Thulium as a sensitizer for the Gd-Eu quantum cutting couple

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The increasing knowledge of the energy level structure of the lanthanides has led to new applications for these ions. The Gd-Eu quantum cutting couple was discovered a few years ago and may be applied in phosphors for fluorescent tubes based on a VUV xenon discharge. The VUV absorption of the phosphor $LiGdF_4:Eu^{3+}$ is poor and therefore a sensitizer is needed. This contribution describes the investigation of using the strong $4f^{11}5d$ VUV absorption bands of thulium ions as a sensitizer for the Gd-Eu quantum cutting couple. In order to serve as an efficient sensitizer for the Gd/Eu couple, the absorption of VUV radiation should be followed by energy transfer to one of the high energy (VUV) energy levels of Gd. From the high energy levels fast relaxation to the ^6G level occurs and this level serves as the starting level for the quantum cutting process (see Fig. 1).

The strongest fd emission bands of Tm in LiYF4 are situated in the VUV region and have a good spectral overlap with the VUV energy levels of Gd. As a result, energy transfer to the high energy levels of Gd is expected resulting in population of the ^6G level. The incorporation of thulium in the quantum cutting phosphor $LiGdF_4$ does indeed result in sensitization of Gd^{3+} but not in downconversion in the Gd-Eu couple. A competing downconversion process, depicted between gadolinium and thulium occurs resulting in infrared emission of thulium, which is not suitable for lighting applications.

In Fig. 2 the emission spectra are shown for LiGdF4:Eu,Tm upon excitation in the fd band of Tm. Comparison of the spectra in Fig. 2 shows that the intensity of the $^5D_0$ emission does not increase relative to the emission from the higher energy ^5D_J levels. This indicates that the desired quantum cutting process is not sensitized by Tm3+ and that the incorporation of Tm3+ even eliminates the Gd/Eu downconversion process upon direct excitation in the 6G level of Gd3+.

To understand what is causing the apparent absence of quantum cutting, a careful inspection of the emission spectra is required. Even though the ratio of the $^5D_0$ to ^5D_J emission is the same in Figs. 2(a) through (c), there is a significant difference in the near-infrared part of the spectrum. Only under VUV excitation an emission is observed in the infrared spectral region around 800 nm. This emission is assigned to $^3H_4$-$^3H_6$ emission from Tm^{3+}. The fact that the $^3H_4$ emission is much stronger upon VUV excitation indicates that there is direct feeding of the $^3H_4$ level of Tm from the $^6G_{7/2}$ level of Gd^{3+} through downconversion.

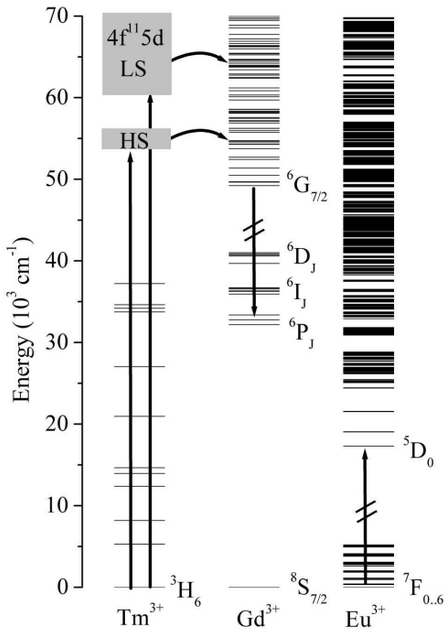

Fig. 1 – Schematic scheme of the desired sensitization and quantum cutting process for $LiGdF_4$:Eu,Tm

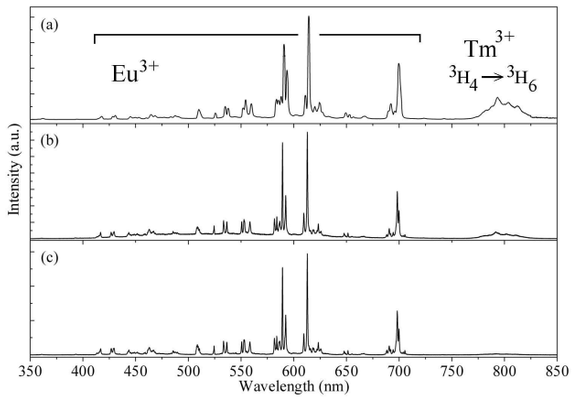

Fig. 2 – Emission spectra of $LiGdF_4$:Eu1%, Tm0.3% upon excitation at 160 nm (a), 202 nm (b) and 273 nm (c) at 300 K.