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Title of the doctoral dissertation:
Synthesis, modeling and spectroscopic evaluation of selected Tm^{3+}, Pr^{3+}, Ho^{3+} doped and Yb^{3+} co-doped colloidal photon avalanching nanoparticles

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Abstract

Among different kinds of energy excitation upconversion (UC) processes, where the emitted photons have higher energy than the one absorbed, photon avalanche – PA is unique due to a highly nonlinear photoluminescence intensity increase in a response to a minute rise of photoexcitation source pump power density. As a result, the dependence of luminescence intensity in a function of pump power density exhibit a characteristic "S"-shape. A characteristic feature of PA process is a distinct PA pump power threshold (PA_{TH}), above which the luminescence intensity increases in highly nonlinear way following power law with power factor, slope (S) of the s-shaped curve, larger than 5. The PA itself, was first observed in the 1979 year in Pr^{3+} doped $LaCl_3$, which were investigated aiming to design of medium IR (MIR) photons quantum counter. From those times, the phenomenon became an interesting topic for many researchers, who have reported it in materials doped with different lanthanide ions. Initially, PA was investigated in bulk crystals, glasses and waveguides, mostly in cryogenic temperatures. However, it became clear that the observation of avalanche emission at the micro or nanoscale would enable a range of new applications of avalanche materials, such as use in bioimaging or in the design of active elements in biosensors. Until recently, obtaining the PA at nanoscale was a challenge, however PA emission was finally demonstrated in Tm^{3+} doped $NaYF_4$ nanocrystals at room temperature (RT) for the first time. The optimal concentration was found as 8% of Tm^{3+}. Typically, cross-relaxation (CR) processes, which are more efficient at high dopant concentrations, lead to luminescence concentration quenching and are competitive to emission or energy UC processes. However, in the case of avalanche emission, CR processes are highly desirable, because they increase an effectiveness

of a positive feedback (energy loop) leading to the multiplication of the population of the level responsible for effective absorption from the excited state. Beside Tm^{3+} doped, PA was observed also in Pr^{3+}, Yb^{3+} co-doped nanocrystals. Nevertheless, the impact of materials size on PA properties have not been studied before and the present dissertation reports it. Two sets of $LiYF_4$ crystals were prepared and studied – the behavior of crystals doped with 3% and 8% Tm^{3+} was compared, with size as a variable parameter. In the first case, nano and microcrystals were compared with the corresponding 3% Tm^{3+} doped single crystal. In the second case, nano and microcrystals with higher, 8% Tm^{3+} doping, were compared. In addition, the nanocrystals came in two versions – a doped core and identical nanocrystals whose surface as passivated with an undoped $LiYF_4$. The materials were excited by a single mode solid-state laser generating 1064 nm wavelength beam and the PA emission at 800 nm and 475 nm was observed. The characteristic properties of avalanche emission – nonlinearity and threshold were investigated. It has been observed that the PA threshold values decrease as the size of the test material increases, simultaneously, an increase in the slope of the "S" curve with decrease of the material size was observed. The presented results related to PA in Tm^{3+} doped crystals were enriched with modeling of the avalanche emission behavior aiming to understand a mechanism of PA observed in Tm^{3+} ions. A practical demonstration of avalanche nanoparticles (ANP) for sub-diffraction imaging was prepared in collaboration. Sub-diffraction imaging of core-shell nanocrystals doped with 3% of Tm^{3+} ions confirmed the possibility to achieve down to 125 nm spatial resolution.

The present dissertation include also the description of PA phenomenon observed in a Pr^{3+} (0.1%, 0.3%, 0.5% or 0.7%) and Yb^{3+} (15%) co-doped core and core-undoped shell $NaYF_4$ nanocrystals. The materials were excited with a single mode diode generating 852 nm wavelength beam and consequently the PA emissions at 482 nm and 607 nm were observed. While multicolor avalanche emission in materials co-doped with Yb^{3+} and Pr^{3+} ions has been previously demonstrated, the results presented in this dissertation contain important, new elements as well as enrich and clarify knowledge. Firstly, an influence of crystals architecture, namely core and core-shell on a PA properties was investigated. Moreover, the influence of broad Pr^{3+} ions concentration (0.1%, 0.3%, 0.5%, 0.7%) on the PA characteristics was reported. Furthermore, some articles wrongly assign the emission of Pr^{3+} ions around 610 nm as coming from the $^1D_2$ level. In a present work, the correct origin of the 607 emission in fluorides was

experimentally verified and attributed to the $^3P_0 \rightarrow {}^3H_6$ energy transition. Moreover, a relatively simple theoretical model of PA in a Pr^{3+}, Yb^{3+} co-doped system was prepared aiming to understand, how particular energy transitions influence the PA emission properties. The phenomenological model evidenced, that under excitation conditions studied here, PA is present only in a Pr^{3+} and Yb^{3+} co-doped materials, in contrast to singly Pr^{3+} doped materials. This feature was also confirmed experimentally. Namely, core and core-shell $NaYF_4$ nanocrystals singly doped with Pr^{3+} ions in a wide range concentration: 0.1%, 0.5%, 1%, 3%, 5%, and 8% were excited with 852 nm, however no emission was observed.

The present dissertation includes also investigations aiming to verify the possibility of obtaining PA in nanocrystals doped with other lanthanide ions. Characteristic features of PA phenomenon were observed in Tm^{3+} (3%, 8%) doped as well as 20% Yb^{3+} and Tm^{3+} (4% or 8%) co-doped cores-shell $NaYF_4$ nanocrystals under 1059 nm photoexcitation. Moreover, $NaYF_4$ nanocrystals doped with Ho^{3+} ions (0.5%, 2%) as well as co-doped with 20% Yb^{3+} and 0.5%, 1%, 2%, 4% or 8% of Ho^{3+} ions were investigated under 1059 nm and 980 nm photoexcitation, however these excitation condition were not suitable to generate PA emission. Furthermore, core and core-shell nanocrystals co-doped with 20% Yb^{3+} and Er^{3+} ions (2% and 20%) were synthesized and will be future investigated under appropriate photoexcitation scheme. In the aforementioned cases, where avalanche emission could not been observed, the most serious challenge is to choose the light excitation wavelength to meet the initial requirements (i.e. effective ESA and unlikely GSA). Learning about the behavior of PA at the micro- and nanoscale is essential to think about future applications of this phenomenon in many disciplines of (bio)technology and biomedical engineering. The presented results contributes to understanding of crystal size dependent PA characteristic properties, and although foreseeable to some extent, this has not been studied so far. The resulting knowledge enable a better understanding the PA mechanism, prediction of the PA features of synthesized materials, and thus the possibility of intentional design of the luminescent properties of these highly nonlinear (nano)phosphors.