Luminescent hybrid materials based on an europium organic complex and borate glasses

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ABSTRACT

Hybrid materials (HM) were synthesized by high temperature reactions of inorganic glass matrices with an organometallic phosphor; B_2O_3 and $80PbF_2$–$20B_2O_3$ were used as glassy matrices. The organometallic complex was tris(4,4,4-trifluoro-1-(2-naphthyl) butane-1,3-dionato-(1,10-phenanthroline) europium (III), ($Eu(NTA)_3(Phen)$). The fabricated HMs were shaped as thin glassy plates. The PL spectra of HMs based on fused B_2O_3 contained only the bands corresponding to Eu^{3+} ion transitions and were similar to the spectra of the $Eu(NTA)_3(Phen)$ powder. For the HM made from an unfused B_2O_3, we observed the 503 nm PL band attributed to the ligand, but the Eu^{3+} lines were more intense. The $80PbF_2$–$20B_2O_3$-based HM had a broad PL band (480 nm), which was more intense than the narrow Eu^{3+} lines. To explain the obtained results, an exchange reaction that was accompanied by partial decomposition of the organic complex in the glass matrix was proposed. The Eu^{3+} displacement in an oxide–fluoride environment led to a decreased PL intensity to values that have typically been attributed to Eu^{3+} doped inorganic glasses. Simultaneously, the ligands formed complexes with Pb, which resulted in an increased PL intensity.

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1. Introduction

Eu^{3+} compounds are undoubtedly the most studied among all lanthanide (III) 1,3-diketonates complexes [1–5]. One of the main reasons for their study is the near-monochromatic red emission of these compounds that is attributed to the strongest $^5D_0 \rightarrow {}^7F_2$ transition in the Eu^{3+} ion, which is located at approximately 615 nm. Another reason is because of the relatively low energy of the resonant $^5D_0$ level (approximately 17,200 cm^{-1}), which matches well with many common ligands [6–8]. Emission lines in such complexes are usually rather narrow, which is very attractive for creating light-emitting devices based on the RGB color model, namely, displays or multicomponent white OLEDs [9,10].

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). All of these properties provide protection to and improve the reliability of the organic constituents or layers that are under the action of temperature, humidity, sunlight.

In our previous research dealing with the fabrication of bulk and film hybrid materials, we considered boron oxide and low melting alkali borate glass systems, that is, Na_2O–B_2O_3 and Li_2O–B_2O_3, as perspective glass matrices. Although alkali borate glass melts appear to be chemically aggressive towards the organic component of metal complex phosphors

(e.g., tris-(8-hydroxyquinoline), including aluminum (Alq_3), indium (Inq_3), and gallium (Gaq_3)), we have succeeded in obtaining luminescent hybrid materials with boron oxide [11]. However, boron oxide is not an ideal candidate for use in a glass matrix: its melt viscosity at 400–500 °C is very high (~2×10^4 Pa·s), and its chemical resistance is insufficient. Hence, the search remains active for a glass matrix that is compatible with hybrid materials.

The presence of a highly polarized cation in lead compounds causes a reduction in the melting temperature and a substantial decrease in the melt viscosity. The replacement of a lead oxide by a lead fluoride results in further reductions of specific glass temperatures and the viscosity. Glasses in the PbF_2–B_2O_3 system have been obtained with compositions that range from 25 to 80 PbF_2 mol% [12,13]. These glasses are chemically stable and are less aggressive than alkali borate glasses.

Thus, boron oxide and oxyfluoride lead-borate glasses, with a high content of lead fluoride, may be good matrices for both bulk and film hybrid materials.

2. Experimental

2.1. General

PbF_2, B_2O_3 and EuF_3 preparations (99.99 wt.% purity grade) were purchased from Sigma-Aldrich, and all solvents were procured from Merck. Commercial B_2O_3 (99.995 wt.%) was placed in a glassy carbon crucible and dried by continuous heating up to 700 °C in a quartz glass

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reactor under a dynamic vacuum ($p = 10^{-3}$ Torr). The material purity was verified by ICP-MS (NexION 300D, Perkin Elmer Inc.).

2.2. Synthesis of ligand — 4,4,4-Trifluoro-1-(2-naphthyl)butane-1,3-dione

This compound was obtained according to a slightly modified procedure [14] that involved the interaction of 2-acetonaphthone (1 eq.) and methyl trifluoroacetate (1.05 eq.) with an excess of NaH (1.2 eq.) in dry THF.

A solution of 17 g (100 mmol) of 2-acetonaphthone (Acros) and 13.5 g (10.5 mmol) of methyl trifluoroacetate in 50 ml of THF was added dropwise, at a rate that maintained moderate hydrogen evolution, to a stirred suspension of 7.2 g (120 mmol) of NaH (60% dispersion in mineral oil, Acros) in 200 ml of dry THF at 0 °C under an argon atmosphere. The resultant thick suspension was kept at room temperature for 8 h, after which it was cautiously decomposed by the addition of 5 ml of dry MeOH, followed by an excess of ice-cold 2 M HCl. The organic phase was then separated, and the water phase was extracted three times by 70-ml portions of dichloromethane. The extracts were mixed together, dried over MgSO₄, and concentrated under vacuum. The solid compound was purified by recrystallization from aqueous methanol. The yield was 21.8 g (82%) of light yellow crystals. M.p. 73–74 °C (75 °C [15]).

The composition was determined from a combustion elemental (HCN) analysis for $C_{14}H_9O_2F_3$: Calculated — C, 63.10; H, 3.38%. Found — C, 63.14; H, 3.41%. ^{1}H NMR (300 MHz, 300 K, CDCl₃) δ: 15.31 (1H, bs), 8.55 (1H, s), 8.00 (1H, d), 7.88 (1H, d), 7.61 (1H, m), 7.21 (1H, m), 6.73 (1H, s). ^{19}F NMR (282.4 MHz, 300 K, CDCl₃) δ: −79.8 (CF₃—).

2.3. Synthesis of complex — europium (III) tris-(4,4,4-trifluoro-1-(2-naphthyl)butane-1,3-dionato)(1,10-phenantroline) — Eu(NTA)₃(Phen)

Different methods have been described for the preparation of this complex [16,17]. Nevertheless, we developed an original procedure using dichloromethane as a solvent.

To a stirred warm (40 °C) solution of 1.36 g (6 mmol) of 4,4,4-trifluoro-1-(2-naphthyl)butane-1,3-dione (HNTA) and 0.36 g (2 mmol) of 1,10-phenantroline in 60 ml ethanol, 4 ml of 0.5 M aqueous EuCl₃ (2 mmol) was added dropwise, which was followed by the addition of 6 ml (6 mmol) of a 1 M NaOH solution in water.

The pH of the resultant suspension was 6.8. The mixture was heated at 50 °C for 4 h, cooled and filtered. The precipitate was dissolved in 50 ml of dichloromethane, washed with water and dried over MgSO₄. The filtered solution was then concentrated to a volume of approximately 5 ml, covered with care by 60 ml of MeOH and sealed. The closed container was left at room temperature. After 1 week, the crystals (X-ray quality) were separated, washed by MeOH (10 ml) and dried to a constant weight at 40 °C at 10^{-2} Torr. The yield was 1.23 g (59%) of light brown crystals.

The determined composition from a combustion elemental (HCN) analysis for $C_{54}H_{32}EuF_9N_2O_6$ (1127.79): Calculated — C, 57.51; H, 2.86; N, 2.48%. Found — C, 57.59; H, 2.83; N, 2.55%. FTIR (KBr, cm^{-1}): 1611, 1591, 1568 (ν_s C=O); 1349 (ν_s C—N); 1295, 1198 (ν_s C–F).

2.4. Synthesis of glass matrix

The glasses were synthesized using PbF₂, B₂O₃ and EuF₃ preparations (99.99 wt.% purity grade) in batches that were 10 g in weight. Glasses were synthesized at 850–900 °C for 0.25 to 0.5 h in closed corundum crucibles. The melt was poured into a steel mold that was heated to 200 °C. To compare the hybrid materials, we synthesized the 79·PbF₂-20·B₂O₃-1·EuF₃ glass as a standard. During synthesis up to 50% of the fluorine volatilized from the melt and up to 10 wt.% of aluminum dissolved in the glass.

2.5. Elemental analysis

Scanning Electron microscopy (SEM, Tescan VEGA3-LMU) equipped with a detector for energy-dispersive spectroscopy (EDS Oxford Instruments X-MAX-50) and AZTec software was used for gathering and
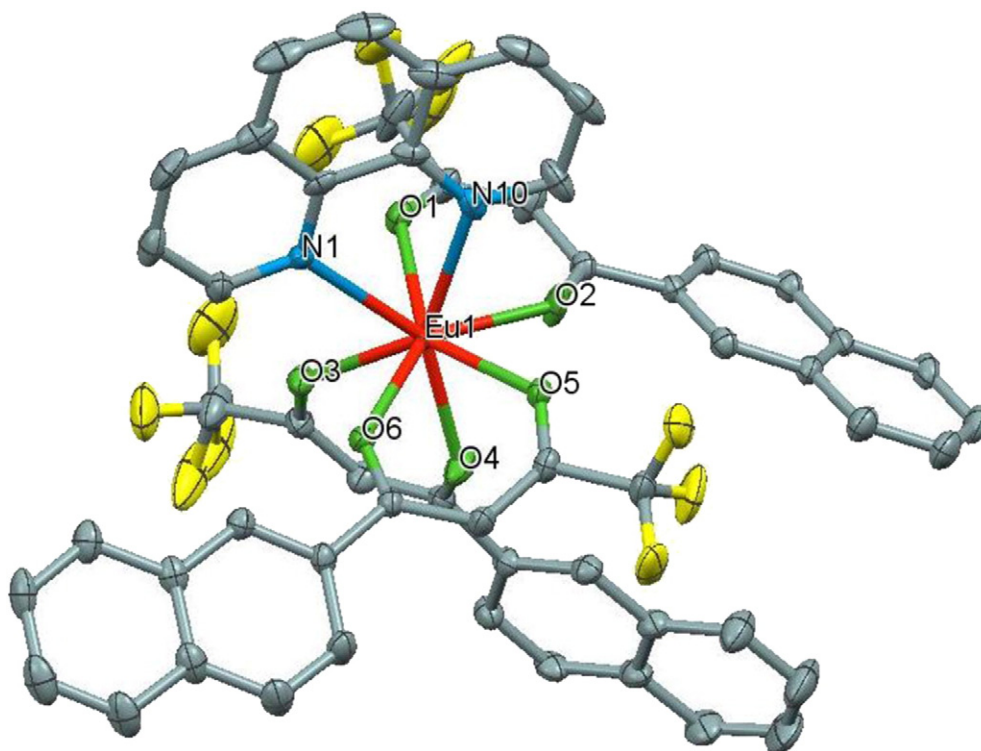

Fig. 1. General view of the Eu(NTA)₃(Phen)·CH₂Cl₂ complex with the representation of atoms via thermal ellipsoids at p = 50%. Hydrogen atoms and a solvate dichloromethane molecule are not shown for clarity. The structural parameters are available in the Cambridge Crystallographic Data Centre (CCDC No. 1057109).