Transparent glass-ceramics: crystallization mechanisms and optical properties

Araceli de Pablos-Martín, Silvia Soria, M. O. Ramírez, Davor Ristic, Giancarlo C. Righini, Luisa E. Bausá, Maurizio Ferrari, Thomas Höche, Alicia Durán, and M. J. Pascual

The optical performance of rare-earth-doped oxyfluoride glass-ceramics with nanocrystals smaller than 20 nm suggests that these materials have a promising future in optics and photovoltaics.

Rare earth (RE)-doped oxyfluoride glass-ceramics possess optical properties of interest for telecommunications and optoelectronics. Specifically, these materials combine the transparency and mechanical and chemical resistance of aluminosilicate glasses with the low phonon energy and facile incorporation of RE ions in the fluoride crystalline phase, which enhances optical emission intensity. Oxyfluoride nano-glass-ceramics have been extensively investigated ever since Wang and Ohwaki\(^1\) developed ytterbium-erbium (Yb\(^{3+}\)/Er\(^{3+}\))-doped lead fluoride nanocrystals within an oxide glassy matrix. Studies have been focused on exploring new crystalline phases and adding different RE ions.\(^2\)\(^-\)\(^7\) A complete overview of this research field is available elsewhere.\(^8\)

In medicine, sodium yttrium fluoride (NaYF\(_4\)) nanoparticles doped with Yb\(^{3+}\)/Er\(^{3+}\) have been reported as analytes (molecules of interest) for detecting DNA.\(^9\)\(^,\)\(^10\) Zhang and Huang\(^11\) reviewed down-conversion applications of IR quantum cutting glass-ceramics containing a range of fluoride-based nanocrystals, including materials used for solar energy. Richards\(^12\) described the advantages of applying up-conversion to photovoltaics, in other words, achieving photon energies that can be more readily absorbed by silicon (Si) solar cells.

Lanthanum fluoride (LaF\(_3\)) is a commonly used fluoride for hosting RE ions in the crystalline phase. Moreover, because to date NaYF\(_4\) is known to be one of the most efficient hosts for green and blue up-conversion (e.g., two IR photons giving rise to one visible photon),\(^13\)\(^,\)\(^14\) RE-doped fluorides of the type AREF\(_4\) (where ‘A’ is an alkali metal) have become the focus of recent attention.\(^15\)\(^,\)\(^16\)

We chose to study nanocrystallization in four different glasses in the oxyfluoride system SiO\(_2\)-Al\(_2\)O\(_3\)-Na\(_2\)O-K\(_2\)O-LaF\(_3\)/YF\(_3\) (where Al is aluminum, and K potassium). Heat treatments at temperatures above the glass-transition temperature induce devitrification of different crystalline phases, depending on the composition.\(^17\) LaF\(_3\), NaLaF\(_4\), KLaF\(_4\), and NaYF\(_4\). Crystalline fraction and crystal size depend on the time and temperature of thermal treatment.

We carried out thermal and structural characterization of samples using several techniques, including viscosity, dilatometry, x-ray and neutron diffraction, quantitative Rietveld refinement, transmission electron microscopy, differential scanning calorimetry, nuclear magnetic resonance, and extended x-ray absorption fine structure. The crystallization mechanism

Continued on next page
is similar in all the LaF$_3$-containing glasses we investigated. The parent glass was initially phase-separated, showing LaF-enriched droplets in the oxide glassy matrix. During heat treatment, formation of a crystal-glass interface enriched in SiO$_2$ occurs (see Figure 1), which acts as a diffusional barrier through the increase of viscosity in this region. Consequently, the crystal size remains in the nanometer range.\textsuperscript{18–21} This mechanism has been confirmed by scanning transmission electron microscopy and electron energy loss spectroscopy (see Figure 1).

We also analyzed the effect on nanocrystallization of adding RE ions (Tm$^{3+}$, Eu$^{3+}$, Yb$^{3+}$, Er$^{3+}$). In particular, the optical characterization of RE-doped glass and glass-ceramics focused on confirming the distribution of RE ions between the glassy matrix and crystals, and on the up-conversion emission processes.

\textit{Figure 2.} (a) Up-conversion spectra of 1mol\% thulium oxide (Tm$_2$O$_3$)-doped 55Si10La glass and glass-ceramic (620°C, 40h) under excitation at 790nm employing a pumping power of 290mW. The inset shows emission spectra under 488nm excitation. (b) Tm$^{3+}$ energy-level diagram showing the up-conversion mechanism. The labels at the peaks in the inset and to the far right in (b) represent transition energies. $\lambda$: Wavelength. a.u.: Arbitrary units. MPR: Multiphonon relaxation. CR: Cross-relaxation.

\textit{Figure 3.} (a) Emission spectra under 488nm of 0.7mol\% Tm$_2$O$_3$-doped 70Si7La glass and glass-ceramic (540°C, 100h). (b) Up-conversion emission spectra of 0.7mol\%-doped 70Si7La glass and glass-ceramic (540°C, 100h) under 790nm excitation.
**Tm-doped LaF₃ glass-ceramics**

Heat treatment of the glass 55Si₁₀La (55SiO₂-20Al₂O₃-15Na₂O-10LaF₃ mol%) doped with 1mol% Tm₂O₃ induced crystallization of LaF₃. We observed a homogeneous distribution of ~19nm LaF₃ nanocrystals after 40h at 620°C. When we excited glass and glass-ceramic samples with a pulsed laser at 790nm, we observed a blue emission. Figure 2(a) shows up-conversion spectra consisting of two contributions at 447 and 477nm, corresponding to ¹D₂ → ³F₄ and ¹G₄ → ³H₆ transitions, respectively. These transitions exhibit slightly higher intensity in glass-ceramic than in the glass, suggesting a more efficient process in glass-ceramic. Moreover, under excitation at 488nm, the emission spectra of the glass and glass-ceramic show the presence of sharp and better-resolved extra peaks located at 607 and 720nm in the glass-ceramic sample—see Figure 2(a), inset—where we attribute to fluoride crystalline environments of Tm³⁺ and which provide evidence for the formation of Tm³⁺:LaF₃ nanocrystals. We measured the variation of the emission intensities as a function of the laser pumping power in both materials, and found evidence of a two-photon process: see Figure 2(b).

**Tm-doped NaLaF₄ glass-ceramics**

Heat treatment of the glass 70Si₇La (70SiO₂-7Al₂O₃-8Na₂O-8K₂O-7LaF₃ mol%) doped with 0.7mol% Tm₂O₃ provoked crystallization of NaLaF₄, with crystal sizes ranging between 12 and 16nm. Figure 3(a) shows photoluminescence emission measurements under 488nm excitation. Glass-ceramics exhibit additional and narrower bands compared with the base glass, indicating the partial location of Tm³⁺ in fluoride crystalline surroundings. Figure 3(b) shows Tm³⁺ up-conversion spectra from excitation at 790nm. Blue emission intensity is much higher in glass-ceramic compared with glass. We selected this composition to produce planar waveguides that are now in development in our group using ionic exchange with silver.

**Summary**

We have presented the general principles of nanocrystallization in oxyfluoride glasses, with special attention to the crystallization of fluoride and double-fluoride phases. Collaboration with other institutions has allowed the optical characterization of these materials, which suggests a promising future for them, for example, in optics and photovoltaics. Finding the best material requires that several factors be improved: crystallization of the appropriate fluoride crystal (including new phases such as sodium lutetium fluoride and lithium lutetium fluoride), a high crystalline fraction, and maximum incorporation of the RE ion into the crystalline structure, among others. We will devote our next steps to this end.

**Author Information**

**Araceli de Pablos-Martín, Alicia Durán, and M. J. Pascual**

Glass Department
Instituto de ceramica y vidrio (ICV-CSIC)
Madrid, Spain

Araceli de Pablos-Martín recently obtained her PhD. She has published seven papers in Science Citation Index (SCI) journals. Her areas of expertise are glass, glass-ceramics, and nanocrystallization.

Alicia Durán is research professor and head of the Glass Department. Her research focuses on glasses, glass-ceramics, and sol-gel materials. She has published more than 180 papers in SCI journals. She is on the steering committee of the International Commission on Glass, associate editor of the International Journal of Applied Glass Science, and editor of the European Journal of Glass Science and Technology and the Journal of Sol-Gel Science and Technology.

M. J. Pascual is a tenured researcher. Her work focuses on glass, glass-ceramic, and crystallization processes. She has published 50 papers in SCI journals and is a council member of the International Commission on Glass, for which she participates in the technical committee TC7 Crystallization in Glasses.

**Silvia Soria and Giancarlo C. Righini**

Photonic Materials and Devices
Carrara Institute of Applied Physics - CNR
Florence, Italy

**M. O. Ramírez and Luisa E. Bausá**

Department of Physics of Materials
Universidad Autónoma de Madrid
Madrid, Spain

**Davor Ristic and Maurizio Ferrari**

Group for Characterization and Development of Materials for Photonics and Optoelectronics
Institute for Photonics and Nanotechnologies - CNR
Trento, Italy

**Thomas Höche**

Center for Applied Microstructure Diagnostics (CAM)
Fraunhofer Institute IWM
Halle, Germany

*Continued on next page*