

Unexpected luminescent and thermal properties of novel tetrakis Eu³⁺-indandionate complex: Experimental and theoretical studies

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Highlights

The highest value of Judd–Ofelt intensity parameter (Ω_2) for the europium compound reported in the literature. The $\text{Et}_4\text{N}^+[\text{Eu}(\text{isovind})_4]^-$ complex presents an abnormal phase transition changing $^5\text{D}_0 \rightarrow ^7\text{F}_J$ luminescence profile.

Resumo/Abstract

Luminescent coordination compounds based on trivalent europium ions (Eu^{3+}) have found wide range of applications in new technologies, such as optoelectronics, molecular thermometers, and biomedical devices. Applications of this materials may be associated with narrow emission bands, which are arise from intra-configurational Laporte forbidden $4f - 4f$ transitions ($^5\text{D}_0 \rightarrow ^7\text{F}_J$). Furthermore, Eu^{3+} ion can act as a powerful spectroscopic probe and the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition are strongly sensitive to small angular variations in the coordination polyhedron. However, the energy structures of the organic ligands in the complexes play the most important role on the Eu^{3+} luminescence sensitization process¹. In this context, this work reports about theoretical, syntheses, characterization, and photoluminescence studies of a series of tetrakis complexes containing tetraethylammonium, $\text{Et}_4\text{N}^+[\text{Ln}(\text{L})_4]^-$ (Et_4N^+ : tetraethylammonium cation, Ln: Gd and Eu, and L: 2-acyl-1,3-indandionate). The Judd–Ofelt intensity parameter (Ω_λ), lifetime (τ), radiative (A_{rad}) and non-radiative (A_{nrad}) coefficients, and intrinsic quantum yield ($\Omega_{\text{Eu}}^{\text{Eu}}$) values were calculated for different temperatures (80 - 475 K) (Table 1). The $\text{Et}_4\text{N}^+[\text{Eu}(\text{isovind})_4]^-$ complex, where isovind: 2-isovaleryl-1,3-indandionate) shows an extraordinarily high value of the intensity parameter ($\Omega_2 = 73.5 \times 10^{-20} \text{ cm}^2$, considering the index of refraction equal to 1.5) and radiative decay rate ($A_{\text{rad}} = 2.468 \times 10^3 \text{ s}^{-1}$) at 300 K. These optical results show an abnormally high emission intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (Figure 1), leading to the highest measured Ω_2 value of the europium materials, to the best our knowledge, reported in the literature. In addition, this complex shows different solid phases at 367 and 460 K, leading significant changes in the band profile assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. The spectroscopic study of luminescent systems has shown very interesting and promising results for applications, such as OLED devices and luminescent thermometers based on Ln^{3+} ions.

Table 1. Experimental intensity parameters (Ω_λ), lifetime (τ), radiative (A_{rad}) and non-radiative (A_{nrad}) coefficients, and intrinsic quantum yield ($\Omega_{\text{Eu}}^{\text{Eu}}$) of $\text{Et}_4\text{N}^+[\text{Eu}(\text{isovind})_4]^-$ complex.

Temperature K	Ω_2 (10^{-20}) cm^2	Ω_4 (10^{-20}) cm^2	τ (ms)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	$Q_{\text{Ln}}^{\text{Ln}}$ (%)
80	63.6	7.9	0.371	2140	555.4	2695	79.4
200	68.4	8.8	0.358	2307	486.3	2793	82.6
300	73.5	8.9	0.330	2468	562.3	3030	81.4
375	77.7	8.8	0.172	2362	3452	5814	40.6
425	83.1	10.8	0.127	2791	10910	13700	20.4
475	90.5	13.1	0.018	3053	52500	55560	5.5

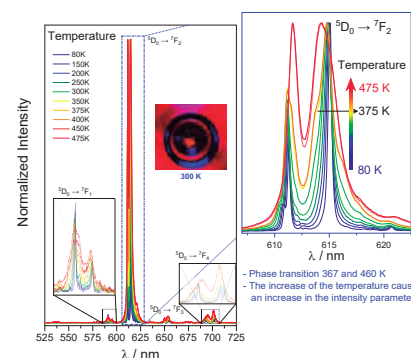


Figure 1. The emission spectra of $\text{Et}_4\text{N}^+[\text{Eu}(\text{isovind})_4]^-$ complex at from 80 to 475 K. Insert: Photograph taken under the 365 nm UV lamp at 300 K.

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