Site-resolved emission of Nd³⁺-doped oxyfluoride nano glass-ceramics

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ABSTRACT

Transparent oxyfluoride glass-ceramics obtained by the adequate heat treatment of Nd³⁺-doped glass with composition SiO₂-Al₂O₃-Na₂O-LaF₃ are investigated. X-ray diffraction (XRD) and high resolution transmission electron microscopy (HR-TEM) show that the precipitated nanocrystals are LaF₃ with a crystal size between 9-12 nm. Furthermore, energy dispersive X-ray (EDX) analysis shows the incorporation of Nd³⁺ ions into the LaF₃ nanocrystals. Site-selective and time-resolved emission and excitation spectra of the ⁴F_{3/2} and ⁴F_{5/2} states, allows to unambiguously isolate the emission of Nd³⁺ ions in LaF₃ nanocrystals which shows well defined spectra, similar to those obtained for pure LaF₃ crystal.

Keywords: Nanocrystalline glass-ceramics; Neodymium; Site-selective laser spectroscopy

1. INTRODUCTION

The search for new rare earth (RE)-doped materials is still a challenge of great interest for a wide range of photonics applications as well as for scientific basic research. For example, fiber lasers and amplifiers emitting at selected wavelengths in the continuous or pulsed time domain are of paramount importance for bioimaging, optical biosensors, light activated therapy, and telecommunications [1-5]. In particular, RE-doped oxyfluoride glass-ceramics containing one or more crystalline phases embedded in the glass matrix, combine the low phonon energy, optical transparency, and RE ions solubility of fluoride crystals with the good mechanical, thermal, and chemical properties of oxide glasses [6,7]. The special interest in these materials is due to the fact that, after the thermal treatment, near the crystallization peak, the rare earth ions are incorporated into a nanocrystalline fluoride phase.

The first transparent glass-ceramic (GC) based on aluminosilicate glass doped with Er³⁺ and Yb³⁺ ions was developed by Wang & Ohwaki in 1993 [8]. It was observed that, exciting Yb³⁺ ions at 970 nm, the green-red upconversion emission from Er³⁺ ions was 100 times more intense than observed from fluoride glass, which suggested the segregation of Yb³⁺ and Er³⁺ ions in the Pb_xCd_{1-x}F₂ nanocrystals (NCs). The first application in the field of Photonics appears in 1995 with the work of Tick et al. [9] concerning Pr³⁺-doped oxyfluoride GC for optical amplification at 1300 nm. Since then, different RE-doped oxyfluoride glass ceramics mainly based on silicate glass matrices and other fluoride crystal phases, such as LaF₃ [10-12], CaF₂ [13], BaF₂ [14], etc. have been proposed as active media for solid state lasers, optical amplifiers, phosphors or to enhance the efficiency of photovoltaic cells [15,16].

Among rare-earth ions, Nd³⁺ has been recognized as one of the most efficient RE ions for solid-state lasers in crystals and glasses due to its intense ⁴F_{3/2}→⁴I_{11/2} emission at around 1.06 μm [17]. Besides the interest of Nd³⁺ ions in the field of IR optical amplification, this ion can also be used as a probe for local ordering due to the close relation between its spectroscopic properties and the local structure and bonding at the ion site [17,18].

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In this work, transparent oxyfluoride glass-ceramics obtained by the adequate heat treatment of Nd^{3+} -doped glass with composition $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-LaF}_3$ are investigated. X-ray diffraction (XRD) and high resolution transmission electron microscopy (HR-TEM) show that the precipitated nanocrystals (NCs) are LaF_3 with a crystal size between 9-12 nm. Furthermore, energy dispersive X-ray (EDX) analysis gives evidence of the incorporation of Nd^{3+} ions into the LaF_3 nano-crystals. Site-selective emission and excitation spectra together with the different lifetime values of the $^4\text{F}_{3/2}$ state depending on the excitation and emission wavelengths allow to isolate unambiguously the emission of Nd^{3+} ions in LaF_3 nanocrystals which shows extremely well defined spectra similar to those obtained for pure LaF_3 crystals. A strong reduction of the lifetimes of Nd^{3+} in the crystalline phase is observed for concentrations higher than 0.1% and attributed to the much higher concentration of Nd^{3+} in nanocrystals with respect to glass matrix.

2. RESULTS AND DISCUSSION

Glasses of composition $55\text{SiO}_2\text{-}20\text{Al}_2\text{O}_3\text{-}15\text{Na}_2\text{O-}10\text{LaF}_3$ doped with 0.1, 0.2, 0.5, 1 and 2 Nd^{3+} (in mol %) have been prepared by melting-quenching by using as raw materials: SiO_2 (Saint-Gobain, 99.6%), Al_2O_3 (Panreac), Na_2CO_3 (Sigma Aldrich, >99.5 %), LaF_3 (Alfa Aesar, 99.9%), and NdF_3 (Alfa Aesar, 99.99%). The batches were calcined at 1200 °C for 2 h, melted at 1650 °C for 1.5 h, and then quenched onto a brass mould. Glasses were melted again for 30 min and quenched onto a cold (-10 °C) brass mould. All the glasses were annealed at 600 °C for 30 min to eliminate residual stresses. From now on, glass samples will be labelled by G0.1, G0.2, G0.5, G1 and G2, for Nd^{3+} concentrations equal to 0.1, 0.2, 0.5, 1, and 2, respectively, while corresponding glass-ceramics will be denoted by GCx.

Glass-ceramic samples were obtained by heat treatments of glass pieces at 620 °C for 1, 3, 5, 20, 40, 80 h, 660 °C-20h, and 680 °C-20h using a heating rate of 10 °C/min [19]. Glass plates (1 cm x 1 cm x 2 mm) were treated and then polished for optical characterization. One glass lamella for each composition was not treated and used as reference glass for comparison with the corresponding glass-ceramics. The heat-treated samples were milled, sieved (<63 μm) and characterised by XRD (Bruker D8 Advance). XRD diffractograms were acquired in the 10-70 ° range, with 0.02 ° step and 1 s acquisition for each step.

2.1 Structural characterization

Figure 1(a) shows the XRD diffractograms of GC1 samples heat treated at 620 °C -20 h, 660 °C- 20 h, and 680-20h. On the bottom the LaF_3 peaks are given (JCPDS 00-032-0483) as reference. For all the compositions, only LaF_3 crystals precipitate in the glass matrix, but the crystal growth kinetics slows down as Nd^{3+} content increases. Figure 1(b) shows the crystal size of GC1 heat treated at 620 °C for different times. As can be seen the crystal size increases during the first 5 h reaching a constant value independent on the time of treatment. For 660 °C-20 h heat treatment bigger crystals are formed but a similar trend as for 620 °C is maintained [19].

Fig. 1. a) XRD diffractograms of GC1 samples heat treated at 620 °C -20 h, 660 °C- 20 h, and 680-20h. b) Crystal size for the sample doped with 1 mol% NdF_3 treated at 620 °C.

High resolution electron microscopy (HR-TEM), including Scanning Transmission Microscopy-High Angle Annular Dark Field (STEM-HAADF) and X-Ray Energy Dispersive Spectroscopy (EDXS), were recorded on a JEOL 2100 field emission gun transmission electron microscope, operating at 200 kV and providing a point resolution of 0.19 nm. The TEM is equipped with an EDXS energy dispersive X-ray spectrometer (INCA x-sight, Oxford Instruments). EDXS analysis was performed in STEM mode, with a probe size of 1 nm. TEM analysis clearly demonstrates the formation of nanocrystals in the heat treated samples. As an example, Fig. 2(a) shows the micrograph of the glass sample doped with 2 mol% of NdF_3 where phase separation droplets are observed. The main size of the droplets in the glass is around 35 nm. The micrographs of the sample doped with 2 mol% of NdF_3 treated at 620°C -40 h (Figs. 2(b) and (c)) show the formation of NCs inside the droplets. The main size of the droplets is similar to the glass sample and the average crystal size is around 10 nm in agreement with the values obtained from the diffractograms.

Fig. 2. HR-TEM of G2 glass (a) and GC2 heat treated at 620°C -40h (b) and (c).

The incorporation of Nd^{3+} ions into the NCs has been demonstrated by Energy Dispersive X-ray (EDX) spectroscopy. As can be seen in Fig. 3, the crystallized droplets show an excess of La, F, and Nd, whereas Si is confined mostly at the interface between the droplets which leads to the formation of a barrier around them. The barrier formation should occur during the first 20 h of treatment since LaF_3 crystals grow up to this time, and constant values are stabilized for longer times. The line along the droplet is the scanning line. The incorporation of Nd^{3+} into crystals of LaF_3 is clearly visible from the EDX curves.

Fig. 3. (a) EDX of the GC2 620°C -40h sample. (b) STEM image of the droplets used for the EDX measurements. The line indicates the scanning line.

2.2 Site-selective luminescence

The $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition of Nd^{3+} ions can show variations in peak wavelength, linewidth, and spectral profile depending on pumping wavelength due to the site-to-site variation of the local field acting on the ions. To obtain information about the different environments for Nd^{3+} ions in these glass-ceramics, emission and excitation spectra have been performed by using a continuous wave (cw) Ti-sapphire ring laser. The fluorescence was analyzed with a 0.25 monochromator, and the signal was detected by a Hamamatsu H10330A-75 photomultiplier and finally amplified by a standard lock-in technique. As an example, Fig. 4(a) shows the normalized emission spectra obtained by exciting at 786 and 802 nm in the $^4I_{9/2} \rightarrow ^4F_{5/2}$ absorption band for the GC sample doped with 0.1 mol% of NdF_3 treated at 620°C-40h. As can be observed in this figure the shape, peak position, and linewidth of the emission band change depending on the excitation wavelength, pointing out that Nd^{3+} ions are in different crystal field sites. The spectrum obtained at 786 nm displays a more resolved structure which indicates a crystalline environment for Nd^{3+} ions, whereas the one obtained under excitation at 802 nm exhibits an inhomogeneous broadened band similar to the glass sample. The emission spectrum obtained under excitation at 786 nm is similar to the one obtained in pure LaF_3 crystals [20]. Moreover, the excitation spectra obtained by collecting the luminescence at 1039 and 1057 nm also show the presence of different environments for Nd^{3+} ions. Figure 4(b) shows the normalized excitation spectra for the same GC sample doped with 0.1 mol% of NdF_3 . The spectrum monitored at 1039 nm presents narrower and well-resolved peaks corresponding to Nd^{3+} ions in the NCs. As concentration increases the spectra become broader and less resolved. Similar results are obtained for the different heat treatments at 620°C-20h, 620°C-40h, and 660°C-20h, which indicates that after a 20 hours treatment at 620°C the Nd^{3+} ions are incorporated in the NCs.

Fig. 4. a) Room temperature normalized emission spectra obtained under excitation at 786 (black) and 802 (grey) nm for the GC treated at 620°C-40h sample doped with 0.1 mol% of NdF_3 . b) Normalized excitation spectra obtained by collecting the luminescence at 1039 (black) and 1057 nm (grey) for the GC treated at 620°C-40h sample doped with 0.1 mol% of NdF_3 .

To clearly identify the emission from the Nd^{3+} ions in the NCs, the emission and excitation spectra have been measured at low temperature, in order to minimize the overlapping of the contributions from Nd^{3+} in the crystalline and amorphous phases due to the thermal population of the higher energy Stark components of the ground and excited states. The low temperature (9 K) excitation spectra are presented in Fig. 5 for the GC samples doped with 0.1 and 1 mol% treated at 620°C-40h. As observed in the spectra obtained at 1039 nm, the low energy band corresponding to the $^4I_{9/2} \rightarrow ^4F_{3/2}$ doublet narrows and splits into two single components as expected for a well defined crystal field site. Moreover, the $^4I_{9/2} \rightarrow ^4F_{5/2}$ band is composed of narrow and well resolved peaks which indicates that the spectra obtained at 1039 nm correspond to Nd^{3+} ions in the LaF_3 nanocrystals whereas the spectra obtained at 1055 nm show broad bands similar to those found in the glass samples. On the other side, the relative intensity of the contributions from Nd^{3+} ions in the NCs and in the amorphous phase changes as Nd^{3+} concentration increases. At low concentrations, the higher intensity corresponds to Nd^{3+} in the crystalline phase.

Fig. 5. Low temperature excitation spectra obtained by collecting the luminescence at 1039 (black) and 1055 nm (grey) for the GC samples doped with a) 0.1 and b) 1 mol% of NdF_3 .

In order to confirm if the features shown by the excitation spectra monitored at 1039 nm can be definitely related to the Nd^{3+} ions in the NCs, site-selective steady-state emission spectra for the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transition were recorded by exciting at 786 and 802 nm. Figure 6 shows the emission spectra at 9 K obtained under excitation at 786 and 802 nm for the GC samples doped with 0.1 and 1 mol%. The spectrum obtained under excitation at 786 nm displays sharp peaks, one of which, at 1039 nm, has no overlapping with the emission spectrum obtained by exciting at 802 nm. However, the sharp peaks disappear and the spectrum becomes broader and similar to the one found in the glass sample for 802 nm excitation. These results indicate that at 786 nm, we excite Nd^{3+} ions in the crystalline phase [21]. As concentration increases, the emission from Nd^{3+} ions in the NCs decreases and the spectra become broader and with less resolved peaks.

Fig. 6. Low temperature emission spectra obtained under excitation at 786 (black) and 802 nm (grey) for the GC samples doped with a) 0.1 and b) 1 mol% of NdF_3 .

The incorporation of Nd^{3+} ions in the LaF_3 NCs and in the glass matrix should be reflected in the lifetime values. The lifetime values should depend on the excitation and emission wavelengths according to the presence of Nd^{3+} ions in crystalline and amorphous phases. Lifetime measurements of the $^4\text{F}_{3/2}$ state were performed at 9 K by exciting the

samples at 786 and 802 nm by using a Ti-sapphire laser pumped by a pulsed frequency doubled Nd:YAG laser (9 ns pulse width), and collecting the luminescence at 1039 and 1055 nm respectively. Under excitation at 786 nm and collecting the luminescence at 1039 nm the decay is single exponential with a lifetime of 688 μ s for the GC sample doped with 0.1% whereas by exciting at 802 nm and collecting the luminescence at 1055 nm the lifetime is 336 μ s. The longer lifetime corresponds to the Nd^{3+} ions incorporated in the NCs. Table 1 shows the lifetime values as a function of Nd^{3+} concentration for the GC samples treated at 620°C-40h. As can be seen, the Nd^{3+} lifetime in the crystalline phase is strongly reduced as concentration increases being 98 μ s for the GC sample doped with 1 mol%. Figure 7 shows the semilogarithmic plot of the experimental decays of the $^4\text{F}_{3/2}$ level for the samples doped with 0.1, 0.2, 0.5, and 1 mol% of NdF_3 under selective excitation (786 nm) and emission (1039 nm) wavelengths at which it is possible to separate Nd^{3+} contribution in the LaF_3 NCs.

Table 1. Low temperature experimental lifetimes of the $^4\text{F}_{3/2}$ level obtained under excitation at 786 and 802 nm collecting the luminescence at 1039 and 1055 nm respectively.

$\%\text{NdF}_3$	$\lambda_{\text{exc}} = 786 \text{ nm}$	$\lambda_{\text{exc}} = 802 \text{ nm}$
	$\tau_{\text{exp}} (\mu\text{s})$	
0.1	688	336
0.2	462	337
0.5	188	332
1	98	295

Fig. 7. Semilogarithmic plot of the experimental decays from the $^4\text{F}_{3/2}$ state obtained under excitation at 786 nm collecting the luminescence at 1039 nm for the GC samples doped with 0.1, 0.2, 0.5, and 1 mol% of NdF_3 .

As can be seen in Table 1 and Fig. 7, there is a strong quenching of the Nd^{3+} lifetimes in the LaF_3 nanocrystals, being much less relevant in the amorphous phase. This behaviour is likely explained by a high diffusion of Nd^{3+} ions from the glass matrix to the LaF_3 nanocrystals, as confirmed in the same system doped with Tm^{3+} studied by XANES with Synchrotron radiation [22].

3. CONCLUSIONS

Nanostructured glass-ceramics obtained by the adequate heat treatment of a Nd^{3+} -doped glass with composition SiO_2 - Al_2O_3 - Na_2O - LaF_3 have been investigated by several techniques. X-ray diffraction (XRD) and high resolution

transmission electron microscopy (HR-TEM) show that the precipitated nanocrystals are LaF_3 with a crystal size between 9-12 nm. Furthermore, energy dispersive X-ray (EDX) analysis shows the incorporation of Nd^{3+} ions into the LaF_3 nano-crystals. The site-selective emission and excitation spectra, together with the different lifetime values of the $^4\text{F}_{3/2}$ state depending on the excitation and emission wavelengths, allow to isolate unambiguously the emission from Nd^{3+} ions in the LaF_3 nanocrystals and to correlate the spectroscopic properties with the structural properties. As the Nd^{3+} concentration is increased beyond 0.1 mol%, a stronger quenching of lifetime is observed for Nd^{3+} ions inside LaF_3 crystals than for those dispersed in the glass matrix. This strong concentration quenching is explained by the much higher concentration of Nd^{3+} ions in the crystalline phase compared to the one in the glass matrix.

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