80SiO2-20LaF3 oxyfluoride glass ceramic coatings doped with Nd3+ for optical applications

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Abstract
Transparent glass ceramic (GC) films and self-supported layers of composition 80SiO2-20LaF3 doped with Nd3+ were prepared by sol-gel method for the first time. GC films were deposited by dip coating on different substrates and heat-treated between 350°C and 850°C for 1, 3, and 80 hours. The structural analysis of thin films was performed by GI-XRD and HR-TEM to check the LaF3 nanocrystals precipitation in the SiO2 matrix, revealing a crystal size lower than 5 nm. The emission and excitation spectra and lifetimes of the films have been obtained for different thermal treatments and Nd3+ contents. The luminescence intensity of the 4F3/2 → 4I11/2 laser transition increases with the treatment temperature and Nd3+ content, whereas a reduction for the luminescence lifetime is observed compared to those observed in bulk samples prepared by melting quenching.

KEYWORDS coatings, glass ceramics, glass manufacturing, optical properties, oxyfluoride, photoluminescence, sol-gel

1 | INTRODUCTION

Rare-earth (RE)-doped materials have gained great interest in the last decade for their use in solid-state lasers, sensing, solar cells, etc.1-7 Silicate glasses were commonly used for these applications due to their good mechanical and chemical properties compared to borate, phosphate, or chalcogenide glasses. However, oxide glasses, especially silicates, have quite high phonon energy (1200 cm⁻¹) that causes nonradiative relaxation with subsequent low optical efficiency.8 Thereby, oxyfluoride GCs have been considered as promising host materials due to their high transparency, low phonon energy of fluoride crystals, and the possibility to effectively host RE ions inside the crystals.9 Moreover, they present high chemical and mechanical stability typical of oxide glasses, in particular silicates and alumino-silicates.

Many oxyfluoride GCs have been prepared by the melting quenching (MQ) method10,11 using several RE ions, as Eu3+,12 Nd3+ for its use as laser material at 1.06 μm,13-15 Pr3+-Yb3+ as down-converter materials,16-18 and Er3+-Yb3+ for up-conversion.19,20 But MQ method presents some limitations such as the high temperature of processing that causes fluorine loss by evaporation. Moreover, phase separation is commonly produced during the quenching, thus limiting the possibility to obtain homogeneous materials with high optical quality. Therefore, many efforts were concentrated to prepare oxyfluoride materials by sol-gel method.21-31 This process allows obtaining purer materials, and compositions impossible or extremely difficult to
obtain by MQ method using much lower temperatures. Furthermore, it is a very flexible and rather cheap method.

In the last years, different authors have reported the development of SiO$_2$-LaF$_3$/LaOF oxyfluoride glass ceramics by sol-gel, highlighting the works of Fujihara et al$^{21-23}$ and Ribeiro et al$^{24}$ Fujihara et al described the preparation of 90SiO$_2$-10LaF$_3$/LaOF thin films doped with Eu$^{3+}$ and reported that the luminescence associated to Eu$^{3+}$ ions increased when the RE ions are introduced in a oxyfluoride GCs matrix compared to silica glass matrix. Anyway, at high temperature (600-900°C) LaOF crystals instead of LaF$_3$ are identified. On the other hand, Ribeiro et al prepared films with the same composition finding that for heat treatment between 600-900°C both LaF$_3$ and LaOF phases appeared. They used these films as planar waveguides at Vis (500-600 nm) and IR (1.44-1.46 μm) wavelengths obtaining losses of 1.8 dB/cm at 632.8 nm.

Different authors have reported the doping of GC materials with RE ions and demonstrated that these ions are preferably incorporated into the crystalline phase and not into the silica matrix, confirming that the sol-gel process is suitable for the synthesis of oxyfluoride GC materials with photonic applications. Biswas et al$^{25}$ prepared 95SiO$_2$-5LaF$_3$ xerogels doped with Er$^{3+}$-Yb$^{3+}$ for up-conversion. Upon Yb$^{3+}$ excitation at 980 nm, Er$^{3+}$ emission from the$^{2}F_{5}$ levels (at 450 and 490 nm) was observed, suggesting that Er$^{3+}$ ions are present in a local environment of very low phonon energy. An Er$^{3+}$ emission$^{3}I_{15/2}$-$^{3}I_{11/2}$ quite broad compared to the emission of Er$^{3+}$ in the LaF$_3$ crystals was observed. The emission had two contributions: one produced by Er$^{3+}$ ions inside the LaF$_3$ crystals and the other associated with the ions near of crystals surface that feel the high phonons of the silica matrix. Velázquez et al$^{30,31}$ have also prepared 95SiO$_2$-5LaF$_3$ xerogels doped with Tb$^{3+}$ and codoped with Dy$^{3+}$ to enhance the UV absorption band and shift this energy to the visible range. The precipitation of LaF$_3$ crystals inside the SiO$_2$ matrix was observed and the lifetimes reported show that around 75% of the RE ions are in the LaF$_3$ crystals. The same materials doped with Pr$^{3+}$-Yb$^{3+}$ ions for Vis UC upon Yb$^{3+}$ excitation at 980 nm were also studied.

Finally, a review of sol-gel monoliths with more than 200 references focused on the preparation of silica and silicate-based materials, especially SiO$_2$-LnF$_3$ GCs, was reported by Kajihara.$^{32}$ However, in all of these works, typical LaF$_3$ concentration was between 5 and 10 mol%; furthermore, the same synthesis procedure was used without modifying the processing parameters. On the other hand, structural characterization of thin films together with optical properties have been poorly evaluated.

The aim of this work was the preparation of 80SiO$_2$-20LaF$_3$ transparent GC films doped with Nd$^{3+}$ using the sol-gel method. The structural characterization was performed by GI-XRD and HR-TEM, whereas the optical properties were investigated using steady-state emission and excitation spectra and lifetimes. This work demonstrates the possibility to prepare completely transparent films with higher LaF$_3$ amount (20 mol%) compared to the materials reported up to now, and opens the door to new compositions with even higher LaF$_3$ content (30-40 mol%) and with promising optical properties of coating and self-supported sol-gel materials.

## 2 EXPERIMENTAL

### 2.1 Preparation of 80SiO$_2$-20LaF$_3$ sols, coatings, and self-supported layers

The 80SiO$_2$-20LaF$_3$ sol was prepared in alcoholic media using tetraethylorthosilicate (TEOS, ABCR, 98%) as precursor of silica, lanthanide acetate (La(CH$_3$COO-nH$_2$O)$_3$), Sigma-Aldrich, St. Louis, MO, 99.9%) and trifluoroacetic acid (TFA, Sigma-Aldrich, 99%) as lanthanide and fluorine sources, respectively. The synthesis of the sol was performed in two steps. First, SOL-1 was obtained mixing TEOS, absolute ethanol (EtOH) and H$_2$O (0.1M HCl) in a molar ratio 1TEOS:9.5EtOH:2H$_2$O and maintained under stirring for 2 hours at room temperature. Water was added drop by drop, to start the hydrolysis process. Then, SOL-2 was prepared from lanthanum acetate (La(ac)), trifluoroacetic acid (TFA), absolute ethanol, and distilled water. The molar ratio was fixed to 1La(ac):5TFA:5EtOH:4H$_2$O. SOL-2 was stirred for 2 hours at 40°C to obtain a homogenous solution. Finally, SOL-1 and SOL-2 were mixed and maintained at room temperature before using.

Doped 80SiO$_2$-20LaF$_3$ sols with 2 ad 3 mol% of Nd$^{3+}$ were also prepared by adding the corresponding molar ratio of neodymium acetate (Nd(ac)) (Nd(CH$_3$CO$_2$)$_3$-xH$_2$O, Sigma-Aldrich, 99.9%) to SOL-2 and then, mixing with the SOL-1.

SiO$_2$ films doped with 3Nd$^{3+}$ were also prepared using the same TEOS:H$_2$O:EtOH ratio as for the 80SiO$_2$-20LaF$_3$ composition but substituting Nd(ac) with Nd(NO$_3$)$_3$ (Sigma-Aldrich 99.9%) because the latter can be easily dissolved in H$_2$O and EtOH without using TFA.

Doped and undoped 80SiO$_2$-20LaF$_3$ films were deposited on silicon wafers and silica substrates by dip-coating method using a withdrawal rate of 30 cm/min. Films were sintered between 350 and 850°C during 1, 3, or 80 hours using a heating rate of 10°C/min. Two-layers films were also prepared on silica substrates using an intermediate heat treatment at 200°C for 20 minutes and a final heat treatment at 750°C for 3 and 80 hours. SiO$_2$-3Nd coatings were also prepared using the same withdrawal rate and varying the heat treatment between 350 and 850°C during 3 hours.
A similar synthesis with a different H₂O/EtOH ratio was used to prepare self-supported layers with composition 80SiO₂-20LaF₃ doped with 0.5 and 3Nd³⁺ (mol%). A wet-gel was obtained by leaving the solution in a sealed container at 50°C for 2 days and then dried for 15 days at 50°C. Finally, the self-supported layers were heat-treated in air at 650°C for 3 hours with a rate of 1°C/min to obtain the precipitation of LaF₃ nanocrystals and giving rise to crack-free transparent GCs.

2.2 | Characterization of coatings and self-supported layers

Ellipsometry measurements were performed using a spectral Ellipsometer (M-2000UTM, J.A. Co., Woollam) to characterize the films deposited onto silica substrates. The spectra were taken between 250 and 1000 nm at two different incident angles: 50° and 60°. The data were fitted using the WVASE32 software with a Cauchy model. From the fitting data, the refractive index (n) (taken at λ = 700 nm) and the thickness of the films were obtained.

Fourier transform infrared spectroscopy (FTIR) of doped and undoped 80SiO₂-20LaF₃ films on Si-wafer substrates was performed in transmission mode, using a Perkin Elmer Spectrum 100 equipment, in the range 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹.

The crystallization behavior was followed by Grazing Incidence X-ray diffraction (GI-XRD) of doped and undoped 80SiO₂-20LaF₃ films on Si-wafer substrates was performed in transmission mode, using a Perkin Elmer Spectrum 100 equipment, in the range 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹.

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After the heat treatment, the self-supported layers were milled and sieved to a particle size less than 60 μm to measure XRD. Diffractograms were acquired in the range 10-70° with a step size of 0.02° and 1 second of integration time using a D8 Advance diffractometer (Bruker, Billerica, MA).

Self-supported layers and coatings on silicon wafers were also characterized by high-resolution electron microscopy (HR-TEM), including scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF). A JEOL 2100 field-emission gun transmission electron microscope operating at 200 kV with a point resolution of 0.19 nm was used. The samples were obtained by scratching the films and depositing the scaled fragments onto carbon-coated copper grids.

2.3 | Optical characterization

Luminescence measurements were performed at room temperature with a single grating monochromator (focal length 0.25 m), an extended IR Hamamatsu H10330A-75 photomultiplier, and amplified by a standard lock-in technique. The films were excited with a tunable Ti:sapphire ring laser (0.4 cm⁻¹ linewidth) in the 770-920 nm spectral range, and the incident beam formed a 25° angle with the sample normal. The emitted light was collected along the direction perpendicular to the films. For all the samples, the excitation power was 700 mW, except for the self-supported layers for which a power of 100 mW was used. Luminescence decay curves were obtained by exciting the samples with a Ti:sapphire laser pumped by a pulsed frequency-doubled Nd:YAG laser (9 ns pulse width), and detecting the emission with a Hamamatsu H10330A-75 photomultiplier. The sample temperature was varied between 9 and 300 K in a continuous-flow cryostat.

3 | RESULTS AND DISCUSSION

Transparent and stable sols were obtained after the synthesis process. The viscosity value was ~ 3 mPas and remained almost unchanged for at least 2 months. Figure 1 shows a picture of 80SiO₂-20LaF₃-3Nd³⁺ film treated at 750°C-80 hours. In the picture, the coating was marked with a yellow line. Homogeneous, transparent and crack-free doped and undoped coatings were obtained in all cases, and for all the sintering temperatures.

80SiO₂-20LaF₃-3Nd³⁺ films deposited on silica substrates were characterized by ellipsometry to obtain the refractive index and thickness as a function of sintering temperature. Figure 2A shows the ellipsometry measurements with the corresponding Cauchy fits for single and double films on SiO₂ substrate treated at 750°C-3 hours. Very good agreement between the measurements and the fits is obtained, thus indicating the good film quality. The thickness and refractive index were obtained by measuring four films to obtain an n average ± standard deviation. Figure 2B shows the corresponding variation in the
thickness and refractive index at $\lambda = 700$ nm for single film treated between 350 and 850°C during 3 hours. The thickness decreases linearly with temperature, from 625 nm at 350°C to 450 nm at 750°C with a slope of 0.4 nm/°C ($R^2 = .96$). Then, an important shrinkage of the coating is observed and the thickness decreases up to 325 nm at 850°C. In the case of refractive index, it increases with temperature. The increment of refractive index is associated with two effects: one with the condensation of the silica network and the corresponding elimination of the residual organic groups, and the other, with the increase in crystallization of LaF$_3$ with temperature. The refractive index increases linearly ($R^2 = .998$) from 1.50 at 350°C to 1.54 at 750°C, but from 750°C a faster increase is observed, the refractive index reaching the theoretical value of 1.56 at 850°C, closer to the LaF$_3$ refractive index (1.60 at $\lambda = 700$ nm). To confirm the precipitation of LaF$_3$ crystals and the effect on the refractive index, SiO$_2$-3Nd doped samples were prepared and treated between 350 and 850°C for 3 hours. The LaF$_3$-free composition shows a refractive index value smaller than that of 80SiO$_2$-20LaF$_3$-3Nd$^{3+}$ films and very close to silica coatings, around ~ 1.45. Moreover, very small change is observed passing from 350 to 550°C, the refractive index passing from 1.44 to 1.45, and for temperature higher than 550°C no change in the refractive index is observed. Instead, for 80SiO$_2$-20LaF$_3$ coatings a remarkable change is obtained increasing the treatment temperature and this is associated to LaF$_3$ crystallization.

Film thicknesses from 450 to 910 nm were obtained for single and multilayer 80SiO$_2$-20LaF$_3$ coatings, respectively, after heat treatment at 750°C during 3 hours (Figure 2).

Figure 3A shows the FTIR spectra of 80SiO$_2$-20LaF$_3$ films deposited on Si-wafer and treated between 150-850°C for 3 h. The FTIR for the untreated film is also shown. B, OH groups area of the films measured in (A) calculated in the range 3750-2850 cm$^{-1}$ [Color figure can be viewed at wileyonlinelibrary.com]
vibrations. Moreover, the absorption bands at 1460 and 1680 cm$^{-1}$ appear associated to C=O vibrations of organic compounds not completely removed. In the range 1350-1090 cm$^{-1}$ several sharp vibration bands appear related to CF$_2$ and CF$_3$ associated to TFA. In the case of 80SiO$_2$-20LaF$_3$-3Nd$^3+$ films treated at 550-850$^\circ$C, a small band between at 845-780 cm$^{-1}$ corresponding to the symmetric stretching vibration of Si-O-Si is also identified. The spectra show a broad band ranging from 850-1250 cm$^{-1}$ ascribed to asymmetric stretching of Si-O-Si bonds. On the other hand, at 1640 cm$^{-1}$ the bending vibration of H$_2$O molecules is identified together with a broad band centered around 3400 cm$^{-1}$ associated with the stretching vibrations of the -OH groups. The presence of -OH groups affects the optical properties, producing a quenching of the luminescence of RE ions due to the high vibration frequency of these groups (three times higher than the phonons of silicate glasses). In our case, these bands decrease with increasing the sintering temperature. Figure 3B shows the semiquantitative evolution of -OH groups as a function of temperature. The mean crystal size was evaluated by the Scherrer’s equation, using the full width at half maximum (FWHM) and position of the XRD peaks. From this equation, the mean size of the nanocrystals is $\sim$ 4 nm.

FIGURE 4 GI-XRD of 80SiO$_2$-20LaF$_3$ films deposited on Si-wafer treated at 550$^\circ$C and 750$^\circ$C for 3 and 80 h. The measurement for the untreated film is also shown for comparison [Color figure can be viewed at wileyonlinelibrary.com]

phase, such as LaOF, can appear. Therefore, it is important to reach a compromise between sintering temperature, presence of hydroxyl groups and the precipitated crystal phase.

To identify the presence of crystalline phases, GI-XRD of 80SiO$_2$-20LaF$_3$ thin films treated at 550$^\circ$C and 750$^\circ$C for 3 and 80 hours was performed (Figure 4). In all the diffractograms, two broad peaks are observed at $2\theta = 27.5^\circ$ and 44$^\circ$, corresponding to crystallization of LaF$_3$ in hexagonal form (JPCD 00-032-0483) and associated to the reflections of (111) and (300)-(113) planes, respectively. The diffraction peaks do not change with temperature probably associated with the small size of LaF$_3$ crystals. However, the nanocrystals sizes cannot be calculated using Scherrer’s equation due to the broad width of the XRD peaks. No diffraction peaks appear in the untreated film.

FIGURE 5 XRD of 80SiO$_2$-20LaF$_3$ self-supported layer treated at 650$^\circ$C for 3 h. The measurement for the untreated (xerogel) sample is also shown for comparison [Color figure can be viewed at wileyonlinelibrary.com]
inset in Figure 6A shows a magnified detail of the lattice structure. The distance between the adjacent lattice corresponds to the plane distance (111) of hexagonal LaF3, the most intense diffraction peak (JPCD 00-032-0483), whose lattice spacing is \( d_{111} = 0.328 \text{ nm} \).\(^{15,29,37}\) No defects, such as planes mismatch, distortions etc, are observed from the analysis of the micrograph. The electron diffraction pattern (Figure 6B) shows diffraction rings and white spots that lay on the diffraction rings. The rings are attributed to certain lattice planes of LaF3. For films treated at 750°C during 3 hours, crystals smaller than 3 nm were observed (not shown). The detection of LaF3 crystals is complicated when the heat-treatment temperature is reduced because very small crystals are expected. Thus, an inhibition of the crystallization process could be associated with the presence of quite high internal stresses in the film that increase when the thickness decreases.

Figure 7 shows HRTEM of the 80SiO2-20LaF3 self-supported layer treated at 650°C-3 hours with nanocrystals homogeneously dispersed having a size around 4 nm, which is consistent with XRD results. Figure 7B and C show the corresponding Fast Fourier Transformation (FFT) image taken from two of the nanocrystals encircled in blue in the HRTEM image. The regular diffraction spots recorded along the zone axis unambiguously demonstrate that the nanocrystal has a single crystalline nature, which can be readily indexed as hexagonal LaF3. The HRTEM interplanar distances are determined to be 0.33 nm and 0.207 nm corresponding to the (111) and (300) lattice planes, respectively, of the LaF3 phase.

The emission spectra for untreated and heat-treated films with different Nd\(^{3+}\) concentrations were obtained at room temperature by exciting at 806 nm in the \( ^4I_{9/2} \rightarrow ^2F_{5/2} \) absorption band. A broad spectrum is observed for all the treated samples with a main peak at around 1060 nm corresponding to the \( ^4F_{3/2} \rightarrow ^4I_{11/2} \) laser transition of Nd\(^{3+}\) ions. As an example Figure 8 shows the room-temperature emission spectra of thin films doped with 3 mol% Nd\(^{3+}\) untreated and treated between 350°C and 750°C for 3 hours. As can be seen, the luminescence of the untreated film is very weak, and increases as the heat-treatment temperature increases. However, the spectra show similar features for the different treatments indicating that no significant changes in the chemical surrounding of the Nd\(^{3+}\) ions occur. These changes should affect the Stark splitting and the spectrum peak structure. The emission spectra for times longer than 3 hours show the same spectral features. The increase in the emission intensity is likely related to the reduction in -OH groups with temperature. Concerning to the peak position, the small red-shift observed as annealing temperature increases has been observed in oxyfluoride thin films and attributed to the
formation of oxygen-rich phases at the expense of fluorine content which produces a small variation on the ligand field acting on the RE ions.38

Figure 9 shows the excitation spectra for the thin films doped with 2 and 3% Nd3+ treated at 650°C-3 hours together with the excitation spectrum of the untreated sample doped with 3% is also included [Color figure can be viewed at wileyonlinelibrary.com] Another important spectroscopic parameter to characterize the luminescent behavior of Nd3+ ions in these films is the decay time of the emitting level. The lifetimes of the 4F5/2 state were obtained by exciting at 806 nm and collecting the luminescence at 1064 nm. The decays deviate from a single exponential function and the lifetimes are unexpectedly short, around 40 µs. Table 1 shows the average lifetimes, calculated by \( \langle \tau \rangle = \frac{\int_0^\infty I(t)dt}{\int_0^\infty I(t)dt} \), where \( I(t) \) represents the luminescence intensity at time \( t \) corrected for the background for the samples doped with 2 and 3% for different thermal treatments. The lifetimes are nearly one order of magnitude shorter than those observed in bulk samples prepared by melting quenching.15 The strong reduction in the lifetimes could be due to the formation of clusters leading to luminescence quenching39,40. Moreover, the effective RE3+ ions concentration into the nanocrystals is much different from the theoretical (or nominal) one, as shown in previous papers were an estimation of the effective RE3+ ions diffusion and incorporation into the crystal phase was given.15,41 The results showed that the effective concentration into the nanocrystals can be one order of magnitude higher than the nominal concentration.

In a previous work on Nd-doped GCs prepared by melting-quenching, the emission of Nd3+ in LaF3 nanocrystals has been isolated using site-selective laser spectroscopy.15 It was observed that as the Nd3+ concentration increases, a stronger quenching of lifetime occurs for Nd3+ ions inside LaF3 crystals with respect to those ions dispersed in the glass matrix. Moreover, by increasing Nd3+ concentration the spectra become broader and less resolved. To clarify if the Nd3+ ions are incorporated in the LaF3 nanocrystals in the sol-gel coatings, the emission and excitation spectra and lifetime of a 80SiO2-20LaF3 self-supported layers doped with 0.5 and 3%, and treated at 650°C for 3 hours were measured. The emission spectrum of this sample, obtained by exciting at 786 nm, is presented in Figure 10A, showing a more resolved structure which

**TABLE 1** Average lifetime of the 4F5/2 state for the 80SiO2-20LaF3 thin films doped with 2 and 3 mol% Nd3+ for different temperatures. The experimental error is 3%

<table>
<thead>
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<th>Sample</th>
<th>(&lt;\tau&gt;) (µs)</th>
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<tr>
<td>Nd 2% 350°C-3 h</td>
<td>38</td>
</tr>
<tr>
<td>Nd 2% 550°C-3 h</td>
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<td>42</td>
</tr>
<tr>
<td>Nd 3% 750°C-3 h</td>
<td>41</td>
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**FIGURE 8** Room-temperature emission spectra of 80SiO2-20LaF3 thin films doped with 3 mol% Nd3+ for different heat treatments. The emission spectrum of the untreated sample doped with 3% is also included [Color figure can be viewed at wileyonlinelibrary.com]
indicates a crystalline environment for Nd$^{3+}$ ions with similar features to those observed in LaF$_3$ crystals. This is also confirmed by the excitation spectrum, Figure 10B, obtained by collecting the luminescence at 1064 nm. The spectrum presents narrow and well-resolved peaks corresponding to Nd$^{3+}$ ions in the nanocrystals. The normalized emission and excitation spectra of the untreated sample with the same Nd$^{3+}$ concentration are included in Figure 10 for comparison. It is worth noting that in the case of the untreated sample the spectral features of both spectra correspond to Nd$^{3+}$ ions in an amorphous environment.

Moreover, the Nd$^{3+}$ emission of the treated sample is around 100 times more intense than that of the untreated one. The decay from the $^4F_{3/2}$ level obtained under excitation at 786 nm collecting the luminescence at 1064 nm deviates from a single exponential function. The average lifetime decreases from 147 $\mu$s to 18 $\mu$s as Nd$^{3+}$ concentration increases from 0.5 to 3 mol%.

Nd$^{3+}$ incorporation into LaF$_3$ nanocrystals was unambiguously confirmed by measurements performed at low temperature. Figure 11A and B shows the emission and excitation spectra, respectively, obtained at 9 K for the samples doped with 0.5 and 3 mol% Nd$^{3+}$. The emission spectrum of the lowest concentrated sample shows sharp peaks which correspond to the emission of Nd$^{3+}$ in LaF$_3$ nanocrystals. As observed in the excitation spectrum, the low energy band corresponding to the $^4I_{9/2}\rightarrow^4F_{3/2}$ doublet narrows and defines 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 indicate that the spectrum corresponds to Nd$^{3+}$ ions in the LaF$_3$ nanocrystals. These results confirm that in the self-supported layer treated at 650°C for 3 hours the Nd$^{3+}$ ions are mainly incorporated in the LaF$_3$ nanocrystals. However, the low-temperature emission and excitation spectra of the untreated sample doped with 0.5 mol% Nd$^{3+}$ show broad and structureless bands according with a predominant amorphous environment for Nd$^{3+}$ ions. Referring to the emission and excitation spectra of the treated sample doped with 3 mol% Nd$^{3+}$, although they show the peaks corresponding to Nd$^{3+}$ in LaF$_3$ nanocrystals they become broader and less resolved than those of the less concentrated sample.
which indicates the presence of different Nd$^{3+}$ environments. This is confirmed by the excitation wavelength dependence of the emission. Figure 12 shows the low temperature emission spectra corresponding to 786 and 806 nm excitations displaying the crystalline and amorphous Nd$^{3+}$ environments, respectively.

In summary, Nd$^{3+}$ incorporation into the LaF$_3$ nanocrystals was observed and by selective excitation of pure Nd$^{3+}$:LaF$_3$ crystals were obtained for self-supported layers doped with 0.5Nd$^{3+}$ and 3%. For coatings similar lifetimes but broader spectra were observed doping with 2 and 3 mol%. This discrepancy could be attributed to a much higher Nd$^{3+}$ effective concentration into the LaF$_3$ nanocrystals. In fact, excessive Nd$^{3+}$ concentration may produce inhomogeneous spectral broadening giving rise to glassy-like luminescence emission. Similar behavior was observed in bulk samples prepared by MQ where it was observed that, increasing Nd$^{3+}$ content, spectra lost resolution and became similar to those of glass.15

4 CONCLUSIONS

Transparent and crack-free 80SiO$_2$-20LaF$_3$ GC films doped with 2 and 3 mol% Nd$^{3+}$ were successfully obtained by sol-gel. Self-supported GC layers of composition 80SiO$_2$-20LaF$_3$ doped with 0.5 and 3Nd$^{3+}$ were also prepared to furtherly study the optical properties. By HRTEM it was shown the precipitation of LaF$_3$ nanocrystals with a size between 3 and 5 nm.

For self-supported layers the Nd$^{3+}$ incorporation into the nanocrystals allows reproducing spectra of pure Nd$^{3+}$:LaF$_3$ crystals, however, the lifetime is strongly quenched as compared to typical lifetime in oxyfluoride GCs. Optical properties of coatings show the increase in luminescence with the heat-treatment temperature due to an increase in the crystal fraction and removal of -OH groups. Much broader emission spectra were obtained as compared to self-supported layers likely due to extremely high Nd$^{3+}$ effective concentration. Further studies are in progress to optimize the RE concentration and glass matrix composition to obtain Nd$^{3+}$-doped films with optimal luminescence properties.

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