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Analysis of upconversion nanoparticles as an active medium for upconversion light sources

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ABSTRACT

In the presented work, we investigated the optical and thermal stability of upconversion nanoparticles based on the three widely used matrices (NaYF₄, Y₂O₃, LaF₃). Analysis of the upconversion emission as a function of pump power density in a wide range revealed a multi-stage functional dependence. The stages of linear growing, saturation and degradation with both reversible and irreversible characters were discovered. For matrices of nanoparticles with low-temperature stability (NaYF₄), the dependence proves to be irreversible that could cause by a change in the structure and chemical composition of the matrix. Reversible dependence occurs in matrices with high-temperature stability (Y₂O₃ and LaF₃) and is caused by multiphonon nonradiative relaxation, which can be temperature-stimulated because of self-heating and low air-cooling of the crystal matrices with low thermal conductivity.

Keywords: upconversion, nanoparticles, luminescence, saturation, degradation, erbium, ytterbium

1. INTRODUCTION

Upconversion nanoparticles (UCNPs) have attracted much interest for many highly demanding applications in bioimaging, photonic devices, chemical sensing and photovoltaic devices due to their unique luminescence properties, which can be tailored by the parameters of the synthesis process and compositions. UCNPs are featured by large Stokes shift, sharp emission bands, high signal-to-noise ratio, and efficient conversion of low energy photon to high energy photon via nonlinear optical process compare to other fluorescent nanoparticles. Recently, it has been shown that under the certain conditions it is possible to establish a population inversion in UPCNs. This observation expands the list of further application towards coherent visible light sources. In terms of visible light lasers, UPNCs would be a very attractive approach due to single stage conversion of near-infrared light into multiple-band visible light in comparison to the existing complicated laser devices such as supercontinuum source.

For many technological applications including the gain material for coherent light sources, it is necessary to increase the efficiency of the upconversion (UC) process. The most efficient structure of UCNPs is a host matrix doped with sensitizer and activator, as which are usually used lanthanide ions. Ladder-like energy structure of lanthanides makes them an ideal material for light conversion to obtain multiple-band luminescence in a wide wavelength range. Excited by infrared radiation a sensitizer in UCNPs sequentially absorbs two or more low energy photons and re-emit in a visible range. Upconversion can be accomplished through several different mechanisms: excited-state absorption or multistep (sequential) absorption, energy transfer upconversion, cooperative sensitization upconversion, and photon avalanche. The chemical composition and structure of the UCNPs determine which mechanism will be dominating. Therefore, it is important to maintain a proper architecture of UCNPs to maximize the luminescence efficiency.

A material of the host matrix has a significant impact on the luminescence efficiency of UCNPs. It is commonly accepted that the host matrix should have as low as possible phonon energy to minimize the probability of non-radiative relaxation and, as a consequence, increase the efficiency of the upconversion process. However, for application in laser systems, for the gain material besides high quantum efficiency, it is essential to exhibit optical and thermal stability.

In the present work, we examined the optical and thermal stability of UCNPs under high pump fluence. We investigated the luminescent properties of nanoparticles with different host matrix compositions Y₂O₃;Yb,Er; NaYF₄;Yb,Er;...
LaF$_3$:Yb,Er in the temperature-dependent and excitation-power-dependent analysis. The study revealed multi-stage functional dependence of luminescence properties strongly correlated with the thermal properties of the matrix.

2. EXPERIMENT

In the experiment, we investigated NaYF$_4$, Y$_2$O$_3$ and LaF$_3$ upconversion nanoparticles doped with ytterbium and erbium. NaYF$_4$:Yb,Er nanoparticles were supplied by Inorganic Materials Chemistry research group (University of Turku, Finland). Nanoparticles were synthesized by the modified thermal co-precipitation method. The median nanoparticle size was 700 nm (Fig. 1a).

Y$_2$O$_3$:Yb,Er were commercially available nanoparticles (PTIR660/UF), which were synthesized by Phosphor Technology Ltd. (Stevenage, England). The percentage of lanthanides, as well as the method and parameters of the synthesis are the trade secret of the manufacturer. The median particle size is 2.5 μm (Fig. 1b).

The colloidal solution of LaF$_3$:Yb,Er crystalline nanoparticles was synthesized by hydrothermal - microwave treatment (HTMW) in Laboratory of Laser Spectroscopy (Institute of Physics, University of Tartu, Tartu, Estonia). Then aqueous colloid was placed on a substrate and dried in an oven at 900°C during 6 hours. Such post-processing is necessary to remove water from the nanoparticles, which quenches the luminescence. The average size of the nanoparticles was 25 nm (Fig. 1c). The content of rare earth elements in LaF$_3$:Yb,Er nanoparticles was as follows: 17 at.% of Yb$^{3+}$ and 3 at.% of Er$^{3+}$.

Fig. 1. SEM images of a) NaYF$_4$:Yb,Er, b) Y$_2$O$_3$:Yb,Er, c) LaF$_3$:Yb,Er nanoparticles.

Fig. 2. Schematically illustration of the setup for measuring the luminescence of UCNPs using 976 nm CW laser diode.
Powder containing UCNP was placed on a horizontal surface and irradiated with the laser beam (Fig. 2). A fiber coupled laser diode II-VI LC96Z600-76 operating in CW regime was chosen as a source of 976 nm pump light. To increase the power density of the exciting radiation, the laser beam was focused on the nanoparticles using a lens system over an area of 20 μm in diameter. After that emitted and reflected light was collected using multimode optical fiber with 200 μm core diameter. The measurements of emission spectra of the upconversion nanoparticles were performed using an optical spectrum analyzer within the range from 350 to 900 nm with 0.5 nm step size.

The emission spectra for NaYF₄:Yb,Er, Y₂O₃:Yb,Er, and LaF₃:Yb,Er UCNPs are shown in Figure 3. All spectra contain red (650 nm) and green (540 and 520 nm) peaks. Red band corresponds to the electronic \( ^{4}F_{9/2} \rightarrow ^{4}I_{15/2} \) transitions of erbium ion. Green band corresponds to the \( ^{4}S_{3/2} \rightarrow ^{4}I_{15/2} \) and \( ^{4}H_{11/2} \rightarrow ^{4}I_{15/2} \) transitions of the same ion. NaYF₄:Yb,Er also emits in violet (409 nm) spectral range. Due to the Stark effect, the energy levels of rare-earth ions are split in a crystalline field of host matrix, so each band contains several peaks.

Besides, the sets of spectra were measured at different pump power for all compositions at room temperature (23°C). Each peak in the spectra was integrated to quantify upconversion luminescence. Integrated values were normalized for comparison purpose. The resulting set of values shows the change in the intensity of the radiation as a function of the pump power density (Fig. 4). The lines are drawn as guides to the eye.

The dependences in Figure 4a correspond to a measurement in which pump power of laser diode increased from 0 to 470 W/mm² (curve 1), then decreased from 470 to 0 W/mm² (curve 2) and after that again increased from 0 to 470 W/mm² (curve 3). At low pump power density, NaYF₄:Yb,Er nanoparticles demonstrated grow of luminescence emission. However,
with a further increase in pump power density, the growth rate slowed down and saturation occurred at 300 W/cm\(^2\) (Fig. 4a). This behavior was observed at all emitted wavelengths. The pump power density exceeding 300 W/cm\(^2\) caused irreversible changes in nanoparticles: upconversion luminescence did not recover to the original intensity after decreasing pump power down to zero. This follows from the mismatch between the curves 1 and 3 in Figure 4a. The curves indicated by arrows 2 and 3 almost coincide, which means that irreversible changes have not occurred until a certain threshold was reached. However, an additional increase in the maximum pump power caused an intensify degradation of upconversion efficiency. Similar behavior was observed for other emission wavelengths.

For \(\text{Y}_2\text{O}_3: \text{Yb,Er}\), and \(\text{LaF}_3: \text{Yb,Er}\) nanoparticles only one cycle of measurement \(0 \rightarrow 470 \rightarrow 0\) W/mm\(^2\) was performed since the curves for forward and backward measurements perfectly coincide (Fig. 4b,c). At low excitation power upconversion emission intensity of \(\text{Y}_2\text{O}_3: \text{Yb,Er}\) grew with increasing pump power density and reached a maximum at 150 W/mm\(^2\) (Fig. 4b). Then a linear decline occurred. A reversible degradation of the upconversion emission (~10\%) was observed for all wavelengths. \(\text{LaF}_3: \text{Yb,Er}\) demonstrated much stronger degradation with exponential decay as seen from Fig. 4c. The position of the maxima for the peak at 521 nm differs due to phonon assistant process.

In the next experiment, we investigated properties of \(\text{NaYF}_4: \text{Yb,Er}\) in more detail. Figure 5 shows the results of three measurement cycles. In each of them the pump power density increased to a certain value and then decreased to zero. With each subsequent cycle, the value of the maximum pump power was stepwise increased in the following way \(410 \rightarrow 470 \rightarrow 530\) W/mm\(^2\). As a result, three hysteresis loops were obtained. The luminescence intensity decreased with each measurement cycle as can be seen from (Fig. 5). It should be noted that at low pump powers, the upper curve of each subsequent loop coincides with the lower curve of the previous loop, which indicates that permanent changes occurred in the \(\text{NaYF}_4: \text{Yb,Er}\) nanoparticles. The following mismatch of the curves appears as consequence that the saturation stage for each subsequent circle starts earlier and stays longer with grow of pump power.

Fig. 5. Dependences of the upconversion emission on the pump power density at room temperature for \(\text{NaYF}_4: \text{Yb,Er}\) nanoparticles for 3 measurement cycles.
We also performed a number of measurements at different temperatures. For these purposes, we used a Peltier element for cooling and heating of UCNPs. The nanoparticles were placed on the Peltier element, which was mounted on a heat sink. Sets of spectra were obtained at four different temperatures of the substrate (0, 20, 40, 60°C). Despite the fact that we could not measure the temperature of nanoparticles directly, this experiment allowed observation of the efficiency of the upconversion process depending on temperature change. The dependences of emission on pump power density at different temperatures of the Peltier element are depicted in Figure 6.

The pumping was carried out until the maximum of the upconversion luminescence (Emission axis) since a further increase of pump power could lead to some changes in nanoparticles. In other words, a relatively small pump power was used, which did not lead to any irreversible changes in nanoparticles. Thus, the samples remained unchanged and measurements made at different temperatures can be compared.

As shown in Figure 6, an increase in temperature led to a decrease of upconversion emission efficiency for all nanoparticles. The dependences for the 654, 541 nm peaks tend to saturate. While the dependence for the 521 nm peak is linear and almost does not depend on the substrate temperature. This can be explained by the fact that $^4S_{3/2}$ (541 nm) and $^4H_{11/2}$ (521 nm) energy levels are thermally coupled. Thus, increasing with temperature non-radiative relaxation from $^4H_{11/2}$ level is
compensated by phonon-assisted population from $^4S_{3/2}$ level. An increase in temperature led to a decrease in the luminescence intensity for all nanoparticle compositions. LaF$_3$:Yb,Er UCNPs demonstrated the strongest luminescence dependence on the temperature among the other samples, because of the lowest maximal phonon energy leading to the strongest temperature stimulation of multiphonon relaxation among presented crystal matrices.

3. STRUCTURAL STUDIES

Y$_2$O$_3$ and LaF$_3$ matrices are known as chemically and temperature stable materials. We did not observe irreversible processes in these compounds, and, therefore, we assumed that there were no structural changes. At the same time, irreversible upconversion degradation occurred with NaYF$_4$:Yb,Er. To identify the causes of this process we conducted a series of structural studies including Raman spectroscopy and energy-dispersive X-ray spectroscopy (EDS). EDS measurement demonstrated certain structural changes, whereas Raman spectra were oversaturated by luminescence background emission and Raman shifts could not be extracted from the obtained data.

![Fig. 7. Magnified SEM image of NaYF$_4$:Yb,Er nanoparticles with tagged areas of EDS measurement and table with percentage of elements in each area.](image)

The nanoparticles were arranged in the form of a flat layer on a substrate and then annealed with a 980 nm pump laser. The substrate with nanoparticles moved along a straight line. In Figure 7, a white rectangle shows a region, which was annealed by the laser. The numbering of the regions in Figure 7 corresponds to the numbering in the table. As can be seen, annealing led to a decrease in the fraction of fluorine and an increase in the fraction of oxygen in the sequence of regions $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$ (region #0 is the reference and contained only original nanoparticles). Thus, intense laser radiation could lead to the formation of an oxide in the NaYF$_4$ matrix. However, we should point out that the surface roughness of the measured areas 0-4 was varied significantly, what could affect the measurement results due to the high sensitivity of the measurement technique to this parameter. The further study by other technique less sensitive to the sample roughness like XFR is required to confirm this observation.

4. RESULTS AND DISCUSSION

The main difficulty in analyzing the upconversion mechanism is that a large number of radiative and non-radiative processes occur simultaneously. Each of them is responsible for the mechanisms that facilitate or hinder the upconversion efficiency. For example, overall upconversion efficiency also decreases if doping concentration exceeds the optimal value.
An increase of concentration shortens the distance between sensitizers that promote energy migration between sensitizers and cross-relaxation between activators. This effect is known as concentration quenching.\textsuperscript{12} Also, non-radiative processes strongly depend on the phonon energies of the host matrix. The more phonons involved in the conversion of optical radiation into vibrational energy of the crystal lattice, the less is the probability of the multi-phonon relaxation process.\textsuperscript{15} By the same mechanism, impurities increase the probability of multi-phonon relaxation. For example, hydroxyl group OH has phonon energy (~3500 cm\textsuperscript{-1}) that is an order of magnitude higher than that of the host matrix.\textsuperscript{16} It worth noting that nanoparticles with identical chemical composition may have different crystal symmetry, and, as a consequence, different upconversion properties. In particular, a $\beta$-hexagonal phase of NaYF\textsubscript{4} has higher upconversion efficiency compared with $\alpha$-cubic phase.\textsuperscript{17-19}

Table 1 shows the physical properties of these matrices.

Table 1. The phonon energy of the matrices, their melting points and thermal conductivities.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Phonon energy, cm\textsuperscript{-1}</th>
<th>Melting point, °C</th>
<th>Thermal conductivity at 300K, W/(m\textperiodcentered K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaYF\textsubscript{4}</td>
<td>350\textsuperscript{20}, ~360 (~45 meV)\textsuperscript{21,22}</td>
<td>638-975 (depending on composition)\textsuperscript{24}</td>
<td>0.9-2.5\textsuperscript{23}</td>
</tr>
<tr>
<td>Y\textsubscript{2}O\textsubscript{3}</td>
<td>550\textsuperscript{25}</td>
<td>2425</td>
<td>27\textsuperscript{26}</td>
</tr>
<tr>
<td>LaF\textsubscript{3}</td>
<td>300\textsuperscript{22}, 350\textsuperscript{27}</td>
<td>1493</td>
<td>5.1\textsuperscript{26}</td>
</tr>
</tbody>
</table>

Among investigated samples, only in case of NaYF\textsubscript{4}:Yb,Er nanoparticles the dependencies of emission on pump power density were irreversibl, which means that there were structural changes in the investigated material. Low thermal stability and conductivity of the host matrix play a major role in this phenomenon. Starting from a certain threshold, the pump power led not only to higher excitation but also overheating of UCNPs. Based on the results of microscope study, we can conclude that laser-induced heating caused the melting of the samples and suggest possible evaporation of fluorine and oxidation of host matrix (table in Fig. 7). Since the melting point and thermal conductivity are quite low (~693-800°C and 0.9-2.5 W/(m\textperiodcentered K)), NaYF\textsubscript{4} was more susceptible to overheating among other UCNPs samples.

Melting points of Y\textsubscript{2}O\textsubscript{3}:Yb,Er, and LaF\textsubscript{3}:Yb,Er are high enough (1493°C and 2425°C, respectively) to withstand intense laser pumping. High thermal stability prevents changes of chemical composition, melting and aggregate state under the influence of laser radiation. Reversible degradation is associated with multiphonon relaxation in these materials. As soon as the pump power decreases, they cool down and restore their upconversion properties. It should be noted that the magnitude of the degradation correlates with the thermal conductivity of the material. Y\textsubscript{2}O\textsubscript{3}:Yb,Er loses 10% of upconversion efficiency having a thermal conductivity of 27 W/(m\textperiodcentered K), while LaF\textsubscript{3}:Yb,Er loses almost 75% having lower thermal conductivity of 5.1 W/(m\textperiodcentered K). This can be explained by the fact that the matrix with a higher thermal conductivity more efficiently dissipates heat induced by the laser pump, therefore, a phonon-induced process is less manifested regardless of the phonon energy value.

5. CONCLUSION

In conclusion, analysis of the upconversion emission as a function of pump power density in a wide range revealed a multi-stage functional dependence. This data are essential knowledge for the efficient light source application of nanoparticles. The stages of linear growing, saturation and degradation with both reversible (Y\textsubscript{2}O\textsubscript{3} and LaF\textsubscript{3} matrices) and irreversible (NaYF\textsubscript{4}) characters were observed. We conducted structural studies of NaYF\textsubscript{4}:Yb,Er nanoparticles and suggested that irreversible degradation is caused by the sequential change of the structure and chemical composition of the matrix under the influence of high-power laser radiation in the ambient environment. In the case of the reversible degradation multiphonon nonradiative relaxation plays the primary role in reducing the intensity of the upconversion luminescence. The type of degradation is defined mainly by the physical properties of the matrix, i.e. its temperature stability (melting point) and thermal conductivity. The behavior of Y\textsubscript{2}O\textsubscript{3}:Yb,Er micro powder illustrates that matrix with higher thermal conductivity more effectively removes laser-induced heat and reduces the degradation of upconversion luminescence.
AKNOWLEDGEMENTS

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