Energy transfer and upconversion in Tm³⁺-doped β-NaYF₄: comparison between models and theory

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Tm³⁺ ions in close proximity interact non-radiatively in different ways so that, for example, blue ${}^{3}H_{6} \rightarrow {}^{1}G_{4}$ excitation (473 nm) results in UV ${}^{1}D_{2} \rightarrow {}^{3}H_{6}$ upconverted emission (361 nm) in a β -NaYF₄: 0.3% Tm³⁺ sample, see Fig 1.

The strength of an energy transfer (ET) interaction can be summarized by a single number: the critical radius R_c . This is the distance at which the probability of ET and radiative decay are equal. At shorter distances ET dominates, while at longer distances radiative decay is more important.

A recent model is able to obtain the R_c of different interactions by fitting luminescence decay curves, see Fig 1(b). [1] For the cross-relaxation interaction shown in Fig. 1(a), this model determines $R_c = 11.8$ Å. An analysis based on the Inokuti-Hirayama model results in $R_c = 12.1$ Å.

An equation due to T. Kushida determines R_c as a function of the donor state lifetime, refractive index, transition energy, emission and absorption oscillator strengths, and spectral overlap. [2]



These parameters have been determined for a β -NaYF₄: 0.3% Tm³⁺ powder sample and a β -NaGdF₄: Yb³⁺, Tm³⁺ single crystal. [1,3] The predicted critical radius is R_c=7.6 Å. The disagreement between the model and theory can be explained by the difficulty in measuring the spectral overlap, due to the disorder in the β -NaYF₄ lattice.

Fig. 1. a) Electronic structure of Tm^{3+} and relevant absorption, emission, and energy transfer processes in β -NaYF₄: 0.3% Tm^{3+} . b) ${}^{1}D_{2}\rightarrow{}^{3}H_{6}$ luminescence decay curve (361 nm) after ${}^{3}H_{6}\rightarrow{}^{1}G_{4}$ excitation (473 nm) with model fit (red line).

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