ACTIVITY REPORT 2012

Project no. 290 din 05/10/2011

2012. Preparation and characterization of the Eu^{3+}-$YLiF_4$ (YLiF) glass-ceramics nanorods.

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. 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. 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 2).

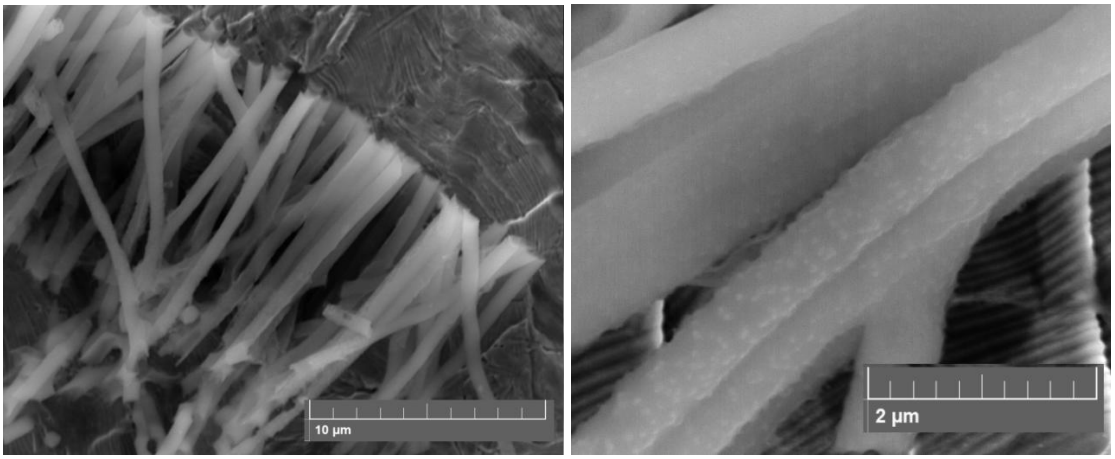

Figure 2 Electron microscopy (SEM) images of the glass-ceramic rods (800nm diameter) recorded at two different magnifications.

Regarding the annealing temperature required for the glass ceramization we have used thermal analysis measurements (Figure 3). In the temperature range from 280 to 360°C we observed a DSC peak at 360°C that was assigned to the decomposition of yttrium trifluoacetate $Y(CF_3COO)_3$ and lithium trifluoacetate ($Li(CF_3COO)$ with the formation of YF_3 and LiF, respectively, accompanied by a weight loss (≈10% mass percent). At 530°C a small but well defined DSC can be observed accompanied by a weight loss (≈1% mass percent). It has been tentatively attributed to crystallization of the $LiYF_4$ nanocrystals (as XRD measurements will show).

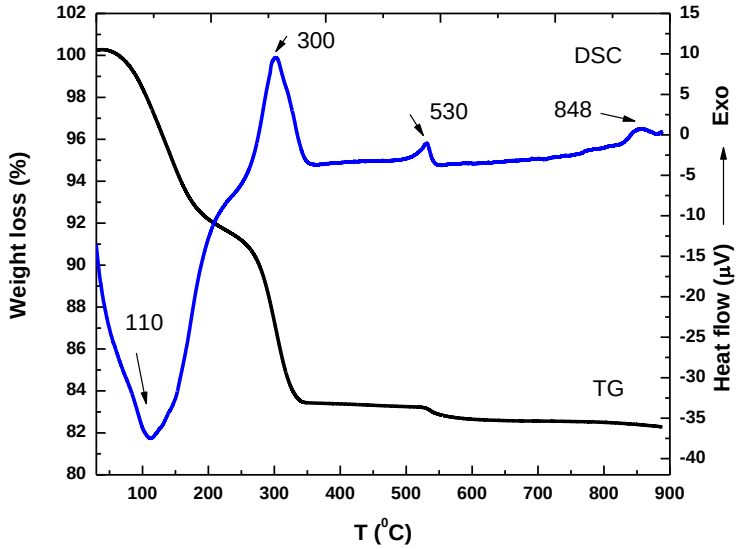

Figure 3. DSC-TG curves recorded on Eu-doped SiO_2-$LiYF_4$ xerogel.

X-ray electron diffraction and Electron microscopy measurements (TEM) have been used to put in evidence and identify the nature of the nanocrystals (Figures 4-5).

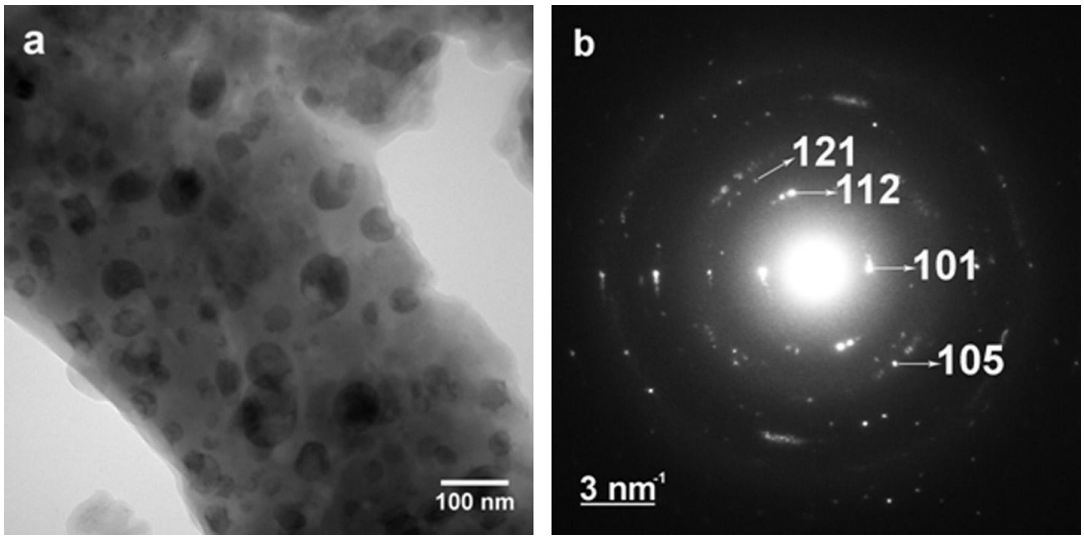

Figure 4 Transmission electron microscopy images of the Eu^{3+}-doped doped $LiYF_4$ glass-ceramics; Miller indices of the main diffraction rings of $LiYF_4$ phase are indicated.

The TEM image of a glass ceramic sample grain containing embedded Eu^{3+}-doped $LiYF_4$ nano-crystals is shown in the Fig. 4. We have observed a distribution of nanocrystals of about tens of nm size. The corresponding Selected Area Electron Diffraction (SAED) pattern in proves the formation of the $LiYF_4$ phase (S.G. $I4_1/a$ (No. 88), *a*= b= 5.164 nm, c= 10.741 nm).

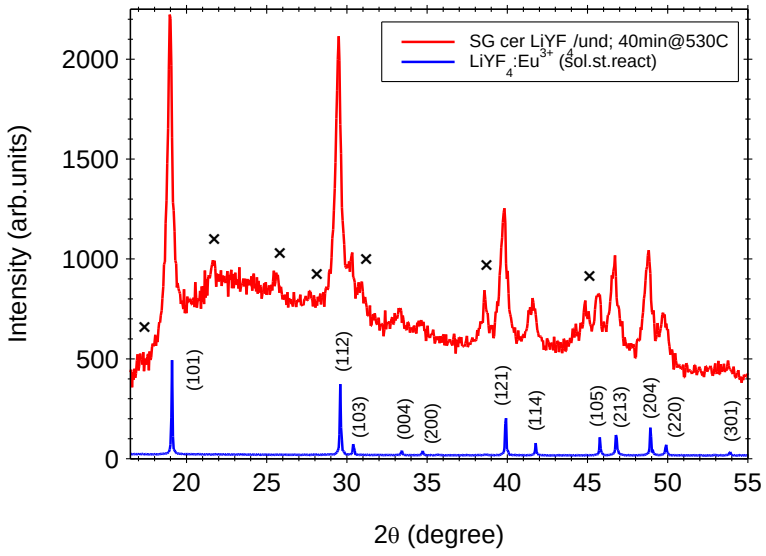

Figure 5. The XRD patterns of the un-doped glass-ceramic sample and $LiYF_4$ pellet (JCCD file no. 081-2254); smaller peaks due to $Y_2Si_2O_7$ phase (JCCD file no. 076-0204) are indicated by crosses.

The XRD pattern of the xerogel has shown that it is completely amorphous without any crystallization peaks (not shown). After subsequent thermal treatments at 530 ^oC we have easily

recognized extra-diffraction peaks due to the $LiYF_4$ crystalline phase precipitation in the glass matrix. From the analysis of the XRD pattern we have extracted the mean size of the nanocrystals which is d≅ 27nm and lattice constants: *a*= b= 5.15743 nm, c= 10.745 nm.

Luminescence processes are strongly influenced by the thermal treatments as can be clearly seen in the Figure 6 where are depicted the PL spectra excited at 394nm recorded on Eu^{3+}-doped initial xerogel and after 450C annealing and glass-ceramic and $LiYF_4$ pellet.

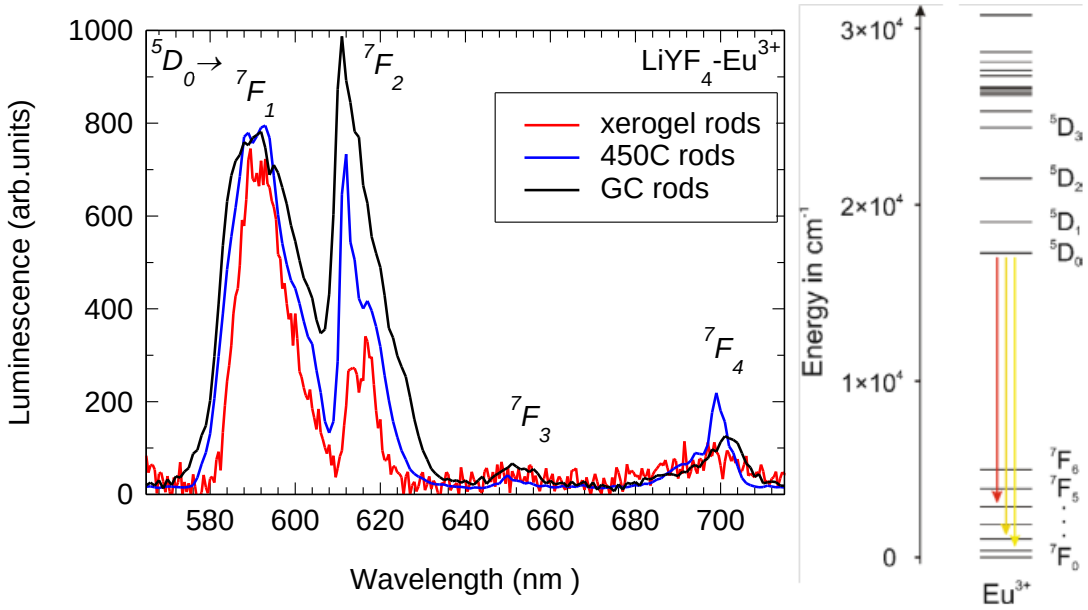

Figure 6. Normalised photoluminescence spectra recorded on Eu^{3+}-doped doped $LiYF_4$ xerogel rods initial and after 450C annealing and glass-ceramic (GC)s nanorods; $^5D_0\rightarrow{}^7F_J$ transitions (J=1-4) of the Eu^{3+}-ion are indicated.

The PL spectrum recorded in the xerogel show several luminescence bands at 578 nm ($^5D_0\rightarrow{}^7F_0$), 591 nm ($^5D_0\rightarrow{}^7F_1$), 612 nm ($^5D_0\rightarrow{}^7F_2$), 650nm ($^5D_0\rightarrow{}^7F_3$) and 698nm ($^5D_0\rightarrow{}^7F_4$) due to the Eu^{3+}-ion transitions. The PL spectrum recorded on xerogel is structureless and relatively weak but after annealing its intensity increases by about 7-8 times and shows a structuring. During ceramization at 530 °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 (Figures 4-5). 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 (Figure 6).

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. Structural

characterization by using electron microscopy (SEM and TEM) and X-ray diffraction (XRD) has shown the formation of glass ceramic microrods with 0.8μm diameter of and 10μm length in which $LiYF_4$ nanocrystals of about 30 nm size are embedded. Photoluminescence measurements have indicated the Eu^{3+}-ions incorporation inside the $LiYF_4$ nanocrystals

References:

1. *"Sol-gel template synthesis of luminescent glass-ceramic rods"*
   M. Secu, C. E. Secu, M. Sima Journal of Nanopart Research (2012) 14:772: