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Journal of Luminescence 114 (2005) 267–274
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Quenching of Pr^{3+} $^1S_0$ emission by Eu^{3+} and Yb^{3+}

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Received 27 September 2004
Available online 14 March 2005

Abstract

Energy transfer between Pr^{3+} and Eu^{3+} is studied by luminescence spectroscopy and time-resolved measurements. In earlier experiments, Zachau et al. (Proceedings—Electrochemical Society, 97 (29) (Luminescent Materials, pp. 314–324, 1998)) observed no energy transfer from the $^1S_0$ level of Pr^{3+} to the $^5D_3$ level of Eu^{3+} for YF_3: Pr, Eu, in spite of the favorable spectral overlap for energy transfer. This unexpected result was not explained. To resolve this issue, we first calculate the critical distance for energy transfer using the Förster theory and show that efficient energy transfer between Pr^{3+} and nearest Eu^{3+} neighbors is predicted. Nevertheless, luminescence experiments show no Eu^{3+} emission upon excitation in the $^1S_0$ level of Pr^{3+} in YF_3: Pr, Eu confirming the results in (Proceedings—Electrochemical Society, 97 (29) (Luminescent Materials, pp. 314–324, 1998)). The experiments do show a strong quenching of the $^1S_0$ emission by Eu^{3+}. The quenching is explained by a low-energy metal-to-metal charge transfer state (Pr^{4+}–Eu^{2+}) for Pr–Eu pairs. Additional support for this quenching mechanism is provided by the observation that addition of Yb^{3+} also quenches the $^1S_0$ emission.

PACS: 78.55.Hx

Keywords: Quantum cutting; Quantum splitting; Cascade; Quenching

1. Introduction

Higher energy efficiencies in luminescent materials can be obtained by the use of quantum-cutting phosphors. A quantum-cutting phosphor is a material that is capable of emitting two visible photons for every (vacuum) ultraviolet photon absorbed. The discovery of such phosphors [1–4] has been an exciting development in the field of luminescence.

Research on quantum-cutting systems started on single ions capable of a cascade emission such as Pr^{3+} [1,2], Tm^{3+} [5] and Gd^{3+} [6]. The Pr^{3+} cascade emission occurs when the 4f5d state is located above the $^1S_0$ state. It was initially observed in highly ionic materials (fluorides) with

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doi:10.1016/j.jlumin.2005.02.001

a small crystal field splitting (see, for example, the review articles from Refs. [7,8]). More recently, it has also been observed in oxides like $LaMgB_5O_{10}$ [9], LaB_3O_6 [10], and $SrAl_{12}O_{19}$ [11]. The first step of the cascade emission is the $^1S_0 \rightarrow {}^1I_6$ transition, where light with a wavelength of ~ 405 nm is emitted. After non-radiative relaxation into the $^3P_0$ level, the second step is a transition from this level to one of the lower lying levels. Typically, radiation of 485 nm ($^3P_0 \rightarrow {}^3H_4$) and of 605 nm ($^3P_0 \rightarrow {}^3H_6$ or $^1D_2 \rightarrow {}^3H_4$) is observed. Despite their high quantum efficiency, phosphors based on the Pr^{3+} cascade emission are not used in lighting applications because of the unfavorable wavelength of the photons emitted in the first step of the cascade (~ 405 nm) [12]. A solution to this problem is to convert the $^1S_0 \rightarrow {}^1I_6$ emission to a more useful visible wavelength by energy transfer to a coactivator. Zachau and coworkers tried to transfer the energy of the Pr^{3+} $^1S_0 \rightarrow {}^1I_6$ transition to suitable coactivators, like the Eu^{3+} ion [13]. Considering the favorable spectral overlap between the $^1S_0$–$^1I_6$ emission of Pr^{3+} and the $^7F_{0,1}$–$^5D_3$, $^5L_6$ absorption lines of Eu^{3+} efficient energy transfer, followed by the well-known red/orange emission from the $^5D_0$ level of Eu^{3+}, is expected. Upon adding Eu^{3+} as a coactivator in YF_3:Pr^{3+}, Zachau et al. did not observe any Eu^{3+} emission upon excitation in the 4f5d bands of Pr^{3+}. Based on these observations, it was concluded that the expected energy transfer does not occur.

This is remarkable, since an important condition for energy transfer, the presence of resonance between the Pr^{3+} $^1S_0 \rightarrow {}^1I_6$ transition and absorptions of the Eu^{3+} ion is fulfilled. In this case, energy transfer can occur by exchange interaction [14] or multipole–multipole interaction [15].

In this work, the system YF_3:Pr^{3+}, Eu^{3+} is studied to solve the puzzle presented in Ref. [13]. First, it is shown that based on dipole–dipole interaction, energy transfer between nearest-neighbor Pr^{3+} $^1S_0 \rightarrow {}^1I_6$ and Eu^{3+} $^7F_{0,1} \rightarrow {}^5D_3$, $^5L_6$ has a similar probability as radiative decay from the Pr^{3+} $^1S_0$ level. As a result, energy transfer and subsequent Eu^{3+} emission should occur. To explain the observed absence of Eu^{3+} emission upon excitation in the $^1S_0$ level of Pr^{3+}, luminescence spectra and time-resolved luminescence were measured for YF_3:Pr^{3+}1%, Eu^{3+} x% ($x = 0$, 5 and 10). The experiments show a strong quenching of the Pr^{3+} $^1S_0$ emission in the presence of Eu^{3+} ions. We attribute this quenching process to non-radiative relaxation via a metal-to-metal charge-transfer state.

2. Experimental

2.1. Sample preparation

Powder samples of YF_3 doped with Pr^{3+} and samples doped with Pr^{3+} and codoped with Eu^{3+}, Yb^{3+} or La^{3+} were prepared by mixing stoichiometric amounts of YF_3, PrF_3, YbF_3, EuF_3 and LaF_3. The mixtures were fired in a tube oven under a nitrogen atmosphere at 650 °C. A sample of YF_3 doped with 1% Pr^{3+}, a sample doped with 1% Pr^{3+} and 5% Eu^{3+} and a sample doped with 1% Pr^{3+} and 10% Eu^{3+} were fired simultaneously. A second batch consisted of YF_3 doped with 1% Pr^{3+}, YF_3 doped with 1% Pr^{3+} and 5% Yb^{3+}, and YF_3 doped with 1% Pr^{3+} and 10% of Yb^{3+}. A third batch consisted of YF_3 doped with 1% Pr^{3+}, YF_3 doped with 1% Pr^{3+} and 5% La^{3+}, and YF_3 doped with 1% Pr^{3+} and 10% of La^{3+}. The phase purity was checked with powder diffraction. YF_3 has space group Pnma and the site symmetry for the cation is C_s [16].

2.2. Optical measurements

Luminescence spectra in the UV/VIS spectral region were recorded with a Spex 1680 spectrofluorometer with a Xe-lamp as excitation source. The excitation light was dispersed by double 0.22 m gratings (1200 l/mm) blazed at 500 nm. A spectrum for the dispersion of the lamp/gratings combination was obtained by division of the excitation spectrum of pyridine 2 dissolved in ethanol by the absorption spectrum of this solution. The signal detected in the excitation spectra was corrected for the lamp/gratings response with this spectrum.

Luminescence spectra involving VUV excitation were recorded on a SPEX 1680 spectrofluorom-