (1).

Comparison of the normalized PL spectra of HM and the initial Liq powder preparation (Fig. 3) showed that the HM spectra are noticeably shifted to shorter wavelengths relative to the initial Liq.

The long-wavelength component of the spectrum with a maximum in the region of 520-530 nm is present, but has a lower intensity than the short-wavelength one. The short-wavelength component is obviously not associated with the Laq₃, Pbq₂ and [PbqF]₂ centers, which luminesce in the longer-wavelength region than Liq. Also, the center cannot be due to specific bonds in the cubic phase of PbF₂ [7]. The center can have a complex structure including Pb and La.

A weak short-wavelength PL component is observed when HMs are obtained by co-precipitation in $(PbF_2 + Liq)$ [19] and $(CaF_2 + Liq)$ [20] systems and it is absent when HMs of the same compositions are obtained by anhydrous methods (melt technique, solid-phase synthesis). It can be assumed that this short-wavelength component is associated with the formation of hydrated metal complexes. Such complexes can exhibit a more intense PL, shifted to the short wavelength region, as compared to non-hydrated analogs [21, 22].

The PL intensity of the best HMs in the $(PbF_2 + LaF_3 + Liq)$ system turned out to be higher than in the $(PbF_2 + Liq)$ [19] and $(LaF_3 + Liq)$ [23] systems, which, in combination with a very short-wavelength spectrum, seems promising for different applications.

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Figure 3. Normalized luminescence spectra of HM (PbF₂-25LaF₃-1Liq) in comparison with the initial Liq. $\lambda^{\text{exc}} = 370$ nm.

4. Conclusions

New luminescent organic-inorganic hybrid materials in the ($PbF_2 + LaF_3 + Liq$) system were obtained by coprecipitation of their aqueous-alcoholic solutions. It has been shown that single-phase HM powders of a cubic structure can be obtained at nominal lanthanum concentrations of more than 15 mol% with direct deposition and more than 20 mol% with reverse deposition. HM exhibit intense luminescence in the region of 390-500 nm with a maximum of 420-440 nm. The most intense luminescence is observed in HM with a nominal lanthanum content of 25 mol%, obtained by reverse precipitation from a solution of inisial nitrates with a concentration of 1.43 M.

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Authorship contribution statement

P Strekalov: Methodology, Investigation, Formal analysis; K Runina: Investigation, Data curation, Resources; M Mayakova: Investigation, Funding acquisition; O Petrova: Investigation, Data curation, Supervision, Writing – original draft; I Avetissov: Validation, Visualization, Conceptualization, Writing – review & editing.

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