ACTIVITY REPORT 2013

Project no. 290/05.11.2011

2013. Optimisation of the optical properties of the Eu^{3+}-doped SiO_2-$YLiF_4$ glass-ceramics nanorods.

Preparation of the glass-ceramics nanorods with different diameters

Eu^{3+}-doped doped $LiYF_4$ glass-ceramics nanorods have been prepared by using the template method and nanoporous polycarbonate membranes (pore diameter size 100, 200 and 800nm), obtained by heavy ion irradiation and chemical etching. The method implies the filling of the pores of the membrane and nanorods/nanowires followed by its separation by dissolving. RE-doped gels have been prepared by using tetraethylorthosilicate (TEOS) as precursor and trifluoroacetic acid (TFA) as fluorine agent. As in this phase the gel is liquid the nanoporous polycarbonate membranes will be used as templates for "growing" RE-doped nanorods from the gel. In the present case the filling process of the pores was carried out by capillarity forces because of the low viscosity of the gel and its fast solidification. After drying of the gel (by forming the xerogel) inside the pores the membrane was removed by dissolving and we have obtained the xerogel nanorods.

Morphological and structural characterisation of the glass-ceramics nanorods

During drying of the xerogel microrods followed by annealing at high temperatures, the liquid located within the gel pores was released and we have observed the volume contraction of the rods to about 35% of the initial value which is restricted mostly on the rod length. However a cracking due to the stress arising from the volume contraction was not observed the rods retaining their morphology (Figure 1) even for smaller diameters down to 100nm.

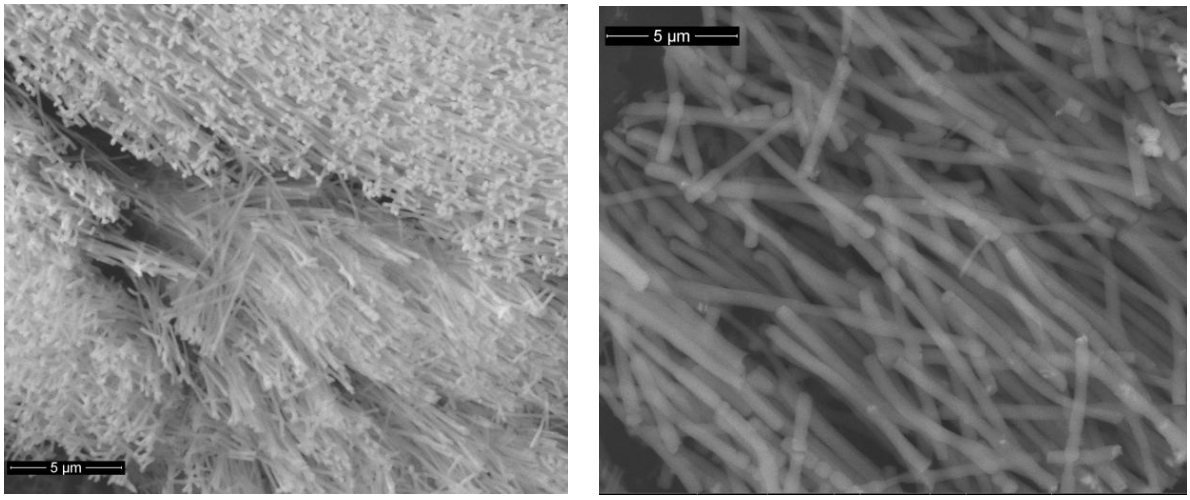

Figure 1. Electron microscopy (SEM) images of the glass-ceramic rods of 100nm and 200nm diameters.

Previous studies (in the 2012 year) perfomed by using transmission electron microscopy and X-ray difraction have indicated the formation of Eu^{3+}-doped $LiYF_4$ nano-crystals inside the glass ceramic microrods with a relatively wide distribution of about tens of nm size.

As the morphology of the glass ceramic rods is preserved even for smaller diameters is quite understandable to suppose that these nanocrystals are formed also for these ones (see Fig. 1) by the same crystallization mechanism. Moroever the small quantities of the material (glass ceramic rods) and sensitivity of the x-ray diffraction technique (of about 2-3%) did not allow to measure the LiYF4 crystallized fraction within the rods and therefore these studies have been performed on "bulk"(powder samples) based on the supposition that the crystallization processes are the same within the "bulk" and rods. This means that we admit that the crystallized fraction (its value) does not depend on the glass ceramic rods size (diameter) but only on the molar composition because the crystallization mechanism involves the formation of the nucleating centres (resulted from the Li and Y acetates at about 300^{o}C) followed by $LiYF_4$ nanocrystalline phase formation.

In order to study ***the influence of the crystallized fraction*** we have prepared SiO_2-$LiYF_4$ doped with Eu^{3+} glass ceramics (as "bulk") with different crystallized fraction. By using different molar ratio Eu:Y:Li:Si we can prepare glass ceramics with different crystallized fraction (see Figure 2 and table). For the crystallized fraction we have computed the ratio from the surface below the LiYF4 diffraction peaks and the whole surface below the entire diffraction pattern.

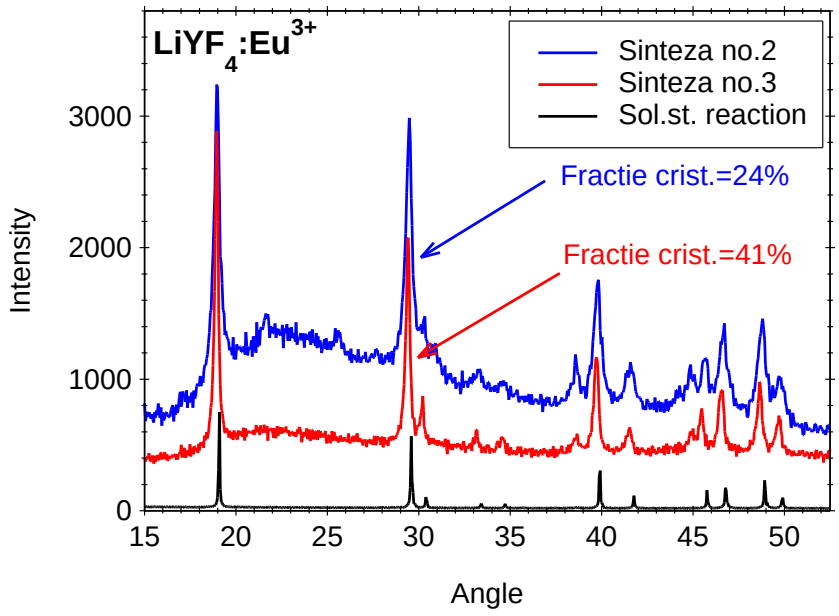

Figura 2. X-ray diffraction patterns of the SiO_2-$LiYF_4$ doped with cu Eu^{3+} (bulk) glass ceramics by comparison to the Eu^{3+} $LiYF_4$ pellet obtained by solid state reaction.

Table

	Molar ratio Eu:Y:Li:Si	**Nature of the crystallized fraction (from XRD)**	**Crystallized fraction (%)** (2teta=0-50)
1	1 : 6.5 : 6.5 : 86	Faza YF_3	**10%**
2	1 : 5.5 : 21.5 : 72	Dominant $LiYF_4$ with Y_2SiO_7	**24%**
3	1 : 10 : 30 : 59.5	Only $LiYF_4$	**41%**

It can be seen that the *nature* of the crystallized phase depends on the Y-Li molar ratio but *its value* depends on the molar ratio between Si and O that has an great influence on the SiO_2 amorphous phase.

Regardind ***the influence of the dopant concentration*** we have measured X-ray diffraction patterns for glass ceramics with different Eu^{3+} concentrations up to 5% (Figure 3). We have observed strong similarities of the patterns that indicates the formation of the $LiYF_4$ nanocrystalline phase. On the other hand, and more important (!), we have not observed new peaks that might be associsted to the formation of other additional/complex phases. These results show a high solubility of the Eu^{3+} ions in the nanocrystallized fraction.

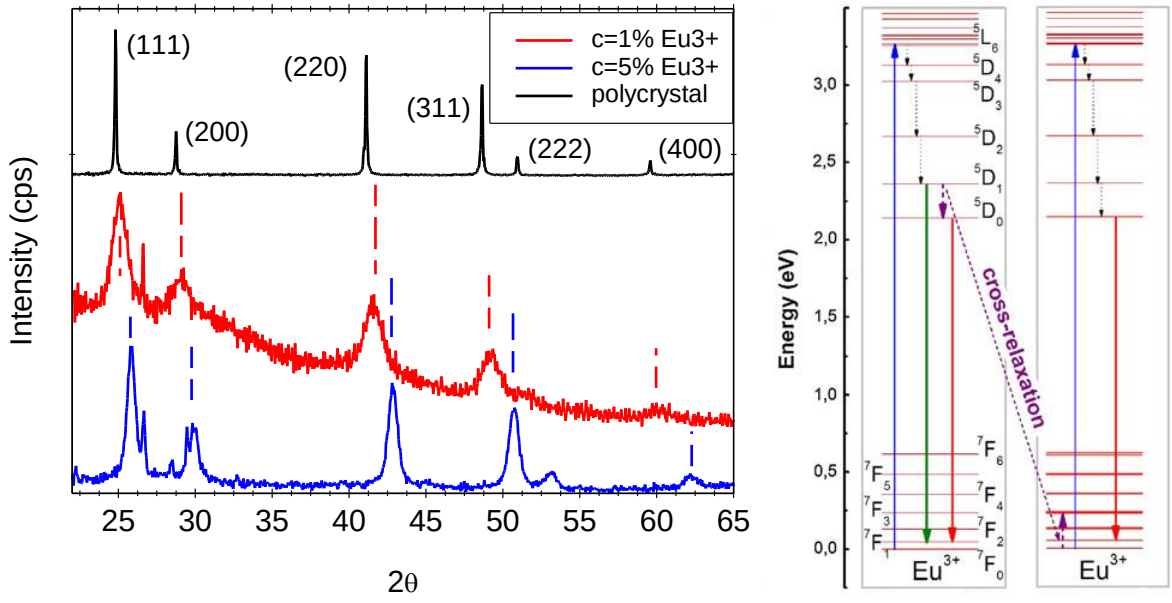

Figura 3. X-ray diffraction patterns of the SiO_2-$LiYF_4$ doped with cu Eu^{3+} (bulk) glass ceramics for two different concentrations by comparison to the undoped polycrystal (left); graphic representation of the "cross-relaxation" processes between two Eu^{3+} ions as a pair.

On the other hand even at 1% dopant concentration there are agglomeration processes of the ions responsible for the Eu^{3+} ions local symmetry descending from de la (S_4) la (C_{2v}). Apparently 1% concentration is small but if we take into account the fraction of the $LiYF_4$ phase the "effective" concentration might reach 20% according to the compositional formula $5LiYF_4$-$1EuF_3$ and this might induce the quenching of the luminescence sigmal by "cross-relaxation" effects (Figure 3).

In conclusion, glass-ceramics microrods with different size and containing Eu^{3+}-doped $LiYF_4$ nanocrystals have been prepared by using sol-gel chemistry within the pores of a polycarbonate template membrane. Photoluminescence measurements have indicated the Eu^{3+}-ions incorporation inside the $LiYF_4$ nanocrystals

References:

1. ***"Eu3+ probe ion for rare-earth dopant site structure in sol-gel derived LiYF4 oxyfluoride glass-ceramic"***

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