Selective excitation in transparent oxyfluoride glass-ceramics doped with Nd³⁺

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Abstract

Transparent oxyfluoride nano-glass-ceramics have been prepared by melting-quenching and doped with five different Nd³⁺ concentrations (0.1-2 mol%) to obtain the most efficient $^4F_{3/2} \rightarrow ^4I_{11/2,13/2}$ emission. It was observed by differential thermal analysis (DTA) that the addition of Nd³⁺ does not affect the crystallization mechanism which corresponds to a diffusion-controlled volumetric process that starts from a constant number of nuclei. Nevertheless, the presence of the dopant affects the kinetics due to the progressive increase of T_g on increasing the Nd³⁺ content. LaF₃ crystals with a size between 9-12 nm are obtained after heat treatments at $T_g + 20-80$ °C as confirmed by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HR-TEM). Energy dispersive X-ray (EDX) analysis shows the incorporation of Nd³⁺ ions into the LaF₃ nano-crystals. Judd-Ofelt analysis from the absorption spectra further demonstrate the incorporation of Nd³⁺ ions into the fluoride phase and the most relevant parameters such as radiative lifetime and stimulated emission cross-section are calculated. A detailed optical characterisation clearly shows that Nd³⁺ ions in the glass-ceramics are incorporated in both crystalline and amorphous phases. Low temperature site-selective emission and excitation spectra, together with the different lifetime values of the $^4F_{3/2}$ state depending on the excitation and emission wavelengths, allow emission from Nd³⁺ ions in the LaF₃ nanocrystals to be identified and correlated with the structural properties. As the Nd³⁺ concentration is increased beyond 0.1 mol%, a stronger quenching of lifetime is observed for Nd³⁺ ions residing in LaF₃ crystals than for those dispersed in the glass matrix. This strong concentration quenching is explained by the much higher concentration of Nd³⁺ ions in the crystalline phase with respect to that in the glass matrix.

1. Introduction

The growing field of photonics demands the design of new rare-earth (RE)-based optical materials for their use in optical telecommunications, solid-state lasers, three-dimensional full-colour displays, solar cells, and other applications [1], [2], [3], [4] and [5]. Oxyfluoride glass-ceramics are promising RE-hosting candidates due to their good processing and optical properties [6]. They combine the good chemical and mechanical stability of oxide-glass matrices with the excellent optical properties of low-phonon-energy fluoride nano-crystals.

Since 1993, when Wang and Ohwaki [7] obtained for the first time transparent oxyfluoride glass-ceramics containing $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$ fluoride crystals doped with Er^{3+} and Yb^{3+} ions, the number of publications on transparent glass-ceramics has grown increasingly. Many compositions have been studied in recent years with the aim of obtaining different crystalline phases. Good review articles concerning oxyfluoride glass-ceramics have been published by A. de Pablos et al. [8] and Federov et al. [9].

A general glass system suitable for preparing glass-ceramics containing LaF_3 nano-crystals by the melt-quenching method is $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-LaF}_3$. The percentage of SiO_2 generally varies between 40-65 mol%, with other components in the following ranges: Al_2O_3 , 18-30 mol%; Na_2O , 10-20 mol%; and LaF_3 10-15 mol %. A relevant parameter for assessing LaF_3 crystallization ability is the ratio $\text{Na}_2\text{O}/(\text{SiO}_2+\text{Al}_2\text{O}_3)$ since La tends to compensate the electrical charge of the $[\text{AlO}_4]$ and $[\text{SiO}_4]$ tetrahedra only in oxygen bonds which are not saturated by Na^+ ions [10].

Many RE ions have been used to dope glass-ceramics with LaF_3 nano-crystals for different photonic applications. These include Er^{3+} for telecommunications at 1.55 μm and for up-conversion (UC), Pr^{3+} for telecommunications at 1.3 μm , Tm^{3+} and $\text{Tb}^{3+}/\text{Yb}^{3+}$ for blue and green UC, $\text{Tm}^{3+}/\text{Yb}^{3+}$ for down-conversion (DC), and Nd^{3+} and $\text{Ho}^{3+}/\text{Tm}^{3+}$ for infrared (IR) laser emission at 1.06 and 2 μm , respectively [11], [12], [13], [14], [15], [16], [17], [18], [19] and [20].

In this paper, an oxyfluoride glass with composition in mol % 55 SiO_2 -20 Al_2O_3 -15 Na_2O -10 LaF_3 (55Si-10La) doped with several Nd^{3+} concentrations (0.1-2 mol %) is investigated. The choice of this glass composition, previously developed in our research group [17], [21] and [22], relies on the fact that very small LaF_3 crystals (~ 10 nm), which is one of the best fluoride hosts for RE ions, can precipitate in the glass matrix. As a consequence, very good transparency is still obtained upon the conversion of the glass into a glass-ceramic. Moreover, this glass system has a peculiar feature: phase separation acts as a precursor to crystallization, with several LaF_3 crystals tending to grow inside phase-separation droplets uniformly distributed throughout the glass matrix, thus impeding formation of clusters. In a previous work, Tm^{3+} -doped 55Si-10La glass-ceramics were studied by X-ray absorption near-edge structure XANES spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy with X-ray synchrotron radiation [23]. These techniques revealed that Tm^{3+} incorporates preferentially into the LaF_3 nanocrystals by diffusion, the concentration of which increases with treatment time. For a thermal treatment of 10 h at 620 $^\circ\text{C}$, the incorporation of Tm^{3+} ions in the LaF_3 nanocrystals was about 17%, reaching 30% for 40 h of heat treatment.

Among the rare-earth ions, Nd^{3+} has been recognized as one of the most efficient for solid-state lasers in crystals and glasses due to its intense $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ emission at around 1.06 μm [24]. Besides the interest of the Nd^{3+} ion for infrared (IR) optical amplification, it 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 [24] and [25]. However, there are few works on the laser properties of Nd^{3+} in transparent oxyfluoride glass-ceramics [26], [27], [28], [29], [30], [31], [32], [33], [34], [35] and [36]. In some of these studies, the spectroscopic properties of Nd^{3+} -containing glass-ceramics differ very

little from those of the precursor glasses, suggesting a more difficult incorporation of Nd^{3+} ions into the crystalline phase compared to other RE ions. Pisarska et al. [28] and [29] did not find any difference in the fluorescence lifetime of the $^4\text{F}_{3/2}$ state in a heat-treated sample of an oxyfluoroborate glass, concluding that Nd^{3+} ions are not incorporated in the crystalline phase. Yu et al. [19] studied Nd^{3+} -doped (0.5-3 mol%) glass-ceramics where LaF_3 precipitates with a crystal size between 10 to 15 nm. It was found that the most promising composition was that containing 0.5 mol% Nd^{3+} , in which glass-ceramics are more efficient than glasses. However, no deeper study of photoluminescence was performed.

In this work, the crystallisation mechanism and the structural and optical properties of Nd^{3+} -doped LaF_3 glass-ceramics are reported for their possible use as laser materials. In particular, the effect of Nd^{3+} ions on the kinetics of crystallisation has been studied and the possibility to selectively separate the emission of Nd^{3+} ions in the glass matrix from those embedded in LaF_3 nanocrystals is presented. 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 allows the emission of Nd^{3+} ions in LaF_3 nanocrystals to be unambiguously identified which shows extremely well defined spectra similar to those obtained for pure LaF_3 crystals [37], [38] and [39].

2. Experimental

2.1. Materials and methods

Glasses of composition $55\text{SiO}_2\text{-}20\text{Al}_2\text{O}_3\text{-}15\text{Na}_2\text{O-}10\text{LaF}_3$ (55Si-10La) doped with 0.1, 0.2, 0.5, 1 and 2 Nd^{3+} (in mol%) have been prepared by melting-quenching using as raw materials: SiO_2 sand (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 as G0.1, G0.2, G0.5, G1 and G2, for Nd^{3+} concentrations of 0.1, 0.2, 0.5, 1, and 2 mol.% respectively; corresponding glass-ceramics will be denoted with GCx.

Glass-ceramics samples were obtained by heat treatments of glass pieces at 620 °C for 1, 3, 5, 20, 40, 80 h and at 660 °C- 20 h, using a heating rate of 10 °C/min. Glass sheets (1 cm x 1 cm x 2 mm) were treated and then polished for optical characterization. One glass slab for each composition was not treated and used as reference glass to compare with the corresponding glass-ceramics.

2.2. Structural characterisation

Non-isothermal crystallisation kinetics were studied by DTA/TG (SDT Q600 - TA Instruments) using 20-30 mg of glass with particle size in the range 1-1.25 mm. DTA curves were obtained with heating rates in the range 10–60 °C/min. From these DTA data, the glass transition temperature T_g , Avrami n parameter and crystal-growth dimensionality m parameter were calculated from the Ozawa equation [40] and the Matusita equation [41] given by equations (1) and (2) respectively:

$$\left(\frac{d[\ln[-\ln(1-x)]]}{d(\ln q)} \right)_T = -n \quad (1)$$

$$\ln \left(\frac{q^n}{T_p^2} \right) = -\frac{mE_a}{RT_p} + \text{Cost} \quad (2)$$

In these relations, x is the partial area of the crystallisation peak calculated for a fixed temperature T and q is the heating rate; T_p and R are the crystallisation peak temperature and the gas constant, respectively. The activation energy for crystallisation E_a was calculated using the Kissinger equation [42]:

$$\ln\left(\frac{q}{T_p^2}\right) = -\frac{E_a}{RT_p} + \text{Cost} \quad (3)$$

The heat-treated specimens were milled, sieved ($<63 \mu\text{m}$) and characterised by XRD (Bruker D8 Advance diffractometer). XRD diffractograms were acquired in the range 2θ 10-70, with a step-size of 0.02° and 1 s acquisition time for each step. The crystal size was calculated using the Scherrer equation [43]:

$$D = \frac{0.94\lambda}{\cos\theta\sqrt{B_m^2 - B_i^2}} \quad (4)$$

where λ is the wavelength ($1.54056 \text{ \AA} - \text{CuK}\alpha_1$), B_m the full width half maximum of the LaF_3 peak (111) and θ its diffraction angle. The factor 0.94 corresponds to spherical crystals. The pseudo-Voigt function was used to fit diffraction-peak parameters. The instrumental broadening B_i has also been taken into account using NaF powder properly milled and sieved ($<63 \mu\text{m}$).

The crystallised fraction of LaF_3 in the glass-ceramics obtained on a heat treatment at 620°C for 40 hours was estimated by quantitative Rietveld analysis employing a method that has been applied to similar compositions [17] and [22]. The glass was finely ground in an agate mortar, sieved through a $60 \mu\text{m}$ mesh then milled again with NaF (99.9%), which was used as internal standard in an appropriate quantity (5-6 wt%) to approximate the peak intensity of the nanocrystalline LaF_3 . XRD powder data for Rietveld analysis were collected over the range $10^\circ \leq 2\theta \leq 90^\circ$ in a stepwidth of 0.0289° and a counting time of 4s per step employing a Bruker D8 high-resolution diffractometer equipped with a solid-state rapid LynxEye detector, and monochromatic $\text{Cu K}\alpha_1$ radiation. Rietveld refinement was performed with the Fullprof program using interpolation of background points to model the amorphous contribution to the pattern.

TEM samples of glasses and glass-ceramics were prepared using sieved powders of size $< 63 \mu\text{m}$. High resolution electron microscopy (HR-TEM), including Scanning Transmission Electron Microscopy-High Angle Annular Dark Field (STEM-HAADF) were recorded on a JEOL 2100 field-emission gun transmission electron microscope operating at 200 kV with a point resolution of 0.19 nm. The microscope is equipped with an energy dispersive X-ray spectrometer (EDXS) (INCA x-sight, Oxford Instruments), which was operated in STEM mode, with a probe size of 1 nm.

Small-angle X-ray scattering (SAXS) measurements were performed using a commercial SAXS system (SAXSess, Anton Paar GmbH). The bulk samples were crushed into fine powders and then compressed into uniform thin pellets for the SAXS measurements. A $\text{Cu K}\alpha$ line beam of $10 \text{ mm} \times 0.4 \text{ mm}$ in size was incident on the samples, and the scattered X-rays were collected using an imaging plate in the q range of $0.01\text{-}0.1 \text{ \AA}^{-1}$. The collected 2D patterns were converted into 1D patterns and treated using the line-beam profile. The 1D SAXS data were then analysed using the Irena software package⁴⁴ to obtain the particle-size distribution.

2.3. Optical characterisation

UV-Vis absorption spectra of optical sheets were measured in the range 300-1000 nm using a Lambda 900-Perkin Elmer double-beam spectrophotometer.

Site-selective, steady-state emission and excitation spectra were recorded by exciting the samples with a continuous wave (cw) Ti:sapphire ring laser (0.4 cm^{-1} linewidth) in the 770–920 nm spectral range. The fluorescence was analysed with a 0.25 m monochromator; the signal was detected by an extended IR Hamamatsu H10330A-75 photomultiplier and amplified by a standard lock-in technique. The sample temperature was varied between 10 and 300 K in a continuous-flow cryostat.

Lifetime measurements 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. Data were processed by a Tektronix oscilloscope.

3. Results and discussion

3.1. Structural properties

Fig. 1a shows DTA curves for G0.1 for the heating rates 10–60 °C/min. The exothermic peak, T_p , at around 670 °C corresponds to the crystallisation of LaF_3 phase. Similar results were obtained for the undoped glass [22]. Fig. 1b shows the variation of T_g and T_p with Nd^{3+} concentration for a heating rate of 10 °C/min, the same rate as used in all heat treatments. On increasing the Nd^{3+} concentration, T_g changes almost linearly from a value of 573 °C for the G0.1 sample to 593 °C for G2, while T_p changes only a few degrees for increasing Nd^{3+} contents. The crystallisation stability parameter, $\Delta T = T_p - T_g$, diminishes notably with higher Nd^{3+} concentration, with G2 glasses showing a higher tendency to crystallise compared to the G0.1 glass. It appears, therefore, that Nd^{3+} ions are acting as nucleating agent, and concomitantly increase the glass-matrix rigidity. This may be explained on considering that incorporation of RE ions usually increases glass viscosity in the high-viscosity regime, i.e for $T < T_g$ [17] and [45]. Additionally, RE incorporation could favour phase separation, which also leads to an increase in viscosity.

Fig. 1 (c) shows the Ozawa plots of G0.1 for six different temperatures. For each plot, an n value was obtained, and then a mean n value was calculated and included in the figure together with the m parameter. Similar n and m values, approximate to 1, were obtained for all compositions. These values correspond to a crystallisation process which starts from a constant number of nuclei and for which crystal growth is diffusion controlled [46]. The same behaviour was also observed for other oxyfluoride GCs [47], [48] and [49]. The addition of Nd^{3+} , even in quite varied concentrations, does not influence the crystallisation mechanism but affects the crystallisation kinetics. Moreover, the crystallisation activation energy, E_a , around 350 kJ/mol, is the same for all compositions and similar to that of the undoped glass [22].

Fig. 1. (a) DTA curves at different heating rates of the G0.1 glass and (b) T_g variation with Nd concentration; (c) Ozawa plots.

Fig. 2(a) shows the XRD diffractograms of GC0.1 samples heat treated at 620 °C for 1, 3, 5, 20, 40 and 80 h and at 660 °C for 20 h. LaF_3 peaks (JCPDS 00-032-0483) are shown at the foot of the figure for reference. For all compositions, only LaF_3 crystals precipitate in the glass matrix; however, the crystal-growth kinetics slows down as Nd^{3+} content increases. Fig. 2b shows the crystal size of GCs at 620 °C for all the Nd^{3+} concentrations; the crystal size for GCs at 660 °C is shown in the inset. On gradually increasing the Nd^{3+} concentration, the crystal size decreases for treatments at 620 and 660 °C. On treatment at 620 °C, LaF_3 crystals grow from 10 nm to 12.5 nm during the first 5 h for the G0.1 glass, but grow less than 1 nm for G2. This may be explained on consideration of the higher T_g of the G2 glass.

For heat treatment at 660 °C-20 h larger crystals are formed but a similar trend as observed for 620 °C is maintained. The inset of Fig. 2(b) shows the crystal growth rate for treatment at 620 °C in the range 1-5 h, since for times longer than 20 h the crystal size does not change with time. Crystal-growth rate decreases from GC0.1 to GC1, maintaining practically the same value for GC2.

Quantitative Rietveld refinements of the LaF_3 crystalline phase with NaF as internal standard were carried out for GCs obtained at the same thermal treatment of 620°C during 40 h. The observed diffraction pattern and the difference between observed and calculated diffraction patterns for 0.1GC are shown in Fig. 2(c).

Fig. 2. (a) XRD diffractograms for G0.1 treated at 620°C for periods in the range 1-80 h and G1 660°C-20h G2; (b) Crystals size for GC samples G0.1, G0.2, G0.5, G1 and G2 treated at 620°C and (inset) crystals growth rate in the range 1-5 h; (c) Observed and difference X-ray powder diffraction profiles of GC0.1 obtained at 620 °C during 40h with 5 mol% NaF internal weight standard. The Bragg peaks of NaF and LaF₃ are indicated by top and bottom vertical bars, respectively. Refinement parameters $R_p = 1.53$; $R_{wp} = 2.0$; $\chi^2 = 1.44$ were obtained.

The following crystalline fractions (wt %) were determined with varying Nd content: 0.1GC (6.4), 0.5GC (9.9), 1GC (8.8), and 2GC (8.2). Although it is difficult to establish a clear tendency, it is apparent that an increase of the crystalline fraction takes place for Nd contents above 0.5 mol %, after which, the crystalline fraction tends to stabilise, or even slightly decrease, which is in good agreement with the smaller nanocrystals obtained with 1 and 2 mol % of Nd (Fig. 2(b)).

Fig. 3a and 3b show HR-TEM images of G2 glass at different magnifications. The inset of Fig. 3a indicates the size of the initial phase-separated droplets present in the glass; their mean size is 34.8 ± 0.4 nm, the FWHM is 18 ± 2 nm. No crystalline structure was observed. Figs. 3c and 3d show images of GC2 treated at 620 °C for 40 h. The amorphous phase-separated droplets in the glass samples formed several crystals inside. The droplet and crystal size distribution are given in the insets of Figs. 3c and 3d, respectively. The mean value of the droplets in the GC sample is 34.0 ± 0.4 nm, similar to that obtained for the glass, but the FWHM gets sharper giving a value of 10 ± 1 nm; the mean crystal size is centred at 10 nm, in agreement with the value obtained by XRD measurements for the GC2 620 °C-40 h sample.

Figs. 3e and 3f present crystal planes along the [100] and [113] directions calculated by FFT of some crystals shown in Fig. 3d, confirming the precipitation of LaF₃ crystals. The plane distances d_{111} and d_{113} , which give the most intense peaks in the XRD diffractogram at 27.5° and 44.7° 2θ , are 0.33 nm and 0.20 nm, in good agreement with the values of 0.323 nm and 0.202 nm reported for LaF₃ in the JCPDS (00-032-0483) and the literature [50], [51] and [52]. Fig. 3g presents the EDX curves across two adjacent droplets circled in red in Fig. 3h; the points 1-2 and 3-4 delimit the first and second droplet, respectively. The yellow line is the scanning line, also represented in Fig. 3g with the droplet size marked by vertical dashed grey lines. EDX analysis of Fig. 3g shows Si enrichment surrounding the phase-separated droplets, which leads to the formation of a barrier of higher viscosity around them.

The barrier formation appears to occur during the first 20 h of heat treatment since LaF₃ crystals grow during this time, and thereafter maintain their size. The incorporation of Nd³⁺ inside the LaF₃ crystals is clearly visible from the EDX curves.

Fig. 3. (a) and (b) HR-TEM of G2 glass; (c) and (d) GC2 heat treated at 620 °C-40 h; (e) and (f) lattice planes of some crystals shown in (d); (g) EDX of the GC2 620 °C-40 h sample along 2 droplets containing several crystals (the yellow and light grey lines indicate the scanning line and droplet size, respectively); (h) STEM image of the droplets used for the EDX measurement where the yellow line is the same as that represented in (g).

Fig. 4a and 4b show the particle volume distribution of G2 and GC2 samples (annealed at 620 °C for 40 hrs) as a function of particle diameter. The insets display the raw SAXS data and theoretical fit using the Irena program, from which the particle volume distribution was obtained. The particles can be classified in two distinctive size groups, group 1 below 10 nm and group 2 between 15 and 60 nm. The group 1 particles seen in both samples may be associated with very small initial phase-separated droplets which could not grow sufficiently to produce crystals. The group 2 particle size is, however, in very good agreement with the results obtained by TEM and is related with the scattering of phase-separated droplets. The calculated average diameters for these two groups of particles were 6 nm and 38 nm for the G2 sample, and 7 nm and 36 nm for the GC2 sample.

The SAXS results were roughly consistent with the TEM results reported in Fig. 3. The slightly larger average size (by about 2 nm) derived from the SAXS analysis compared to the TEM results could be due to the difference between particle-volume distribution (SAXS) and particle-number distribution (TEM), with the former having more weighting on the larger particles. One interesting feature is that the two groups of particles showed opposite growth behaviour upon thermal annealing: the group 1 particle-size distribution became broader while that of the group 2 particles became narrower after 40 hrs of annealing at 620 °C, which was consistent with the TEM observation. The thermal annealing also significantly enhanced the relative volume fraction of group 1 particles. New particles between 10 and 15 nm in diameter appeared in the GC2 sample after thermal annealing, which were probably related to the crystals as seen from the TEM and XRD results.

Fig. 4. SAXS data (insets) and derived particle-volume distribution of G2 (a) and GC2-620 °C treated for 40 hrs (b).

3.2. Absorption and emission properties

A further proof of Nd^{3+} incorporation in the LaF_3 crystals comes from UV-Vis absorption spectra in Fig. 5, in which GCs samples are compared with glasses. Figs 5a

and 5b show the absorption coefficient for the G0.1, G0.2, G0.5, G1 and G2 glasses and for the corresponding GC samples treated at 620 °C for 40 h. The bands observed in the spectra correspond to transitions from the fundamental level ($^4I_{9/2}$) to each of the excited levels of Nd^{3+} ions. The glass samples present characteristic inhomogeneously-broadened absorption bands. However, in the case of the GC samples, the absorption bands are resolved better, indicating the incorporation of Nd^{3+} ions in the LaF_3 nanocrystals precipitated during the heat treatments.

Fig. 5c presents the $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ absorption bands of G0.1 and G2 glasses, along with GC0.1 and GC2 glass-ceramics treated at 620 °C for 40 h, in greater detail. The absorption bands $^4I_{9/2} \rightarrow ^4F_{7/2}, ^4S_{3/2}$ and $^4I_{9/2} \rightarrow ^4F_{5/2}, ^2H_{9/2}$ in the GC samples are shown in the inset. Similar behaviour is also appreciable in the GC samples treated at 620 °C and 660 °C for 20 h. The $^4I_{9/2} \rightarrow ^4G_{5/2}$ transition is well known to be a hypersensitive transition, exhibiting an electric quadrupole character which is strongly dependent on the ligand field. A clear change in the absorption band allows the Stark components in the GCs to be better resolved. The sharpening of the band in comparison to the initial glass indicates the presence of Nd^{3+} ions inside the LaF_3 crystals. This is most clearly visible in the G0.1 sample, whereas on increasing the Nd^{3+} content, the difference between glass and GCs is less apparent.

Fig. 5. (a) Absorption spectra of glasses G0.1, G0.5, G1, G2 and (b) GCs treated at 620 °C-40h; (c) comparison of absorption transitions $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ and (inset) $^4I_{9/2} \rightarrow ^4F_{7/2}, ^4S_{3/2}$ and $^4I_{9/2} \rightarrow ^4F_{5/2}, ^2H_{9/2}$ in G0.1, G2, GC0.1 620 °C-40 h and GC2 620 °C-40 h.

The absorption bands of the glass and GC samples doped with 2 mol% Nd³⁺, together with the values of the refractive index and Nd³⁺ concentration, have been used to determine the Judd-Ofelt parameters [53] and [54]. Using this theory, the calculated oscillator strengths can be expressed as a function of the reduced-matrix elements $\langle U^{\lambda} \rangle$ which are almost independent of the ion environment. To estimate the J-O parameters (Table 1), the values reported by Carnall et al. for Nd³⁺ in LaF₃ [55] were employed. As is well known, the spectroscopic parameter Ω_2 is proportional to the covalent nature of the chemical bonding between rare-earth ions and ligand ions [56]. As observed in Table 1, Ω_2 decreases from 3.23x10⁻²⁰ in the glass sample to 2.82-2.89 x10⁻²⁰ in the GC materials. That is, the heat treatment induces a reduction in the degree of covalence between Nd³⁺ and its nearest neighbours. The decrease of Ω_2 further confirms the incorporation of Nd³⁺ ions into the precipitated nanocrystals. Moreover, the sum of the J-O parameters decreases for the GC samples due to the decreasing covalency of the bond between the Nd³⁺ ion and surrounding anions in accordance with reported results [57]. The strength of the hypersensitive ⁴I_{9/2}→⁴G_{5/2} transition, which is greatly affected by the environment of Nd³⁺ ions, is dominated by the Ω_2 parameter contribution, increasing with both the ligand polarisability and asymmetry of the surrounding environment [53] and [54]. The oscillator strength of this transition is reduced from 1796x10⁻⁸ in the glass to 1609 x10⁻⁸, 1581x10⁻⁸, and 1591x10⁻⁸ in the GC 620 °C C-20 h, GC 620 °C-40 h, and GC 660 °C-20 h samples, respectively. This tendency confirms that the ligand field around the Nd³⁺ ions changes as a consequence of the heat treatment and crystallisation process.

Table 1. Judd-Ofelt parameters and r.m.s. deviation for precursor glass and GC samples doped with 2 mol% Nd.

Sample	Ω_2 (x10 ⁻²⁰)	Ω_4 (x10 ⁻²⁰)	Ω_6 (x10 ⁻²⁰)	r.m.s.
Glass	3.23	6.23	5.03	5.35·10 ⁻⁷
GC2-620°C-20h	2.85	5.57	4.37	5.25·10 ⁻⁷
GC2-620°C-40h	2.82	5.48	4.31	5.16·10 ⁻⁷
GC2-660°C-20h	2.89	5.45	4.17	5.35·10 ⁻⁷

The spontaneous emission probabilities from the ⁴F_{3/2} to ⁴I_J states were calculated from the J-O parameter and used to obtain the radiative lifetimes.

The ⁴F_{3/2}→⁴I_{11/2,13/2} steady-state fluorescence spectra were measured at room temperature for all samples by exciting with a Ti:sapphire laser at 802 nm in resonance with the ⁴I_{9/2}→⁴F_{5/2}, ²H_{9/2} absorption band. Fig. 6 shows the emission for the samples doped with 2 mol% Nd. It can be seen that the emission is inhomogeneously broadened due to site-to-site variations in the local ligand field. The fluorescence band for the ⁴F_{3/2}→⁴I_{11/2} emission was integrated and divided by the peak intensity to yield an effective linewidth [57]. From the measured effective linewidth and the spontaneous emission probability of the ⁴F_{3/2}→⁴I_{11/2} laser transition, calculated from the J-O parameters, the stimulated emission cross-section of this transition may be evaluated as [58]:

$$\sigma_p(\lambda_p) = \frac{\lambda_p^4}{8\pi n^2 \Delta\lambda_{eff}} A[(^4F_{3/2});(^4I_{11/2})] \quad (5)$$

where λ_p is the peak fluorescence wavelength, n is the refractive index, $\Delta\lambda_{eff}$ is the effective linewidth of the ⁴F_{3/2}→⁴I_{11/2} transition, and $A[(^4F_{3/2});(^4I_{11/2})]$ is the radiative transition probability for this transition.

The stimulated emission cross-section for the ⁴F_{3/2}→⁴I_{11/2} transition and other relevant parameters are presented in Table 2. The peak position remains unchanged for the GC samples and the effective linewidth slightly increases with the time of heat treatment.

This behaviour, together with the lower radiative transition probability for the $^4F_{3/2} \rightarrow ^4I_{11/2}$ emission for the crystallised samples, leads to smaller stimulated emission cross-sections for the GC samples, in the range of values found in silicate glasses (0.9-3.6 pm^2) [24].

Fig. 6. Room-temperature emission spectra of the $^4F_{3/2} \rightarrow ^4I_{11/2,13/2}$ transitions of Nd^{3+} ions (2 mol%) obtained under excitation at 802 nm.

Table 2. Room-temperature emission properties of Nd (2 mol%) in the glass and glass-ceramic.

Sample	n	$\lambda_p(\text{nm})$	$\Delta\lambda_{\text{eff}}(\text{nm})$	$\sigma_p(\text{pm}^2)$	$\tau_R(\mu\text{s})$
Glass	1.523	1057	35.95	2.8	345
GC2-620°C-20h	1.525	1057	37.16	2.4	390
GC2-620°C-40h	1.526	1057	37.60	2.3	395
GC2-660°C-20h	1.526	1057	38.94	2.2	398

The steady-state emission spectra exhibit similar spectral features for all concentrations and heat treatments. However, the excitation spectra of the GC samples doped with 0.1, 0.2, and 0.5 mol % performed in the spectral range 765-910 nm monitored at 1057 nm show a fine structure superimposed on the broad $^4I_{9/2} \rightarrow ^4F_{5/2,3/2}$ bands of the glass, confirming the partial incorporation of Nd^{3+} ions in the nanocrystals. In the samples doped with 1 and 2 mol%, Nd^{3+} ions are responsible for the main contribution to the spectra in the amorphous environment. As an example, Fig. 7 shows the excitation spectra for the samples doped with 0.1 and 1 mol% where better resolved peaks are observed for the lower Nd^{3+} concentration.

Fig. 7. Room temperature excitation spectra of the ${}^4I_{9/2} \rightarrow {}^4F_{5/2,3/2}$ transitions of Nd^{3+} obtained by collecting the luminescence at 1057 nm for the samples doped with (a) 0.1 mol% NdF_3 and (b) 1% Nd.

The decays of the ${}^4F_{3/2}$ state were obtained by exciting with a pulsed Ti:sapphire laser at 802 nm in the ${}^4I_{9/2} \rightarrow {}^4F_{5/2}$ absorption band at 295 K. Fig. 8 shows the logarithmic plot of the experimental decays of the ${}^4F_{3/2}$ level for the samples doped with 0.1 and 1 mol% of NdF_3 at room temperature. The decays of the samples doped with 0.1 mol% may be described to a good approximation by a single exponential function, whereas the decays of the samples doped with 1 mol% deviate from a single exponential and the lifetime decreases.

Fig. 8. Logarithmic plot of the room temperature experimental decays from the ${}^4F_{3/2}$ state for the samples doped with (a) 0.1 and (b) 1 mol% of NdF_3 . The decays were obtained by exciting at ${}^4I_{9/2} \rightarrow {}^4F_{5/2}$ transition and monitored at 1057 nm.

Table 3 lists the lifetime values for all the samples. The lifetime values for the samples with concentrations higher than 0.1 mol% correspond to the average lifetime defined by:

$$\langle \tau \rangle = \frac{\int I(t) dt}{I_0} \quad (6)$$

where $I(t)$ is the intensity at time t . According to these radiative lifetimes, the quantum efficiencies ($\eta = \tau_{\text{exp}}/\tau_{\text{R}}$) are around 99 and 41% for the glass samples doped with 0.1 and 2 mol%, respectively. This strong reduction of the quantum efficiency for increasing Nd concentration indicates the presence of non-radiative cross-relaxation processes such as $({}^4F_{3/2}, {}^4I_{9/2}) \rightarrow ({}^4I_{15/2}, {}^4I_{15/2})$. The lifetime of the GC samples is longer than those of glass samples for all the concentrations, which suggests a fluoride environment for Nd^{3+} ions according to their incorporation in the nanocrystals. The results are similar for the three heat treatments which indicate that after 20 h at 620 °C, the rare-earth ions are largely incorporated into a crystalline environment.

Table 3. Experimental lifetimes of the ${}^4F_{3/2}$ level obtained under excitation at 802 nm by collecting the luminescence at 1057 nm as a function of Nd^{3+} concentration and heat treatment. The radiative lifetime is shown in the last column.

Sample	0.1%	0.2%	0.5%	1%	2%	τ_{R} (μs)
Glass	343	298	268	192	143	345
GC2-620°C-20h	382	350	308	251	187	390
GC2-620°C-40h	385	354	310	254	191	395
GC2-660°C-20h	388	360	315	254	197	398

3.3. Site-selective spectroscopy

To obtain further information about the different environments for Nd^{3+} ions in the glass-ceramics, emission spectra were performed by exciting at different wavelengths along the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}$ absorption band. Fig. 9(a) shows the emission spectra obtained by exciting at 786 and 802 nm for the GC samples doped with 0.1 mol% of Nd^{3+} treated at 620 °C-40 h. The figure reveals the strong difference between spectra of differing excitation wavelength, which indicates that Nd^{3+} ions are in different crystal-field sites. The spectrum obtained at 786 nm shows a more resolved structure, indicating a crystalline environment for the Nd^{3+} ions. In contrast, that obtained under excitation at 802 nm shows a more inhomogeneous broadened band similar to that of the glass sample. Moreover, the excitation spectra obtained by collecting the luminescence at 1039 and 1057 nm also reveal the presence of different environments for Nd^{3+} ions. Fig. 9(b) shows the excitation spectra for the same sample doped with 0.1 mol% of Nd^{3+} . The spectrum monitored at 1039 nm presents narrower and well-resolved peaks corresponding to Nd^{3+} ions in the nanocrystals. As concentration increases, the spectra become broader and less resolved.

To clearly identify emission from Nd^{3+} in the nanocrystals, the emission and excitation spectra were measured at low temperature, thereby minimising the overlapping of contributions from Nd^{3+} in the crystalline and amorphous phases due to the lower 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. 10 for the GC samples doped with 0.1 and 1 mol%. As observed in the spectra obtained at 1039 nm, the low-energy band corresponding to the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$ doublet narrows and divides into two single components, as expected for a well-defined crystal-field site. Moreover, the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}$ band is composed of narrow and well-resolved peaks which indicate that the spectra obtained at 1039 nm correspond to Nd^{3+} ions in the LaF_3 nanocrystals. Conversely, the spectra obtained at 1057 nm show broad bands similar to those found in the glass samples.

Fig. 9. (a) Room-temperature emission spectra obtained under excitation at 786 and 802 nm for the GC1 sample doped with 0.1 mol%; (b) excitation spectra obtained on collecting the luminescence at 1039 and 1057 nm for the GC treated at 620 °C-40 h sample doped with 0.1 mol%.

Fig. 10. Low-temperature excitation spectra obtained on collecting the luminescence at 1039 and 1057 nm for the GC samples doped with (a) 0.1 and (b) 1 mol%.

In order to confirm if the features shown by the excitation spectra monitored at 1039 nm can be unambiguously related to the Nd^{3+} ions in the nanocrystals, site-selective steady-state emission spectra for the $4F_{3/2} \rightarrow 4I_{11/2}$ transition were recorded by exciting at 786 and 802 nm. Fig. 11 shows the normalized emission spectra at 9 K obtained under excitation at 786 and 802 nm for the GC samples doped with 0.1 and 1 mol%, showing quite different emission spectra depending on the excitation wavelength. The spectrum obtained under excitation at 786 nm shows sharp peaks, one at 1039 nm which does not overlap with the emission spectrum obtained by exciting at 802 nm. In the latter, the sharp peaks disappear and the spectrum becomes broader and similar to that found in the glass sample. These results indicate that in the glass-ceramic samples excited at 786 nm, Nd^{3+} ions mainly reside in the crystalline phase. As concentration increases, the emission from Nd^{3+} ions in the nanocrystals decreases, and the spectra become broader with more poorly resolved peaks. Similar emission spectra are obtained by exciting the $4I_{9/2} \rightarrow 4F_{3/2}$ band at 861.5 and 876 nm.

Furthermore, the existence of different environments for the Nd^{3+} ions in the LaF_3 nanocrystals is also reflected in the lifetimes of the $4F_{3/2}$ state, the values of which should depend on the excitation and emission wavelengths. Lifetime measurements of the $4F_{3/2}$ state were performed by exciting the samples at 786 and 802 nm, and collecting the luminescence at 1039 and 1057

nm, respectively (Fig. 12). Under excitation at 786 nm and collecting the luminescence at 1039 nm, the decay is a 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 1057 nm, the lifetime is 336 μ s (Table 4). The longer lifetimes corresponds to the Nd³⁺ ions incorporated in the nanocrystals. This lifetime is highly dependent on Nd concentration, decreasing to 98 μ s for the GC samples doped with 1 mol%.

Fig. 11. Low temperature emission spectra obtained under excitation at 786 and 802 nm for the GC samples doped with (a) 0.1 and (b) 1 mol%.

Fig. 12. Logarithmic plot of the experimental decays from the $^4F_{3/2}$ state obtained under excitation at 786 nm (blue lines) and 802 nm (pink lines) for the GC samples doped with (a) 0.1 and (b) 1 mol%.

Table 4. Experimental lifetimes, at low temperature, of the $^4F_{3/2}$ level obtained under excitation at 790 and 802 nm collecting the luminescence at 1039 and 1057 nm, respectively.

%Nd	$\lambda_{\text{exc}} = 786 \text{ nm}$	$\lambda_{\text{exc}} = 802 \text{ nm}$
	$\tau_{\text{exp}} (\mu\text{s})$	$\tau_{\text{exp}} (\mu\text{s})$
0.1	688	336
0.2	462	337
0.5	188	332
1	98	295
2	29	233

As observed, there is a strong quenching of the lifetimes of Nd^{3+} in the LaF_3 nanocrystals, but much less so in the amorphous phase. This behaviour is likely explained from the considerable 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 [23]. In this previous work, the ionization energy E_0 of Tm^{3+} , calculated from the derivate function of the XANES spectra, increased during the crystallisation process, from the glass to the glass-ceramic. It was concluded; therefore, that part of the RE ions existed in a fluorine-rich environment, since the electronegativity of fluorine is higher than that of oxygen. Additionally, the decrease in FWHM of the Tm^{3+} absorption-edge peak from the glass to the glass-ceramic indicated a higher symmetry and, correspondingly, crystallinity of the Tm^{3+} environment in the glass-ceramics. Thus, an increase of the crystalline fraction with the heat treatment time at 620 °C, from 10 to 40 h, was concluded to occur simultaneously with the diffusion process, resulting in the incorporation of around 30% of Tm^{3+} in the LaF_3 crystalline structure after 40 h. Starting from the crystalline fractions obtained by Rietveld refinement, the ratio of the concentration of Tm^{3+} in the crystalline phase to that in the

glass matrix was calculated (with an error of $\sim 25\%$), to be approximately 12 for treatment times of 40 h.

In the present work, the same composition is used doping with Nd^{3+} . The GCs were obtained in similar conditions and the crystalline fractions calculated from Rietveld analysis are in close agreement with those obtained in the previous work [23]. In the present case, the crystalline fraction depends on the Nd content.

As discussed previously, for treatment times of 40 h, the diffusion process should be essentially complete, as indicated by the constant crystal size for treatments of 20 h and longer. If a silica-rich diffusion barrier is established, no further Nd^{3+} diffusion will take place and so it is possible to consider that around 30% of the Nd^{3+} ions will be in the crystalline phase. Using the same method followed in [23], the respective Nd^{3+} contents in the amorphous and crystalline phases were calculated, with an error $\sim 25\%$, and are shown in Table 5.

Table 5. Crystal fraction in wt% of glasses treated at 640 °C-40 h with different Nd^{3+} contents, along with the respective concentration of Nd^{3+} in the glass matrix and LaF_3 NCs.

%Nd	wt% crystallisation	% Nd in glass	% Nd in NCs
0.1	6.4	0.076	1.2
1	8.8	0.65	8.58
2	8.2	1.3	17.16

The relative concentrations of Nd^{3+} in the glass matrix and LaF_3 nanocrystals could explain the strong quenching of the Nd^{3+} emission for Nd^{3+} contents higher than 0.1%, whereas in the glass matrix no significant quenching is observed. Further work is in progress to confirm these calculations by measuring all the samples by XAS-XANES.

4. Conclusions

The crystallisation mechanism of transparent glass-ceramics in the system 55Si-10La doped with increasing Nd^{3+} concentrations was confirmed as a diffusion-controlled process starting from a constant number of nuclei already present in the initial glass. The addition of Nd^{3+} increases the Tg of the glasses and appears to affect the crystallisation kinetics. As the Nd^{3+} content increases, the crystallised fraction also increases indicating that Nd^{3+} ions likely play a role as nucleating agent. Nevertheless, smaller crystals are obtained for the higher Nd^{3+} content. TEM and SAXS techniques have provided complementary information about the size and distribution of phase separation droplets and nanocrystals in the base glass and their evolution in the corresponding glass-ceramics.

Preferential incorporation of Nd^{3+} in the crystalline phase was confirmed by HR-TEM-EDX and several types of optical property measurement. These include splitting of the absorption and emission bands together with reduction of the Ω_2 parameter in the glass-ceramic samples as compared to the glass samples and site-selective spectroscopy obtained under excitation of the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}/^4\text{F}_{5/2}$ transitions.

Low-temperature site-selective emission and excitation spectra together with different lifetime values of the $^4\text{F}_{3/2}$ state depending on the excitation and emission wavelengths allow emission from Nd^{3+} ions in the LaF_3 nanocrystals to be isolated and, in turn, correlation of the spectroscopic and structural properties. The optimum amount of dopant corresponds to 0.1 mol%; strong quenching of the lifetime of Nd^{3+} in the LaF_3 nanocrystals occurs for higher concentrations.

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