

# Energy transfer and upconversion in Tm<sup>3+</sup>-doped β-NaYF<sub>4</sub>: comparison between models and theory

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Tm<sup>3+</sup> ions in close proximity interact non-radiatively in different ways so that, for example, blue <sup>3</sup>H<sub>6</sub>→<sup>1</sup>G<sub>4</sub> excitation (473 nm) results in UV <sup>1</sup>D<sub>2</sub>→<sup>3</sup>H<sub>6</sub> upconverted emission (361 nm) in a β-NaYF<sub>4</sub>: 0.3% Tm<sup>3+</sup> sample, see Fig 1.

The strength of an energy transfer (ET) interaction can be summarized by a single number: the critical radius R<sub>c</sub>. 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<sub>c</sub> 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<sub>c</sub> = 11.8 Å. An analysis based on the Inokuti-Hirayama model results in R<sub>c</sub> = 12.1 Å.

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

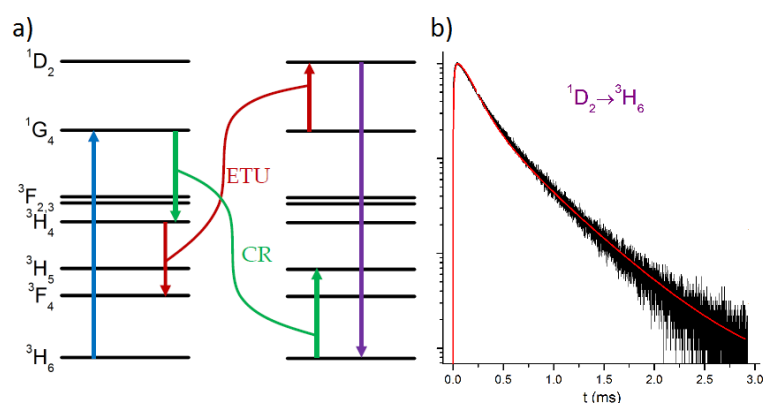


Fig. 1. a) Electronic structure of Tm<sup>3+</sup> and relevant absorption, emission, and energy transfer processes in β-NaYF<sub>4</sub>: 0.3% Tm<sup>3+</sup>. b) <sup>1</sup>D<sub>2</sub>→<sup>3</sup>H<sub>6</sub> luminescence decay curve (361 nm) after <sup>3</sup>H<sub>6</sub>→<sup>1</sup>G<sub>4</sub> excitation (473 nm) with model fit (red line).

These parameters have been determined for a β-NaYF<sub>4</sub>: 0.3% Tm<sup>3+</sup> powder sample and a β-NaGdF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup> single crystal. [1,3] The predicted critical radius is R<sub>c</sub> = 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-NaYF<sub>4</sub> lattice.

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