Influence of temperature on emission decay curves of Europium(III)-based oxides, fluorides and complexes

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Abstract
The present work shows the dependence of emission lifetime of the $^5D_0$ level of Eu$^{III}$ ion as a function of the sample excitation energy and of the temperature. In order to provide a satisfactory explanation for the observed data, the shape of emission decay curves of this ion, situated in different chemical environments, were analyzed under several excitation wavelengths and in temperatures ranging from 77 K to 300 K. These lifetime values are influenced by the presence or absence of intermediate energy levels and by the balance between intramolecular energy transfer rates and the magnitude of non-radiative decay processes.

Keywords: Luminescence, Lifetimes, Europium(III).

Introduction
The emission lifetime is one of the most important properties of any luminescent materials, where lanthanide ions may be used as activators. Their typically long emission lifetime values are due to the metastable states originated from 4f orbitals that are shielded from the ligand charge distribution around the ion, originating f-f electronic transitions forbidden by selection rules. The Eu$^{III}$ is one of the well studied ions of the series, showing red emission that arises from the $^5D_0 \rightarrow ^7F_J$ transitions, especially $J = 0, 1, 2, 4$. Despite of the relevance of such parameter, the discrepancies between the emission lifetimes obtained for the same lanthanide-doped material as a function of excitation wavelengths are scarcely reported. An interesting analysis of lifetime dependence on excitation energies and the presence of intermediate energy levels was done by Ferreira et al. for a variety of Eu$^{III}$-containing compounds.

In a previous undergraduate research work of our group, this emission lifetime dependence was also verified for Y$_2$O$_3$:Eu$^{III}$, LaF$_3$:Eu$^{III}$, and the complexes [Eu(tta)$_3$(H$_2$O)$_2$], [Eu(tta)$_3$(tppo)$_2$] and [Eu(tta)$_3$(phen)], which the present work is trying to elucidate.

Results and Discussion
The emission decay curves of all the mentioned compounds, prepared and characterized in the context of the first project, were measured using a time correlated single photon counting (TCSPC) system; the analyses were performed in ten different values of temperatures, selected evenly between 77 K and 300 K using a liquid nitrogen cryostat coupled to a spectrofluorometer. Considerable variation of emission lifetime values with the excitation energy was observed for both Y$_2$O$_3$:Eu$^{III}$ and LaF$_3$:Eu$^{III}$ bulk inorganic solids. On the other hand, the complexes [Eu(tta)$_3$(H$_2$O)$_2$], [Eu(tta)$_3$(tppo)$_2$] and [Eu(tta)$_3$(phen)], showed a smaller emission lifetime variation as a function of excitation energy than the observed for the inorganic solids. Moreover, higher lifetime values were verified when the excitation was done at high intensity bands of the excitation spectra, especially for the complexes. It was not verified a significant change in the shape of the emission decay curves of any sample, independently of the excitation wavelength, as a function of temperature. However, the trend of the emission lifetime values versus temperature curves typically shown maximum and minimum regions, indicating the temperatures where non-radiative decay processes become more important. That was observed for all the analyzed compounds, regardless if the excitation energy is transferred from the ligands to the activator ion or if the Eu$^{III}$ ion is directly excited.

Conclusions
The present study show the variation of emission lifetime values as a function of the excitation energies and for Y$_2$O$_3$:Eu$^{III}$ and LaF$_3$:Eu$^{III}$ bulk solids and for the complexes [Eu(tta)$_3$(H$_2$O)$_2$], [Eu(tta)$_3$(tppo)$_2$] and [Eu(tta)$_3$(phen)]. It was also observed their dependence with the temperature, despite the shapes of emission decay curves have not changed for any sample. This indicates that they are influenced by the presence of intermediate energy levels and by the balance between intramolecular energy transfer rates and the magnitude of non-radiative decay processes.

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