Spectroscopic evidences of Nanocrystallization in oxyfluoride Nd$^{3+}$doped glass due to laser irradiation

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A local crystalline formation in a Neodymium doped oxyfluoride glass has been obtained using laser irradiation. It has been studied the intense emission around 880 nm originated from the $^{4}$F$_{3/2}$ (Nd$^{3+}$) level when the glass structure changes to a glass ceramic structure due to the irradiation of the laser beam. The emission spectra and the lifetime values obtained before and after the irradiation with 500 mW (effective power at sample surface) reveal that the desvitrification process made by the laser power beam has been successfully achieved. Our micro-luminescence results shows that nanocrystals of βPbF$_2$ have been created by the laser action, confirming in this way that the transition from glass to glass ceramic has been completed.

Introduction

The lanthanide ion Nd$^{3+}$ is one of the most interesting luminescent ions to be used for their laser applications due to the $^{4}$F$_{3/2} \rightarrow ^{4}$I$_{11/2}$ transition centred at about 1064 nm. Rare-earth doped transparent oxyfluoride glass ceramics, in which rare-earth ions are selectively incorporated into the fluoride nanocrystals embedded among the oxide glassy matrix, possess great potential applications in the field of solid luminescence due to the combination of the advantages of both fluorides and oxides: low phonon energy environment of fluoride crystalline for luminescent ions, and desirable mechanical and chemical properties of oxide glasses. This new material has attracted great attention in the continuous research for the novel photoelectric devices, and is usually fabricated by controlled crystallization of fluoride phase in oxide glassy matrix through thermal process using a furnace. Recently, laser irradiation to glass has received much attention as a new tool of micro and nanofabrication. Compared with current techniques such as photolithography and reactive ion etching, which requires numerous processing steps and fabrication masks, laser induced micro and nanofabrication have the advantage of being mask less, allowing single step and very fast processing.

Experimental

The transparent glass sample was prepared starting with the following composition in mol%: 30 SiO$_2$, 15 Al$_2$O$_3$, 29 CdF$_2$, 22 PbF$_2$, (4-x) YF$_3$ and 1 NdF$_3$. The glasses were obtained by melting the components at 1050 °C for 2 hours and finally casting the melt into a slab on a stainless steel plate at room temperature. One of the glasses was heated at 470 °C for 36 h to obtain a transparent glass ceramic for comparison purposes of the irradiated zone.

For laser irradiation we have used an Argon laser on multiline emission configuration. Laser beam was focused with a 10x microscope objective, and the effective power that arrived into the sample was 500 mW. The motorized stage speed was fixed on 125 µm/s. After irradiation process, the damaged zone has 100 µm of width in the orthogonal direction to “burning path”.

Results and Discussion
On Fig. 1 we can clearly appreciate an intermediate appearance of irradiated area emission spectra, between glass sample (outside damage area) and from glass ceramic 1\% Nd mol sample. Our micro-luminescence measurements give us quantitative information about two kind of spectroscopic changes associated to laser irradiation process. Fig. 2 shows the deep contrast between spectroscopic signal from damage area (narrower emission line, a clear signal of crystallization) and non-irradiated areas that keep their glass-like spectrum. In the same way, we have measured a relevant red shift of the emission line collected on irradiated area with respect to non-damaged areas.

With that kind of spectroscopic data, we have proofs of laser induced nano-crystallization process within oxyfluoride glass sample.

Conclusions

On summary, a crystalline environment has been created in the 1 mol\% Nd\textsuperscript{3+} doped glass by laser irradiation at 500 mW since the laser intensity is high enough to stimulate the formation of a glass ceramic structure. The rise of temperature in the irradiated zone due to the increasing laser power produces a local redistribution of the glass structure and leads to a permanent modification of the micro and nanostructure and its properties. The optically active rare earth ions are majority hosted in precipitated fluoride nanocrystals.

References:


Figures

**Fig 1:** Emission spectra of the \textsuperscript{4}F\textsubscript{3/2} and \textsuperscript{4}F\textsubscript{5/2} levels of Nd\textsuperscript{3+} ions of the irradiated point (narrow magenta line), outside the damage (dashed green line) and from a 1 mol\% of Nd\textsuperscript{3+} oxyfluoride glass ceramic sample (wide black line).

**Fig 2:** Full Width Half Maximum data obtained from luminescence signal (\textsuperscript{4}F\textsubscript{3/2} to \textsuperscript{4}I\textsubscript{9/2} transition line) of a scan transversal to irradiated line direction. So it's possible to compare -on the same data set- irradiated and non-irradiated areas.