Quantum cutting by cooperative energy transfer in $Yb_xY_{(1-x)}PO_4$: Tb^{3+}

P. Vergeer, T.J.H. Vlugt, M.H.F. Kox, M.I. den Hertog, J.P.J.M. van der Eerden and A. Meijerink*
Condensed Matter and Interfaces, Debye Institute, Utrecht University, P. O. Box 80000, 3508 TA Utrecht, The Netherlands

The recent discovery of visible quantum cutting phosphor has been an exciting development in the search for luminescent materials with a high energy efficiency. In luminescent devices such as fluorescent tubes or plasma display panels, the phosphors used nowadays convert one UV photon into one visible photon by dissipating roughly 50% of the absorbed energy into heat. The efficiency gain in quantum cutting materials is based on the principle that a quantum cutting phosphor is able to emit two visible photons for every (vacuum) ultraviolet photon absorbed. The energy of the two emitted photons is at most half the energy of the absorbed photon, leading to the necessary redshift of the absorbed radiation without losing energy efficiency.

Quantum cutting materials may also be applied in solar cells[3]. If conversion of one UV/VIS photon into two IR photons is realized, energy losses by thermalization of electron-hole pairs are minimized. The most widely used solar sells are based on crystalline Si. Therefore, the development of solar cells would greatly benefit from a quantum cutting phosphor with the energy of its emission located just above the bandgap of Si.

We present experimental evidence for cooperative energy transfer from Tb^{3+} to two Yb^{3+} ions and a determination of the energy-transfer rate. Energy transfer from Tb^{3+} to Yb^{3+} was investigated by luminescence measurements on $(Yb_xY_{1-x})PO_4$ doped with 1% Tb^{3+}. Time-resolved luminescence experiments were analyzed using Monte Carlo simulations based on theories for phonon-assisted, cooperative, and accretive energy transfer. The luminescence decay curves of the $^5D_4$ emission from Tb^{3+} show an excellent agreement with simulations based on cooperative energy transfer via dipole-dipole interaction, while a phonon-assisted or an accretive energy transfer mechanism cannot explain the experimental results. The energy-transfer efficiency in $YbPO_4$: Tb^{3+} 1% is 88%, which allows for a total quantum efficiency (visible and near-infrared) of 188%. The energy-transfer rate to two nearest-neighbour Yb^{3+} ions is 0.26 ms^{-1}. Application of cooperative energy transfer has prospects for increasing the energy efficiency of crystalline Si solar cells by photon doubling of the high energy part of the solar spectrum.

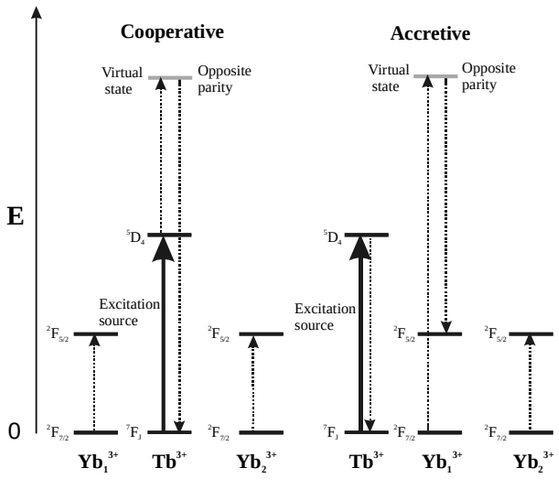

Fig. 1 - Schematic representation of the cooperative and accretive pathways for energy transfer from Tb^{3+} to Yb^{3+}. The bold arrows indicate excitation of Tb^{3+} into the $^5D_4$ state, after which energy transfer may occur. The energy transfer processes are depicted by the dotted lines. In both mechanisms a virtual state is involved. For the cooperative mechanism, the virtual state is located on Tb^{3+}. For the accretive mechanism, the virtual state is located on Yb^{3+}.

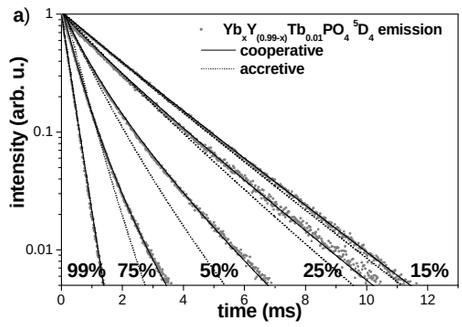

Fig. 2 - Luminescence decay curves of the Tb^{3+} $^5D_4$ emission for various concentrations of Yb^{3+}. The dots are the experimental results. The solid lines are simulated curves using a cooperative dipole-dipole model. Dashed lines are simulated curves using an accretive dipole-dipole model.