Wrocław, 04.01.2024

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"**Evaluation of luminescent properties of photon avalanching nano-, micro- and bulk crystals: novel materials, characterization methods and applications**"

Abstract

Photon avalanche (PA) is a fascinating phenomenon in the realm of photophysics. PA process was first observed in 1979 by Jay S. Chivian in a bulk $LaCl_3:Pr^{3+}$ crystal, while looking for materials suitable for medium infrared (IR) photon counting [1] until recently, this phenomenon was observed mostly at low temperatures in bulk crystals or optical fibers. However, in 2021 all the characteristic features of PA emission were demonstrated for the first time in nano-sized 8% Tm^{3+} doped β-$NaYF_4$ crystals. PA phenomenon is one type of upconversion (UC). PA is a cascade process that occurs in lanthanide ion doped crystals when photons of lower energy trigger a series of subsequent energy transfer processes (such as excited state absorption and cross-relaxation) and ultimately lead to photon emissions of higher energy characterized by highly non-linear multicolor luminescence intensity growth upon small increase of photoexcitation intensity which occurs above a certain pump power threshold. This power law relationship can reach non-linearities much above 10. The second characteristic feature of PA is the significant prolongation of the pump power dependent luminescence rise time (even up to hundreds of ms) for the excitation powers close to the threshold. Therefore, the major motivation behind current dissertation was to design and optimize tools to study PA phenomenon, as well as to evaluate new nano and micromaterials against the possibility to observe PA emission. Because no commercial instrumentation to study PA properties exist on the market, as part of the doctoral thesis I was involved in designing, building and optimizing an unique measuring system that was capable to count photons flux in wide 1 to 10^9 counts per second range over a large range of photoexcitation power density (10^2-10^7 Wcm^{-2}). The system is based on an optical microscope and detection is done in various alternative ways: spectrophotometer enables recording pump power dependent emission spectra, while

luminescence intensity and luminescence kinetics can be recorded utilizing set of three PMT's connected to a dedicated photon counter.

Using this custom made microscopic system, I investigated spectroscopic and avalanche properties of nano- and microcrystals doped with various concentrations and combinations of lanthanide ions such as Tm^{3+}, Nd^{3+}, Pr^{3+}, Yb^{3+}, Ho^{3+}. Among the others, I measured the dependence of the luminescence intensity on the pump power density, as well as the PA rise and decay times for the Tm^{3+} avalanching ions. This dissertation delves into the fundamental principles behind PA in nano and microcrystals, exploring the role of size, composition, matrices and crystal structure in governing this process. I was discussing the mechanisms by which PA can be initiated and controlled within these crystals. Additionally, I investigated the impact of crystal size, dopant concentration in microcrystals, evaluated the impact of various matrices and shell thickness in nanocrystals on PA emissions in Tm^{3+} ions. Moreover, I confirmed the occurrence of PA in Tm^{3+} doped $LiYF_4$ nanocrystals for the first time. Additionally, I explored how the presence of gold nanorods on the surface of crystals affected PA emission. Additionally, I also studied the behavior of PA in Yb^{3+} sensitized Pr^{3+}-doped nanocrystals under 852 nm and the influence of temperature on the visible PA emission. Furthermore, temperature measurements were conducted in crystals doped with Nd^{3+} ions under 1059 nm, but although anti-Stokes emission was observed and temperature dependent, no PA features were discovered.

PA is of particular interest in nanocrystals and microcrystals due to their unique size-dependent properties. These tiny crystalline structures, ranging from several nanometers to a dozen micrometers in diameter/length, exhibit remarkable optical properties that make them ideal candidates for harnessing the PA effect in the view of many potential applications in nano-bio-technology. PA can be used, among the other for (bio)sensing, (bio)imaging, optoelectronics, optical signal processing or optical computing. Materials demonstrating PA can also improve optical resolution in fluorescent microscopes and serve as luminescent nanothermometers with high relative temperature sensitivity. Some of these applications were also within the scope of my interest in the dissertation.

In summary, the scope of my interests in the dissertation covered wide range of activities in optical system design, versatile photophysical characterizations of various novel nano and micromaterials potentially capable to demonstrate photon avalanching phenomenon as well as evaluating their potential for luminescence thermometry and imaging applications.