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Effects of dispersion by Gd^{3+} upon europium diphenylphosphinate luminescence

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Abstract

A series of binary diphenylphosphinates with Eu^{3+} and Gd^{3+}were prepared. The compounds have the general formula $Gd_{1-x}Eu_x(DPP)_3$, where x ranges from 0 to 1. The spectroscopic measurements show interesting behavior. The intensity of the $^5D_0 \to {}^7F_2$ transitions decreases relative to $^5D_0 \to {}^7F_1$ with an increase in europium dispersion. Inside the temporal domain, the same decrease is observed with increasing delay after excitation. The lifetimes are also affected, which can be seen in the $x = 1$ compound, where the decay is a first-order process and lifetime values are 4.81 ms. In the binary compound, as an effect of dispersion, the lifetime of the $^5D_0$ level measured at the $^5D_0 \to {}^7F_1$ transition increases with europium dispersion, and the average along the series is 6.25 ms. The decay measured at the $^5D_0 \to {}^7F_2$ transitions reveals a second-order process with lifetimes ranging from 1.90 to 6.00 ms.

Keywords: Phosphors; Chemical synthesis; Crystal structure and symmetry; Optical properties; Luminescence

1. Introduction

Trivalent gadolinium has been used as a host lattice builder on lanthanide-based luminescent compounds not only because of the similarity of their ionic radii, but also because it shows a suitable energy level gap. The first excited level is 32 000 cm^{-1} above the fundamental level so that it is optically inactive inside this large range, and it is possible to take advantage of the highest levels. Under 200 nm excitation there is the possibility of emitting two photons per each photon absorbed. This phenomenon was reported in Refs. [1–3] and is known as quantum cutting, photon-cascade emission or downconversion. Gd^{3+} can only give rise to one visible photon [4]. Recently Wegh et al. [5] obtained evidence of two visible photons on lithium fluorides doped with Gd^{3+} and Eu^{3+}. The authors proposed that, by improving the system, the quantum yield could approach 200%. This yield is useful for phosphors that are excited by noble-gas discharges in new mercury-free devices.

The luminescence of lanthanide organic complexes is of great interest due to their high emission efficiency. We studied diphenylphosphinate–lanthanide systems, which have shown other equally suitable characteristics for luminescent materials, such as thermal stability and low hygroscopicity [6]. Trivalent europium in a diphenylphosphinate complex, $Eu(DPP)_3$, exhibits an unusual $^5D_0 \to {}^7F_2/{}^5D_0 \to {}^7F_1$ ratio ($\cong$ 1). This pattern is characteristic of europium in high-symmetry sites without an inversion center.

The present work reports the spectroscopic behavior in the UV–visible region of europium diphenylphosphinate dispersed with Gd^{3+}. A series of binary diphenylphosphinates $Gd_{1-x}Eu_x(DPP)_3$ was prepared, where $x = 0.01$, 0.05, 0.10, 0.15, 0.20, 0.50 and 1.00; these will be referred to as Eu 1, 5, 10, 15, 20, 50 and 100%, respectively.

2. Experimental

The compounds were prepared using the method described in previous work [6]. Phosphorus and lanthanide contents were determined by atomic emission spectrometry (ICP) using a Thermo Jarrel Iris/AP Duo spectrometer. The amounts of carbon and hydrogen were determined using a CE Instruments EA 1110 elemental analyzer. Differential thermal analysis (DTA) and thermogravimetric (TG) curves were obtained in a dynamic nitrogen atmosphere at a heating rate of 10°C min^{-1} using a TA Instruments SDT 2960 thermogravimetric analyzer. X-ray powder diffraction patterns were obtained using a Siemens

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D5000 diffractometer with Cu Kα radiation. Emission spectroscopy of polycrystalline samples was performed at 300 K using a Spex 2121 spectrofluorometer and a Spex 1934 D phosphorimeter to carry out the temporal measurements.

3. Results and discussion

The results of the elemental analysis showed that the expected Eu^{3+} molar percentages were attained. The thermogravimetric curves indicated that the binary compounds have a slight hygroscopicity and the water molecules are not coordinated to lanthanide ions. The magnitude of the measured lifetimes (Table 1) corroborates this conclusion [7].

The diffraction patterns of the binary compounds display few differences from that of the pure compound (Eu 100%) [6] so that their structures are expected to be very similar.

The excitation spectra are shown in Fig. 1. The broad band centered at 273 nm can be ascribed to phenyl group absorptions [6]. For f–f transitions the $^7F_0 \rightarrow {}^5L_6$ line at 393 nm is the strongest.

As expected for all compounds, the excitation by the ligands is stronger than that by the ions. However, it is not obvious the fact that the europium bands decrease relative to phenyl group bands when the europium dispersion increases (on the Eu 50% spectrum). This phenomenon can be understood as energy migration among ligands. The energy absorbed by the diphenylphosphinate anions, which are not in the coordination sphere of europium, is transferred to the europium and so it contributes to the emission intensity.

The emission spectra in Fig. 2 present the bands of the $^5D_0 \rightarrow {}^7F_J$ transitions [6]. These spectra show different characteristics as a function of either the europium molar

Table 1
Lifetimes (ms) of $Gd_{1-x}Eu_x(DPP)_3$ compounds under excitation at 273 nm

Eu (mol%)	36 delays between 0 and 17 ms Measured at:	
	593 nm	610 nm
1	6.00	6.42–2.10
5	6.53	6.31–2.20
10	6.43	5.90–1.98
15	5.97	6.04–1.93
20	5.87	5.77–1.88
50	6.04	6.04–1.77
100	4.81	4.80

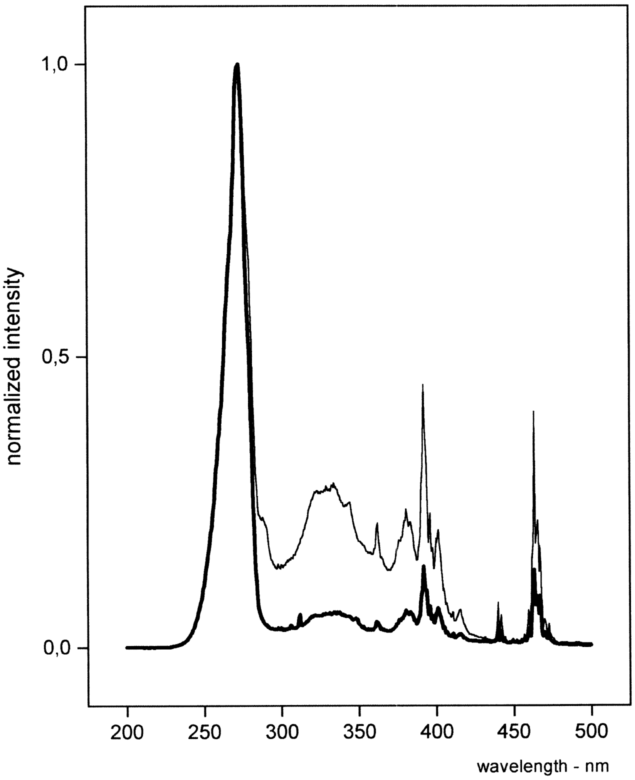

Fig. 1. Excitation spectra of Eu 100% (upper curve) and Eu 50%; curves normalized at 273 nm, $\lambda_{ems} = 593$ nm.

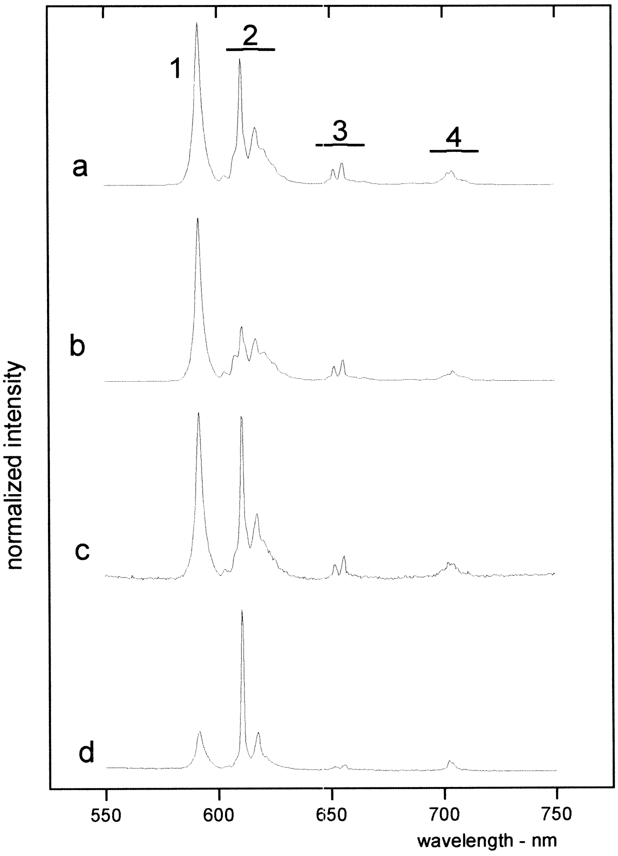

Fig. 2. Emission spectra: (a) Eu 100%, $\lambda_{exc} = 273$ nm; (b) Eu 1%, $\lambda_{exc} = 273$ nm; (c) Eu 1%, $\lambda_{exc} = 393$ nm; (d) Eu 1%, $\lambda_{exc} = 463$ nm on (a) the Eu^{3+} transitions from the $^5D_0$ level to: (1) $^7F_1$, (2) $^7F_2$, (3) $^7F_3$, (4) $^7F_4$. Normalizations: (a, b and c) at 593 nm; (d) at 610 nm.

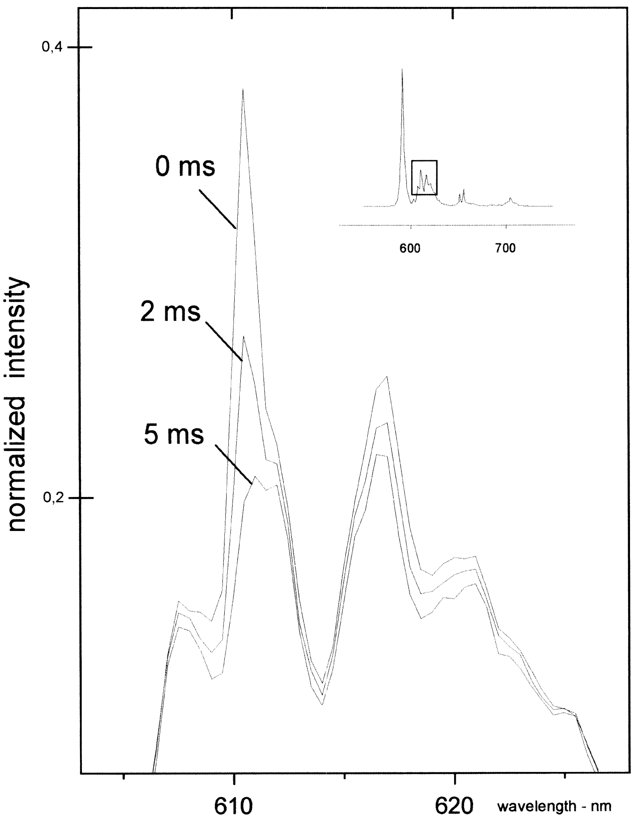

Fig. 3. Time-resolved emission spectra for Eu 1% with increasing after-flash delay. In detail: the $^5D_0 \rightarrow {}^7F_2$ transitions. Normalizations at 593 nm.

concentration or of the wavelength excitation. For Eu 100%, the same spectra are obtained under f–f or ligand excitation. However, for Eu 1% the relative intensities of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions vary for different wavelength excitation. This suggests the presence of more than one site of symmetry, the excitation mechanisms of which are different. The same tendency is observed for intermediate europium compounds. The decrease of the relative intensities of the $^5D_0 \rightarrow {}^7F_2$ transitions in the time-resolved spectra of Fig. 3 is also observed for all compounds with the exception of Eu 100% and Eu 50%

The decay process order observed from the time-resolved spectra point to the presence of two or more sites of symmetry in the binary compounds.

4. Conclusions

The results indicate that dispersion by gadolinium diphenylphosphinate creates one or more new sites from that of the europium complex Eu 100%. Utilizing the 273 nm band the ligands are directly excited and the energy spreads equally over the different sites present. Using excitation at 463 nm, the europium levels more likely excited are those whose sites of symmetry are lower. It can also be seen that the dispersion reveals the existing sites in europium diphenylphosphinate. Complex mechanisms of energy transfer are probably present. Calculations of their rates and quantum yield determinations can help to elucidate this matter. We are also planning to perform spectroscopic measurements under VUV excitation.

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References

[1] J.L. Sommerdijk, A. Bril, A.W. de Jager, J. Lumin. 8 (1974) 341.
[2] W.W. Piper, J.A. de Luca, F.S. Hamilton, J. Lumin. 8 (1974) 344.
[3] W.W. Piper, J.A. de Luca, F.S. Hamilton, J. Lumin. 9 (1974) 288.
[4] R.T. Wegh et al., Phys. Rev. B 56 (21) (1997) 13842.
[5] R.T. Wegh et al., Science 283 (1999) 663.
[6] E.B. Stucchi et al., J. Alloys Comp. 89 (1998) 275.
[7] W. de W. Horrocks Jr., D.R. Sudnick, J. Am. Chem. Soc. 101 (2) (1979) 338.