

**"ETTORE MAJORANA" FOUNDATION AND  
CENTRE FOR SCIENTIFIC CULTURE**

**Antonino Zichichi - Director**

**INTERNATIONAL SCHOOL OF ATOMIC  
AND MOLECULAR SPECTROSCOPY**

**Baldassare Di Bartolo – Director**

**23rd Meeting**

**Workshop on**

***ADVANCES IN THE STUDY OF LUMINESCENT MATERIALS***

**Erice, Italy; June 20-26, 2006**



**San Rocco Courtyard of the Majorana Centre**

**PROCEEDINGS**

**Edited by**

**Ottavio Forte**

# Upconversion Luminescence Transients

Markus Pollnau

MESA+ Research Institute for Nanotechnology, University of Twente,  
P.O. Box 217, NL-7500 AE Enschede, The Netherlands

## Abstract

Inhomogeneous active-ion distributions in laser materials lead to strong deviations of upconversion versus direct luminescence transients from the quadratic law of energy-transfer upconversion. Measured luminescence decay curves in  $\text{LaSc}_3(\text{BO}_3)_4:\text{Nd}^{3+}$  and  $\text{GdVO}_4:\text{Nd}^{3+}$  confirm experimentally the predicted deviations. Differences in energy migration within the metastable level of  $\text{Nd}^{3+}$  are identified.

For several decades, energy-transfer upconversion (ETU) in rare-earth-ion doped systems has been studied intensively, partly because of the fundamental interest in the physical nature of this process, but also because of the availability of near-infrared pump sources for the ETU excitation of visible luminescence and laser emission and because ETU can introduce a loss channel for devices emitting in the infrared region.

We investigate fundamentally the behavior of infrared luminescence emitted directly from a metastable level after excitation by a short laser pulse and visible luminescence emitted after ETU from this metastable level to higher-lying levels [1]. Although these two luminescences are connected by the same metastable level and influenced by the same ETU process, they probe different classes of ions. Whereas the infrared luminescence probes all ions, the visible luminescence probes only the class of ions susceptible to ETU [2]. A simple analytical model predicted that such luminescence decay curves exhibit a super-quadratic dependence of upconversion on direct luminescence decay [3].

The  $\text{Nd}^{3+}$  ion can serve as a model system for such investigations. It exhibits strong ETU from the metastable  $^4\text{F}_{3/2}$  level (Fig. 1). When doped into oxide matrices, the  $^4\text{F}_{3/2}$  level is the only metastable level within the 4f subshell. The  $\text{Nd}^{3+}$  energy levels excited by ETU decay by fast multiphonon relaxation and, hence, the weak visible fluorescence emitted from these levels represents a quasi instantaneous reaction on the dynamics of the  $^4\text{F}_{3/2}$  metastable level.

$\text{LaSc}_3(\text{BO}_3)_4$  and  $\text{GdVO}_4$  crystals with different  $\text{Nd}^{3+}$  concentrations were provided by the University of Hamburg, Germany, and the General Physics Institute, Moscow, Russia, respectively. Experimental results obtained after short-pulse laser excitation near 800 nm (for an example, see Fig. 2) show that the upconversion (VIS) decay is much faster than the square of the direct (IR) decay, indicating the superquadratic behavior of ETU that fundamentally derives from the inhomogeneous active-ion distribution in the host. The experimental decay curves are described in a new model taking into account isolated, paired, and clustered ions. Comparison between  $\text{LaSc}_3(\text{BO}_3)_4$  and  $\text{GdVO}_4$  shows that static ETU in  $\text{LaSc}_3(\text{BO}_3)_4$  [4] leads to a more

superquadratic behavior, in agreement with model predictions. These findings question many interpretations of upconversion luminescence in solid-state laser materials.

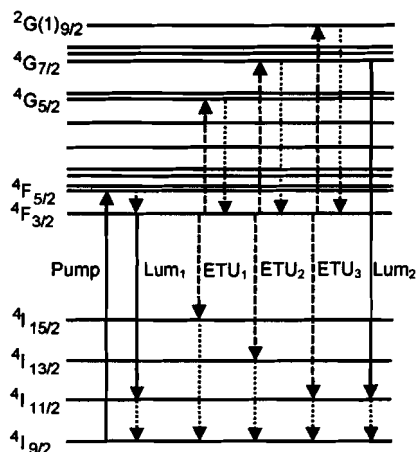


Fig. 1. Partial energy-level scheme of Nd<sup>3+</sup> indicating the relevant processes: pump excitation at 800 nm, direct (LUM<sub>1</sub>) and upconversion (LUM<sub>2</sub>) luminescence, ETU processes, and fast multiphonon relaxation (dashed arrows).

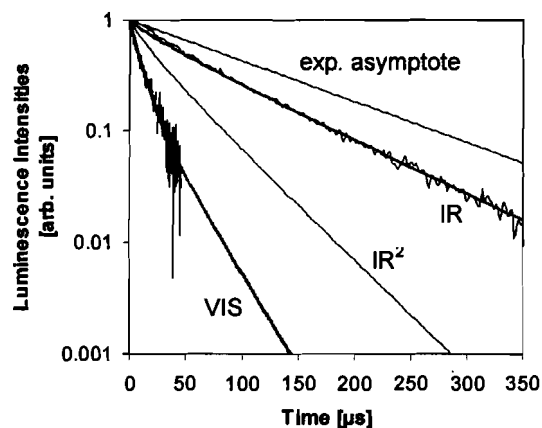


Fig. 2. Measured direct (IR) and upconversion (VIS) luminescence intensities in LaSc<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>:(10%)Nd<sup>3+</sup> together with model results (solid lines) for direct (IR) and upconversion (VIS) decay as well as the exponential asymptote and the square of direct (IR) decay [1].

## References

- [1] M. Pollnau, L. Laversenne, H.G. Limberger, S. Bigotta, A. Toncelli, and M. Tonelli, "Superquadratic behavior of upconversion luminescence transients in rare-earth-ion doped laser crystals", EPS-QEOD Europhoton Conference on Solid-State and Fiber Coherent Light Sources, Lausanne, Switzerland, 2004, Europhysics Conference Abstracts, Vol. 28C, paper TuD6.
- [2] M. Pollnau, D.R. Gamelin, S.R. Lüthi, H.U. Güdel, and M.P. Hehlen, "Power dependence of upconversion luminescence in lanthanide and transition-metal-ion systems", Phys. Rev. B 61, 3337 (2000).
- [3] M. Pollnau, "Decorrelation of luminescent decay in energy-transfer upconversion", J. Alloys Compd. 341, 51 (2002).
- [4] D.A. Zubenko, M.A. Noginov, V.A. Smirnov, and I.A. Shcherbakov, "Different mechanisms of nonlinear quenching of luminescence", Phys. Rev. B 55, 8881 (1997).