ACTIVITY REPORT 2014

Project no. 290/05.11.2011

2014. Optimisation of the optical properties of the Eu^{3+}-doped SiO_2-$YLiF_4$ glass-ceramics nanorods.

During this stage of he project we have continued with the investigations of the optical properties of the SiO_2-$YLiF_4$ glass-ceramics nanorods and we started the study the „up-conversion" properties of the Eu^{3+}-doped $YLiF_4$ nanocrystals in silicate glass matrix.

Synthesis. Eu^{3+}-doped doped $LiYF_4$ glass-ceramics nanorods have been prepared by using the template method and nanoporous polycarbonate membranes (pore diameter size about 800nm), obtained by heavy ion irradiation and chemical etching.

Photoluminescence measurements has been used to track the crystallization processes by using Eu^{3+}-dopant ion as "sample probe" since its incorporation inside the nanocrystallites induces drastic modifications of the luminescence spectra like an increase of the luminescence intensity and structuring of the spectra.The PL spectra in both *bulk and rods xerogel* are quite similar, and the Eu^{3+} ions are embedded in the pores of a three-dimensional SiO_2 macromolecule with a coordination symmetry around the ions close to the $\underline{D}_{3h}$. During ceramization at 800 °C silica network is formed due to the progressive enhancement of dehydration-condensation reactions. This process is accompanied by the precipitation of the $LiYF_4$ nanocrystals in the glass-ceramic microrods.

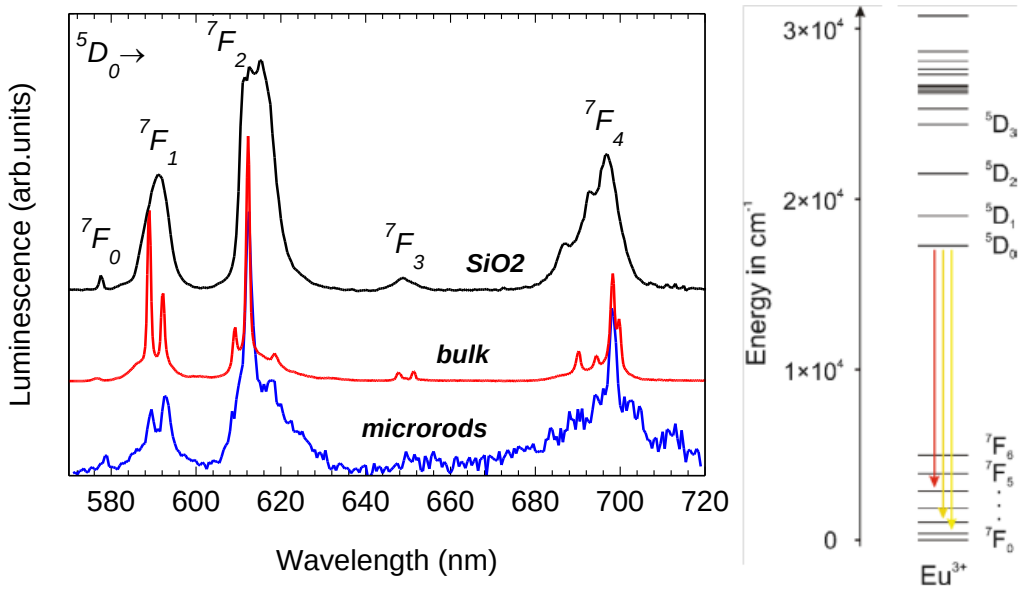

Figure 1. Normalised photoluminescence spectra recorded on Eu^{3+}-doped glass ceramic bulk and microrods by comparison to the silica glass using 394 nm excitation; $^5D_0 \rightarrow {}^7F_J$ transitions (J=1-4) of the Eu^{3+}-ion are indicated.

The Stark splitting of the PL bands which is due to the degeneracy level removal by the crystal field indicating that a number of Eu^{3+}-ions are taken inside the nanocrystals. The measurements have indicated that the precipitation mechanism of the nanocrystals in the glass-ceramic microrods and in the bulk glass-ceramic is quite similar.

Photoluminescence spectra and decay curves recorded in the Eu^{3+}-doped SiO_2-$LiYF_4$ glass ceramic bulk and rods have been discussed using group-theoretical arguments. The photoluminescence spectra are very similar in the glass ceramic "bulk" or microds (Figure 1) indicating a close environment in both cases; Eu^{3+} ions are embedded dominantly inside the $LiYF_4$ nanocrystals most probably as Eu-O center and/or dimer centers in low symmetry (C_{2v}) sites; oxygen ions were incorporated in their neighborhood during the glass ceramization.

Time resolved photoluminescence measurements provide valuable information about the non-radiative rates. We have observed differences in the photoluminescence lifetimes recorded on the glass-ceramic nanorods compared to the "bulk" (Figure 2).

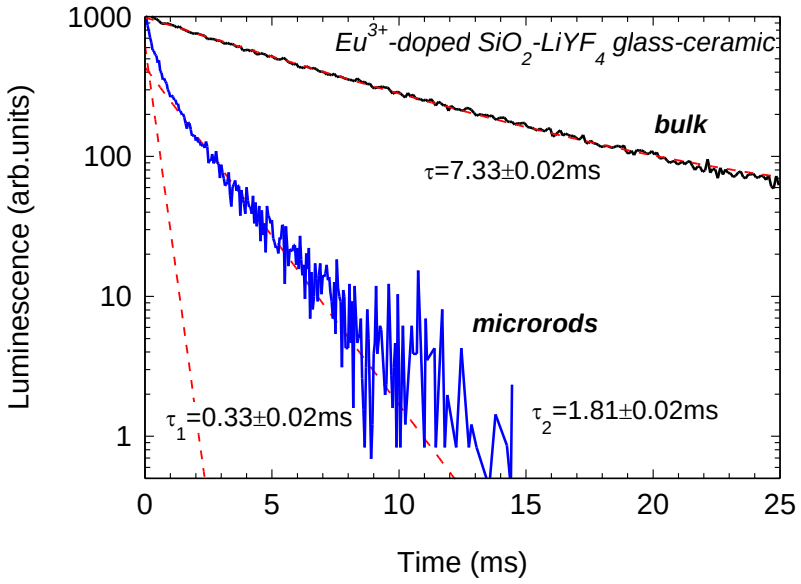

Figure 2. Photoluminescence decays (solid curves) recorded at 617 nm on Eu^{3+}-doped SiO_2-$LiYF_4$ glass ceramic bulk and microrods. and $LiYF_4$ pellet (solid curves); the decays were fitted with single exponential decays (dotted curves).

In the first case there are two characteristic times; the shorter time of 0.33ms was assigned to the radiative decay of the Eu^{3+} ions in the silicate glass matrix (being close to values obtained in the silicate xerogels) and the longer time of 1.81ms to the Eu^{3+} ions present in the nanocrystals. The last value is much shorter than that recorded in the Eu^{3+}-doped SiO_2-$LiYF_4$ glass ceramic "bulk" of about 7.3ms indicating higher non-radiative decay rates in the nanorods.

In order to get a deeper insight on the luminescence properties of the Eu^{3+}-doped SiO_2–$LiYF_4$ Glass-ceramic microrods and bulk glass-ceramic we will use the Judd–Ofelt theory. This theory is widely used to compute the JO intensity parameters $\Omega_{2,\ 4,\ 6}$ and the coefficient of spontaneous emission (radiative) *A* of the *J-J'* transition. Then it can predicted important radiative properties of Ln^{3+} ions in host matrix as the relative contribution to the emission spectrum (the branching ratio β) for any of the rare-earth transitions as well as the radiative lifetime (τ_R). In the particulat case of Eu^{3+} ions the coefficient of spontaneous emission (radiative) *A* of the *J-J'* transition can be computed from the photoluminescence spectra and photoluminescence lifetimes measurements; the results are tabulated in the Table below.

Table. Decay rates of radiative (A_{rad}), non-radiative (A_{nrad}) and total (A_{tot}) processes of $^5D_0 \rightarrow {}^7F_J$ transitions, luminescence lifetimes (τ) and quantum efficiencies (η)

Sample	$A_{rad}(s^{-1})$	$A_{nrad}(s^{-1})$	$A_{tot}(s^{-1})$	τ **(ms)**	η **(%)**
SiO_2 -$LiYF_4$- Eu^{3+} glass ceramic (microrods)	221	831	1052	0.95	15
SiO_2 -$LiYF_4$- Eu^{3+} glass ceramic (bulk)	130	9	139	7.33	95
SiO_2-Eu^{3+} glass	232	1018	1250	0.8	19
Eu^{3+}-doped SiO_2 -$LiYF_4$ (pellet)	120	2	122	8.16	100

As can be seen in the table, the non-radiatie rate is much higher in the glass ceramic rods compared to the bulk that they might be related to the quasi-unidimensional morphology of the nanorods: there might be an influence of the dimensional constraints imposed by the membrane pores during xerogel formation and subsequent glass ceramization.

Up-conversion (UC) luminescence is a process in which the sequential absorption of two or more photons leads to the emission of light at shorter wavelength than the excitation wavelength (Figure 3); it is an anti-Stokes type emission.

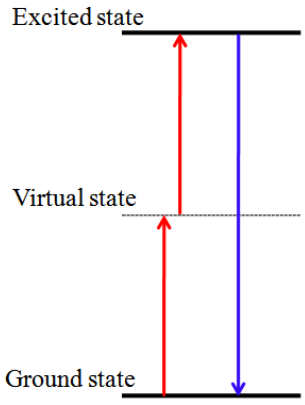

Figure 3 Graphic representation of the „up-conversion" phenomenon.

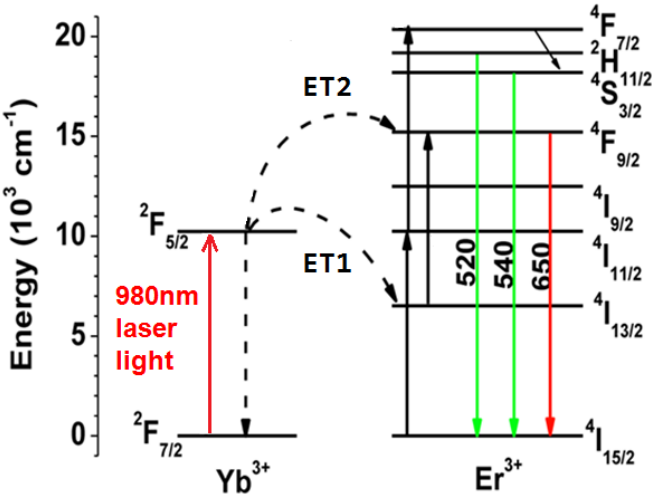

Figure 4 Figure 3 Graphic representation of the mechanism involved in the „up-conversion" phenomenon in the Yb-Er doped systems.

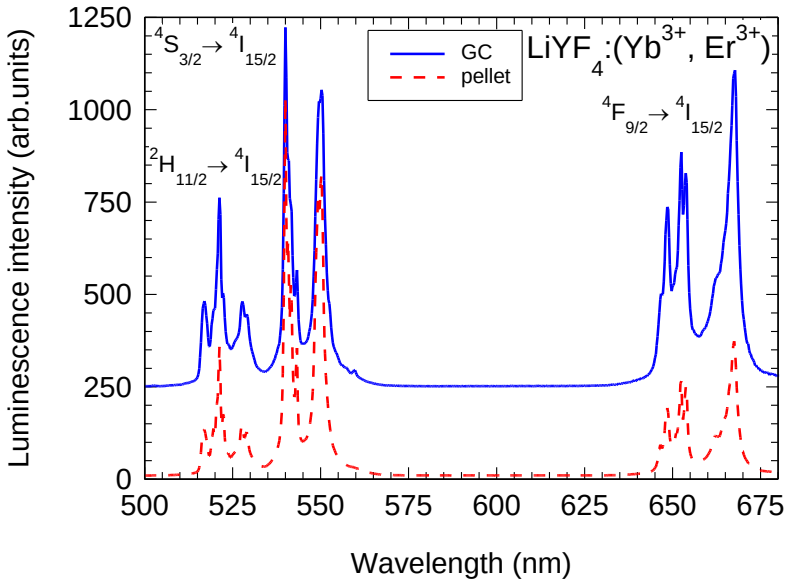

Figure 5. „Up-conversion" spectra recorded on SiO_2-$LiYF_4$: (Yb^{3+},Er^{3+}) glass ceramic and pellet.

We have started the investigation of the UC properties of the **(**Er3+-Yb3+) doped YLiF glass-ceramic; preliminary measurements have shown UC luminescence on the (Yb,Er)-doped SiO_2-$LiYF_4$ glass ceramic (Figure 5).

In conclusion glass-ceramics microrods containing Eu^{3+}-doped $LiYF_4$ nanocrystals have been prepared by using sol-gel chemistry within the pores of a polycarbonate template membrane. Photoluminescence spectra and decay curves recorded in the Eu^{3+}-doped SiO_2-$LiYF_4$ glass ceramic bulk and rods have been discussed using group-theoretical arguments. As the photoluminescence spectra are very similar both cases this indicates a similar environment of Eu^{3+} ions: they are

embedded dominantly inside the $LiYF_4$ nanocrystals in low symmetry (C_{2v}) sites.The measurements have indicated that the precipitation mechanism of the nanocrystals in the glass-ceramic microrods and in the bulk glass-ceramic is quite similar. the non-radiatie decay processes are much higher in the glass ceramic rods compared to the bulk an effect that might be related to the quasi-unidimensional morphology of the nanorods, i.e an influence of the dimensional constraints imposed by the membrane pores during xerogel formation and subsequent glass ceramization.

References:

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3. *„Up-conversion luminescence of Er^{3+}/Yb^{3+} co-doped $LiYF_4$ nanocrystals in sol-gel derived oxyfluoride glass-ceramics"*

C.E. Secu and M. Secu (submitted to Journal of Alloys and Compounds (2014)

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