**Title** : *Transparent oxyfluoride nano-glass-ceramics doped with rare earths for photovoltaic applications*

**Candidate** : *Giulio Gorni (g.giulio_88@libero.it)*

**Supervisor** : *Dr. M$^a$ Yolanda Castro Martin (castro@icv.csic.es)*

**Assistant Supervisor** : *Prof. Stefano Pelli (stefano.pelli@unifi.it)*

Photovoltaic (PV) technologies for solar energy conversion are promising routes to green and renewable energy generation. The main problem to improve the efficiency of PV energy conversion is associated with the spectral mismatch between the energy distribution of photons in the incident solar spectrum and the band-gap of semiconductor materials. Therefore, currently efforts have been focused in the modification of the PV cells and making them more efficient. A possibility is to convert the solar spectrum to shift the maximum part of available solar energy to the range 950-1100nm, where Si-cells show the best energy conversion efficiency. To reach this goal, luminescent materials have been synthesized and used to minimize the losses in the solar-cell-based energy conversion process.

Oxyfluoride nano-glass-ceramic materials doped with rare earth ions are very good candidates. In this case, the good chemical and mechanical properties of oxide glasses are mixed with the low phonons energy of fluoride crystals, especially $LaF_3$ . The rare earths give all the interesting properties to the host, allowing the wavelengths conversion processes. In particular, the combinations Pr-Yb and Ce-Tb-Yb are good examples of down-conversion processes.

Glass materials have been produced using the classical melting-quenching (MQ) method and the more innovative sol-gel (SG) method which is a chemical process. Using an adequate processing condition, glasses are converted in glass-ceramics with nano-sized crystals.

$SiO_2$-$LaF_3$ transparent bulk materials (by MQ) doped with Pr-Yb and Ce-Tb-Yb, and powders, bulks and thin films materials (by SG) doped with Pr-Yb have been prepared and characterized. Finally, the down-conversion process of solar energy has been studied.

By MQ three different oxyfluoride glass materials have been prepared; $55SiO_2$-$10LaF_3$ 0.1-0.5 Pr-Yb, $55SiO_2$-$10LaF_3$ 0.5-1 Pr-Yb and $55SiO_2$-$10LaF_3$ 0.2-1-1 Ce-Tb-Yb.

By SG the $90SiO_2$-$10LaF_3$, $80SiO_2$-$20LaF_3$, $70SiO_2$-$30LaF_3$, $60SiO_2$-$40LaF_3$ compositions have been considered but only 90-10 and 80-20 compositions have been doped with 0.1-0.5 Pr-Yb and 0.5-1 Pr-Yb.

The crystallization mechanism of materials prepared by MQ and SG has been studied by thermal analysis and compared. Bulk materials by MQ have a crystals growth in 2D in a disk-like shape, while powders and bulk materials by SG have crystals growth on the surface and in 3D, respectively.

After heat treatment, glasses are converted in nano-glass-ceramics and the crystalline properties (phase and size) have been studied by X-Ray-Diffraction (XRD).

In the case of glass-ceramics by MQ, crystals size changes with the temperature and increase between 12-26 nm. For sol-gel materials, powders crystals size varies between 20-40nm however, the size decreases for bulk materials (≤5nm). At 850°C, new crystalline phases appear together with $LaF_3$.

Transparent thin films obtained by dipping and SG method have been characterized. Coating thickness between 350-1200nm have been obtained.

The realization of sol-gel materials has to be considered successful because there are few results in literature, however, more studies are necessary. Moreover, for high La content (30-40mol %) no results are present in the literature.

The down-conversion process of glasses and glass-ceramics by MQ has been observed by photoluminescence spectroscopy. In particular, for the couple Pr-Yb, the excitation of $Pr^{3+}$ at 442 nm and the corresponding emission at 980 nm due to $Yb^{3+}$ has been measured. For Ce-Tb-Yb doped materials, $Ce^{3+}$ ions are excited at 300nm and a small emission at 980nm corresponding to $Yb^{3+}$ ions has been observed.

The best results have been obtained, for each composition, for glass-ceramics treated at 660°C/20h. The down-conversion process is better for glass-ceramics than for glasses.

These preliminary results show the possibility to produce down-conversion materials, although further studies will be necessary to optimize the process.