

New Fluorescent Hybrid Materials Based on Eu-Complexes in Oxyfluoride Glass and Glass-Ceramic Matrix

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Received 09 December 2015; accepted 22 February 2016

Abstract

Hybrid materials were synthesized using a high temperature reaction. We used $80\text{PbF}_2-20\text{B}_2\text{O}_3$ glass as an inorganic matrix and various phenanthroline complexes europium(III) – as organic phosphors. The photoluminescence spectra of hybrid materials were measured just after synthesis and after heat treatment. We suggested that an exchange reaction between a Eu-complex and a glass matrix had occurred.

Keywords

hybrid materials, photoluminescence, europium coordination compounds

1 Introduction

Hybrid materials (HM) based on metal-organic phosphors and inorganic glasses are promising materials for developing new light emitting devices [1-3]. Organic luminescent materials are highly efficient under optical and electric excitation. However, most of them are extremely unstable in air and need protection. The embedding of organic materials into transparent matrices may solve the degradation problem and lead to the manufacturing of new materials. Inorganic glass matrices are stable at higher temperatures than organic polymers, lacquers and compounds and their thermal expansion coefficients are less than those of organic matrices. In general, glasses are characterized by a high hardness and chemical resistance, as well as a resistance to radiation, especially UV.

In our previous research concerning on the fabrication of bulk and film hybrid materials, we considered boron oxide [2-3] as a glass matrix. However, boron oxide is not an ideal candidate for application as a glass matrix: its melt viscosity at 400–500 °C is very high ($\sim 2 \times 10^4$ Pa*s), and its chemical resistance is insufficient. We made glasses in the $\text{PbF}_2-\text{B}_2\text{O}_3$ system in the 25-80 mol% PbF_2 composition range [4-5]. These glasses have lower melting temperatures and viscosity index. Our latter research dealt with HM based on $\text{PbF}_2-\text{B}_2\text{O}_3$ glass and $\text{Eu}(\text{NTA})_3(\text{Phen})$ [6] demonstrated a possibility to fabricate transparent and stable glassy HM's.

2 Experimental

Different methods of preparation of europium (III) complexes have been described [7-8]. Syntheses of organic ligands were carried out according to a slightly modified procedure [9-10] using dichloromethane as a solvent.

The glasses were synthesized in 10 g batches using PbF_2 , B_2O_3 , and EuF_3 as initial materials (99.99 wt% purity grade for all). Syntheses were conducted at 850–900 °C during 0.25 to 0.5 h in closed corundum crucibles. The melt was casted into a steel mold. To compare HM's properties, we synthesized the 79 $\text{PbF}_2-20 \text{B}_2\text{O}_3-1 \text{EuF}_3$ glass as a standard. During the synthesis up to 50 % of the fluorine volatilized from the melt and up to the 10 wt% of aluminum oxide had been dissolving in glass.

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The HM's were synthesized using a high temperature fast rate reaction. Formerly prepared $80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3$ glass was melted at $800\text{-}850\text{ }^\circ\text{C}$ then cooled down to $600\text{ }^\circ\text{C}$. Afterwards we added $0.1\text{ - }0.15\text{ wt\%}$ organo-metallic phosphors and the system were stirring during 30 seconds. The samples were obtained by a rapid casting into a steel mold. The produced HM's looked like transparent yellowish glassy plates without visible bubbles and trace inclusions.

A heat treatment of samples was performed in several temperature-time regimes at temperatures above T_g and various durations from 0.5 to 4 h.

A Fluorolog FL3-22 spectrofluorimeter (Horiba Jobin Yvon) with double-grating excitation and emission monochromators was used for luminescence measurements of the inorganic glass, organic phosphors Eu(III) complexes, the as-synthesized HM's and the HM's after the heat treatment (the wavelength range from 400 to 700 nm with the 0.1 nm step). PL was excited by a Xenon 450W Ushio UXL-450S/O lamp ($\lambda = 370\text{ nm}$) or a pulsed diode laser ($\lambda = 370\text{ nm}$, $\Delta\tau = 1.5\text{ ns}$, with 100 kHz). The latter was used for photoluminescence decay kinetics measurements. All of the luminescence measurements were carried out at room temperature.

3 Results and discussion

To produce HM's we used different asymmetric Eu(III) phenanthroline complexes, as organic phosphors (Table 1).

Photoluminescence (PL) spectra of Eu-complexes demonstrated narrow lines in the red spectrum range with maximum at $\lambda = 611\text{ nm}$ corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition in Eu^{3+} ion (Fig. 1).

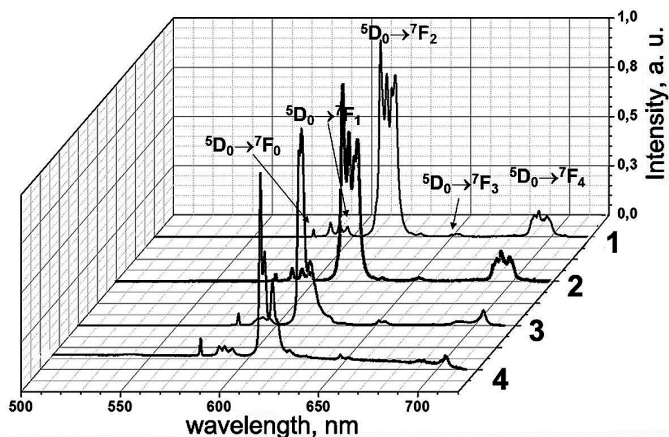


Fig. 1 PL spectra of pure crystalline powder Eu(III) complexes (numbers correspond to the sample numbers in Table 1)

Table 1 Structures and abbreviation of metal-organic phosphors

N	Phosphor	Abbreviation	Structures of complexes
1	4,4,5,5,6,6,7,7,8,8,9,9-tridecafluoro-1-(1-methyl-1H-pyrazol-4-yl)nonane-1,3-dionato-(1,10-phenanthroline) europium	$\text{Eu}(\text{L}^2)_3(\text{Phen})$	
2	4,4,5,5,6,6,6-heptafluoro-1-(1-methyl-1H-pyrazol-4-yl)hexane-1,3-dionato-(1,10-phenanthroline) europium	$\text{Eu}(\text{L}^1)_3(\text{Phen})$	
3	Tris(4,4,4-trifluoro-1-(2-naphthyl) butane-1,3-dionato-(4,7-diphenyl-1,10-phenanthroline) europium	$\text{Eu}(\text{NTA})_3(\text{Bath})$	
4	Tris(4,4,4-trifluoro-1-(2-naphthyl) butane-1,3-dionato-(1,10-phenanthroline) europium	$\text{Eu}(\text{NTA})_3(\text{Phen})$	

All the obtained complexes contained Eu^{3+} ion in an asymmetric position. This resulted to the higher PL intensity of a hypersensitive electron-dipole ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition in contrast with a ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition. The ratio of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2/{}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition intensities was as high as 20-30. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ band was not splitted which proved a phase purity of the analyzed complexes [11].

An easy melting $80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3$ glass was used as a glassy matrix for HM's creation. It is proved that the phosphor powders have the brightest luminescence lines. In the cases of the glass and HM's PL lines are significantly broadened comparing with powder phosphors. The broadening is attributed to a formation of several luminescence centers with similar structures. HMs exhibited PL with varying intensities in the range of emission colours from red to green. The PL spectra of the HM's based on pirazyl-containing Eu-complexes (Fig. 2 lines 1, 2) had a distinguished line of Eu^{3+} ion transition ($\lambda_{\text{max}} = 611$ nm), but for the HM's based on a naphthyl ligand (Fig. 2 lines 3, 4), the PL in the short-wave part ($\lambda = 400\text{-}580$ nm) was more intense (Fig. 2).

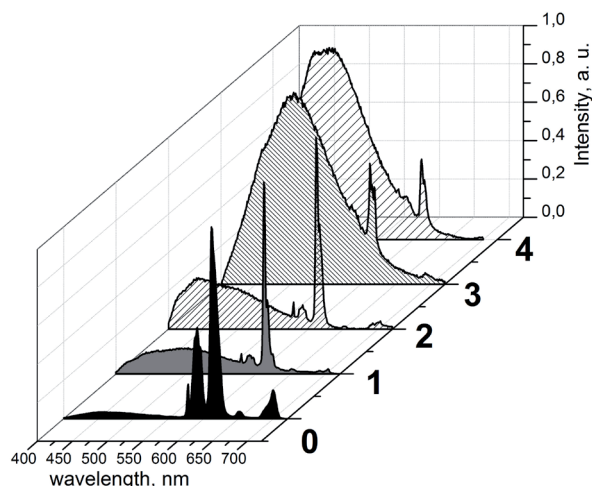


Fig. 2 PL spectra of as-synthesized $79\text{PbF}_2\text{-}20\text{B}_2\text{O}_3\text{-}1\text{EuF}_3$ glass (0) and HM's (1-4) (figures correspond to the sample numbers in Table 2)

Table 2 Structures and abbreviation of metal-organic phosphors

N	Composition	Maximum peak wavelength, nm	Chromaticity coordinates (CIE)
0	$79\text{PbF}_2\text{-}20\text{B}_2\text{O}_3\text{-}1\text{EuF}_3$	612	X=0.5498 Y=0.3427
1	$80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3 + \text{Eu}(\text{L}^2)_3(\text{Phen})$	611	X=0.3476 Y=0.3272
2	$80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3 + \text{Eu}(\text{L}^1)_3(\text{Phen})$	611	X=0.2938 Y=0.2630
3	$80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3 + \text{Eu}(\text{NTA})_3(\text{Bath})$	504	X=0.2592 Y=0.3749
4	$80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3 + \text{Eu}(\text{NTA})_3(\text{Phen})$	480	X=0.2054 Y=0.2769

We have assumed that there is an exchange reaction accompanied by a partial decomposition of the organic complexes. The similar reaction was described in [3] for the HM based on tris(8-hydroxyquinoline) aluminum (Alq_3) with boron oxide.

During the reaction Eu^{3+} ions embedded into a glass matrix and this caused the reduction of the PL intensity to values typical for inorganic glasses doped by Eu^{3+} ion. Simultaneously, the ligands were bonding into complexes with Pb^{2+} ions.

The HM based on the Pb complex demonstrated more intense PL. The Pb complexes with similar ligands had been described in [12-13], but the spectral-luminescent properties of these compounds had not been studied. The Pb-complex formation was confirmed by PL peak's positions which cannot be attributed to transitions between the levels of the individual ligands [14] or Eu^{2+} ion PL in a glass [15].

The PL decay kinetics of the $\text{Eu}(\text{L}^2)_3(\text{Phen})$, when excited by a Xenon 450 W Ushio UXL-450S/O lamp ($\lambda_{\text{exc}} = 355$ nm), was described by two exponents with lifetimes of 105 μs and 223 μs [6], which correlated with the data [16]. However, at the excitation by the pulsed laser ($\Delta\tau = 1.5$ ns) we succeeded in fitting the short lifetime components of the decay kinetics for all studied Eu^{3+} -based materials. The decay kinetics was described by two exponents with lifetimes of approximately 0.2 and 3 μs . The first exponent responsible for the fast decay step agreed with the data [14].

Analysis of the PL decay kinetics of the HM's under study showed that there was no difference in the short lifetime component. But the long lifetime component of PL decay kinetics measured for different Eu^{3+} lines showed that the lifetimes differed more than in two times (Fig. 3): for $\lambda = 612$ nm $\tau = 320$ ms, for $\lambda = 528$ nm $\tau = 134$ ms.

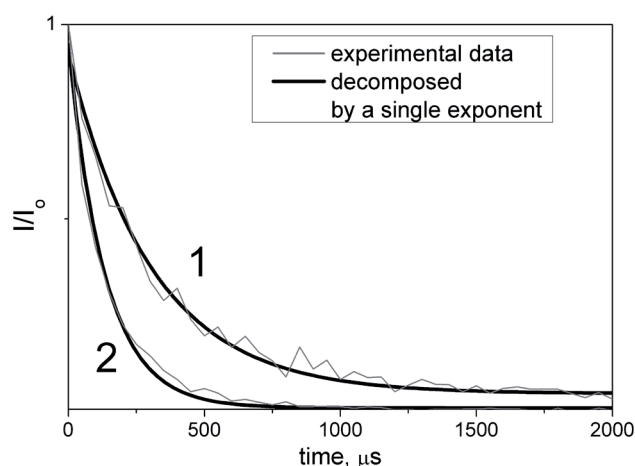


Fig. 3 Decay kinetics of luminescence HM $80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3 + \text{Eu}(\text{NTA})_3(\text{Bath})$: $\lambda_{\text{em}} = 612$ nm (1), $\lambda_{\text{em}} = 528$ nm (2), excited by $\lambda_{\text{exc}} = 370$ nm Xenon 450W Ushio UXL-450S/O lamp

A heat-treatment resulted in a partial crystallization of a glass matrix and changing of a PL spectrum (Fig. 4). We observed the presence of a wide band and changing in the Eu^{3+} ion line position. The latter shifted from 611-612 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) for the case of glass or organic ligands with non-centrosymmetric fields to 580 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$) for the case of cubic crystallites $\text{Pb}_{1-x}\text{Eu}_x\text{F}_{2+x}$ having a centrosymmetric crystalline field.

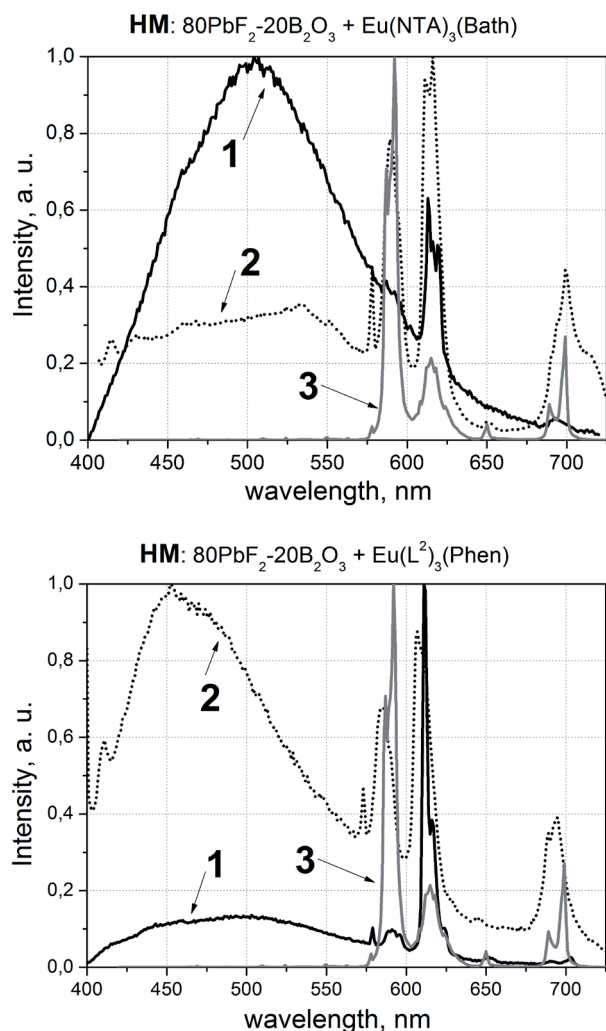


Fig. 4 PL spectra of HM's: 1 – HM as-synthesized, 2 – HM after heat-treatment on 400 °C, 2 h, 3 – polycrystalline $\text{Pb}_{1-x}\text{Eu}_x\text{F}_{2+x}$

Change of the environment and, accordingly, the symmetry of the Eu^{3+} ion can be detected by the monitoring of the ratio of the PL intensities of hypersensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ and the weakly sensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions (Table 3). The Eu environment in the metal complex is non-centrosymmetrical. In the case of HM's the symmetry increased and a still greater increase was observed for partially crystallized HM's. Most likely, this resulted from an intrinsic crystallization of a fluoride cubic phase containing Eu^{3+} ions. This trend confirmed our hypothesis that the Eu^{3+} ions were moving from the organic ligand's field into a glass matrix field and at a further heat treatment they were embedding into a crystalline phase. Ligands bind with glass components and stay in the glass.

Table 3 PL intensities ratio for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions

Luminescent material	The ratio of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition intensities
Phosphor $\text{Eu}(\text{NTA})_3(\text{Bath})$	31.5
HM as-synthesized $80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3$ + $\text{Eu}(\text{NTA})_3(\text{Bath})$	9.3
HM after heat-treatment $80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3$ + $\text{Eu}(\text{NTA})_3(\text{Bath})$	1.6
Phosphor $\text{Eu}(\text{L}^2)_3(\text{Phen})$	20.1
HM as-synthesized $80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3$ + $\text{Eu}(\text{L}^2)_3(\text{Phen})$	10.7
HM after heat-treatment $80\text{PbF}_2\text{-}20\text{B}_2\text{O}_3$ + $\text{Eu}(\text{L}^2)_3(\text{Phen})$	1.3
Glass $79\text{PbF}_2\text{-}20\text{B}_2\text{O}_3\text{-}1\text{EuF}_3$	2.1
Glass after heat-treatment $79\text{PbF}_2\text{-}20\text{B}_2\text{O}_3\text{-}1\text{EuF}_3$	1.6
Polycrystalline $\text{Pb}_{0.95}\text{Eu}_{0.05}\text{F}_{2.05}$	0.2

4 Conclusions

We developed a synthesis technique for new luminescent materials by conducting a high-temperature exchange reaction between an inorganic glass matrix and organic complexes.

This process offers the prospects of developing synthesis methods for novel, highly pure luminescent materials without the use of solvents in a non-oxidizing atmosphere.

Acknowledgement

The research was financially supported by the Russian Science Foundation (grant N 14-13-01074).

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