Raport stiintific

privind implementarea proiectului in 290/05.11.2011 perioada ianuarie-decembrie 2016

Within the actual stage we have continued with the morphological characterisation and the study of up-conversion effects (by avalanche) shown by (Ho^{3+}-Er^{3+}) doped SiO_2-$YLiF_4$ glass-ceramics

Morphological characterisation of the glass-ceramics nanorods has been made by using scanning electron microscopy (SEM) and elemental analysis (Energy Dispersive X-ray Spectroscopy-EDX) measurements. Previous SEM images of the glass ceramic microrods recorded at two different magnifications have shown an uniform distribution of microrods of about 0.8μm diameter and 10 μm length with nanostructures of about 60-70nm inside them.

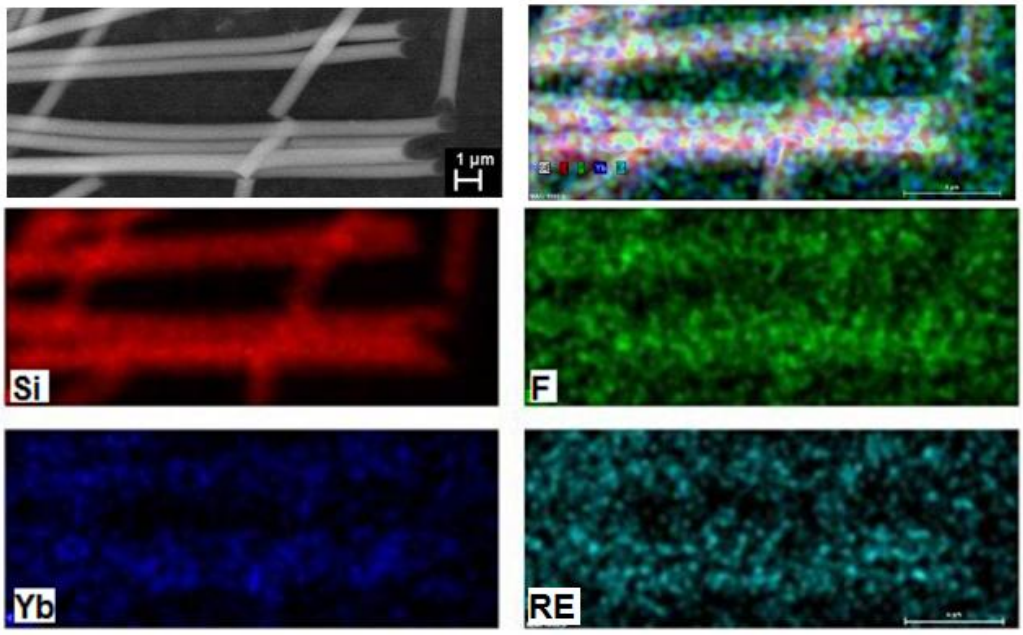

Figure 2. SEM image of the glass-ceramic microrods by comparison to the elements distribution obtained by the EDX measurements.

As can be observed in the Figure 1 elements distribution characterization has shown a uniform distribution of the elements within the microrods.

The upconversion "avalanche" mechanism of the green upconversion emission of Ho-Yb doped $LiYF_4$.

The "up-conversion" avalanche mechanism denotes a particular type of upconversion [E. Osiac, I. Sokolska and S. Kuck PHYSICAL REVIEW B, VOLUME 65, 235119]. In such a process, weak ground state absorption (GSA) leads to a small population in an intermediate level, the so-called "reservoir level". The ESA process from this reservoir level is very strong, thus bringing the excitation in the emitting level. An efficient feed-back mechanism, e.g. cross relaxation (CR),

connects the emitting level, the reservoir level and the ground level, thus enhancing efficiently the population in the reservoir level. There are several "signatures" of the avalanche mechanism: first, the pump power dependence in logarithmic scale of the up-converted emission shows a specific shape beginning with a slope of 2, than around a threshold value of the pump rate a powerful increase with a slope larger than 2 occurs, which is finally followed at high pump powers by a saturation behavior.

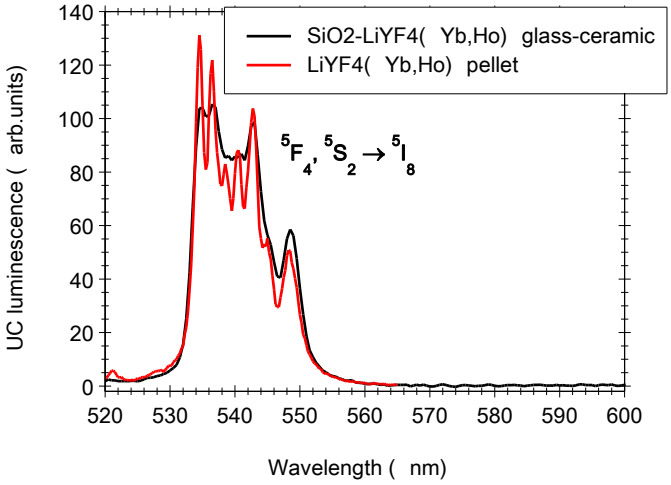

Figure 2. "Up-conversion" luminescence spectra recorded on (Ho^{3+}-Er^{3+}) doped SiO_2-$LiYF_4$ glass-ceramics and pellet under 810nm laser light pumping.

In order to make the avalanche mechanism more efficient we have codoped the Ho^{3+}:YLiF4 system with Yb^{3+}. The Yb^{3+}-ion is one of the most used sensitizer. It is very easily introduced in large concentrations in an appropriate assuring a good homogeneity of the Ho^{3+}-Yb^{3+} system due to the energy migration process inside the Yb^{3+} ion system. In a Ho^{3+}-Yb^{3+} codoped material, the upconversion mechanism is rather complex because in addition to the processes among Ho^{3+} ions, energy-transfer and back-transfer channels between the two kinds of ions.

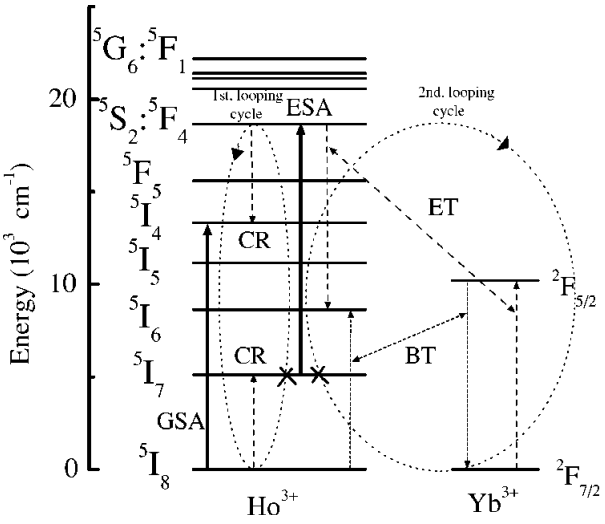

Figure 2. Energy levels scheme of Ho^{3+} and Yb^{3+} ions. The upconversion process leading to the ($^5F_4$, $^5S_2$) → $^5I_8$) "green" luminescence and the two looping cycles that feed the $^5I_7$ intermediate level are indicated.

The upconversion mechanism of the green upconversion emission (($^5F_4$, $^5S_2$) → $^5I_8$) of Ho-Yb doped systems upon excitation at around 810 nm, see Fig. 1 starts with a weak GSA to the $^5I_4$ level, which relaxes non radiatively to the $^5I_6$ and, then, radiative and nonradiative deexcitation to the $^5I_7$ level takes place [F. Lahoz et al. PHYSICAL REVIEW B 71, 045115 (2005)]. One Ho $LiYF_4$(Yb4%, Ho1%) ion in the $^5I_7$ excited level can absorb an excitation photon (ESA: $^5I_7 \rightarrow {}^5S_2 : {}^5F_4$ transition), which brings the Ho3+ ion to the $^5S2 : {}^5F_4$ level. From this level two relaxation channels are possible. One is cross-relaxatio (CR) process between Ho^{3+} ions [CR: ($^5S_2 : 5F_4$, $^5I_8$) → ($^5I_7$, $^5I_4$)] . Another is $Ho^{3+} \rightarrow Yb^{3+}$ energy transfer (ET) and $Yb^{3+} \rightarrow Ho^{3+}$ back transfer [ET: ($^5S_2 : {}^5F_4$, $^2F_{7/2}$)→ ($^5I_6$, $^2F_{5/2}$) and BT: ($^2F_{5/2}$, $^5I_8$) → ($^2F_{7/2}$, $^5I_6$)]. The Ho^{3+} ions in the $^5I_6$ relax to the $^5I_7$ level and a new ESA can occur, repeating the mechanism in a cycle. It can be observed that two looping cycles compete in feeding the 5I7 intermediate level. The first one takes place between Ho^{3+} ions, while the second one needs the assistance of Yb^{3+} ions to happen.

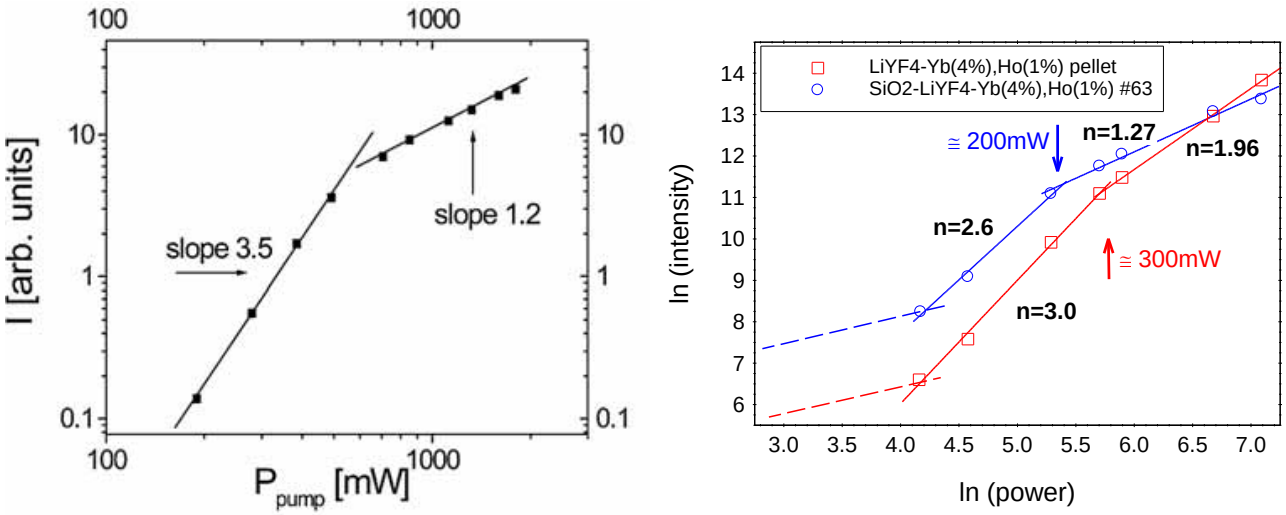

Fig. 5 – Pump power dependence in logarithmic scale of the (($^5F_4$, $^5S_2$) → $^5I_8$) green emission for $LiYF_4$(Yb, Ho) crystal (left) and a SiO_2-$LiYF_4$(Yb,Ho) glass ceramic and a $LiYF_4$(Yb4%, Ho1%) pellet under 810 nm excitation.

In order to prove the existence of the avalanche mechanism in the Ho-Yb glass-ceramic system the pump power dependence of the green emission intensity were registered for both 810 nm laser light pumping by comparison to the $LiYF_4$(Yb,Ho) pellet the results being presented in the and are presented in Figure 5. As the efficiency of the processes is very low the studies were performed on glass-ceramic powders supposing that the mechanism is similar. It can be observed that the threshold to the "saturation" regime is higher for the pellet (about 300mW) compared to the glass ceramic (about 200mW) and we might suppose that the same happens with the energy avalanche „treshold".

Theoretical analysis based on gain/losses of the $^5I_7$ (aprox. 5000cm^{-1}) level according to the pumping „loops" depicted in the Figure 2 has shown that the energy avalanche „treshold" is given by:

$$P_{\text{th}}(mW) = 2.64 \times 10^{-16} \frac{LS}{K\sigma_{\text{ESA}}}.$$

where σ_{ESA} represents the ESA process cross-section, *S* is the laser spot size and *K* constant can be calculated (from the probablility rates of the CR, ET and BT processes). Supposing that both σ_{ESA} and *S* have about the same values (the experimental parameters being the same) it means that the smaller value of the energy avalanche „threshold" for the glass ceramic is related to a higher value of the *K* constant. This one is strongly deopendent on the Yb^{3+} concentration and increases with this one. Therefore we assign the smaler value of the energy avalanche „threshold" for the glass ceramic to a high „*local*" concentration of the Yb^{3+} ions within the glass ceramic; the same conclusion was reached for the Eu^{3+} doped glass ceramic powder or nano-rods. This explanation agres with the reduction of the avalanche pump power threshold experimentally observed when the Yb^{3+} concentration increases. As we observed that in the glass-ceramic rods the Eu^{3+} „*local*" concentration might be even higher than in the bulk, it might be expected that the threshold to be even smaller for the glass-ceramic nanorods.

In conclusion, we have observed the up-conversion „avalanche" luminescence properties of Ho^{3+}/Er^{3+} co-doped SiO_2-$LiYF_4$ glass ceramic and we compared to the pellet. Laser pump power dependencies of UC are similar for the two cases and showed a slightly smaller value for the glass ceramic, an experimental fact assigned to a higher „local" Yb^{3+} concentration.

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