Crystallization effect on rare-earth activated biocompatible glass-ceramics

R. Balda^{a,b,*}, D. Sola^b, J.I. Peña^c, J. Fernández^{a,b}

^aDepartamento de Física Aplicada I, Escuela Técnica Superior de Ingeniería, Universidad del País Vasco UPV/EHU, Alda. Urquijo s/n 48013 Bilbao, Spain

^bMaterials Physics Center CSIC-UPV/EHU and Donostia International Physics Center, 20080 San Sebastián, Spain

^cInstituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC
50018 Zaragoza, Spain

*wupbacrr@bi.ehu.es

ABSTRACT

In this work we report the influence of the crystallization stage of the host matrix on the spectroscopic properties of rare-earth ions in $\text{CaSiO}_3/\text{Ca}_3(\text{PO}_4)_2$ biocompatible eutectic glass-ceramics grown by the laser floating zone technique. The microstructural analysis shows that either a growth rate increase or a rod diameter decrease leads the system to a structural arrangement from three (two crystalline and one amorphous) to two phases (one crystalline and one amorphous). The crystalline phases correspond to apatite-like and Ca_2SiO_4 structures. Site-selective laser spectroscopy allows to distinguish between crystalline and amorphous environments for the Nd^{3+} ions and to correlate the spectroscopic properties with the microstructure of these eutectics.

Keywords: Rare earth doped materials, laser floating zone technique, biocompatible glass-ceramics.

1. INTRODUCTION

Directionally solidified eutectic ceramic oxides are composite materials grown from the melt whose characteristics can be controlled by the solidification conditions. In addition to their excellent mechanical properties, microstructural stability, and corrosion resistance up to temperatures very close to their melting point [1], the unique features of the eutectic microstructure allow to extend their use to functional applications by the addition of rare earths (RE) to the eutectic system. From the point of view of optical spectroscopy, eutectics made from large optical bandgap materials present the unusual characteristic of being at the same time a monolith and a multiphase material where active ions can be placed in a different field environment in the same material, as in $\text{ZrO}_2\text{-CaO}$ eutectics activated with Er^{3+} ions [2,3].

Among different eutectic compositions, the $\text{CaSiO}_3/\text{Ca}_3(\text{PO}_4)_2$ (W-TCP) eutectic composite presents two unconventional and interesting properties. This eutectic is a bio-active ceramic material for human bone replacement since calcium silicate is bioactive and tricalcium phosphate presents an exceptional biocompatibility and a close chemical similarity to biological apatite present in bone tissues. The features, microstructure, bioactivity, biocompatibility, and *in vitro* and *in vivo* behaviors of this binary system have been widely studied, mainly in its glassy form [4-6]. Recent studies have focused on the devitrification process of this glass for obtaining glass-ceramic materials through thermal treatments in order to develop W-TCP implants with a better bioactivity and improved mechanical properties [7-9]. In the second place, it is possible to produce a good optical quality glass by fast directional solidification of the $\text{CaSiO}_3/\text{Ca}_3(\text{PO}_4)_2$ binary eutectic system. The study of the spectroscopic properties of Nd^{3+} and Er^{3+} ions in this glass shows that the lifetimes and emission cross-sections of the 1.06 μm (Nd^{3+}) and 1.5 μm (Er^{3+}) emissions are equivalent to those of the best commercially used alkaline-silicate glasses [10]. Moreover, laser emission at 1.06 μm (Nd^{3+}) under pulsed pumping has been observed which shows a behavior close to a Q-switch operation [11]. The variety of quasi-isolated crystal field site distributions of Nd^{3+} ions in this glass matrix allows for a broad band tunability (10 nm) of the laser as a function of the pumping wavelength [11,12].

In this work we report the influence of the crystallization stage of the host matrix on the spectroscopic properties of Nd^{3+} ions in W-TCP eutectic glass-ceramics doped with 1 and 2 wt% of Nd_2O_3 , grown by the laser floating zone (LFZ) technique. Site-selective laser spectroscopy in the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}/^4\text{F}_{5/2}$ transitions of Nd^{3+} ions have been used to investigate the crystal field changes felt by Nd^{3+} ions as a consequence of the sample crystallization stage. The differences among the spectral features of the site-selective excitation and emission spectra of Nd^{3+} ions allow to distinguish between crystalline and amorphous environments for the rare-earth ions and to correlate the spectroscopic properties with the microstructure of these eutectics. The microstructural analysis of the glass-ceramic samples shows the existence of three (two crystalline and one amorphous) or two phases (one crystalline and one amorphous) depending on the growth rate and rod diameter. The crystalline phases correspond to apatite-like and Ca_2SiO_4 structures. The latter, which has some attractive bioactive properties, is not observed in the glass-ceramics obtained by thermal treatments.

2. EXPERIMENTAL

2.1 Samples fabrication

The precursor rods were obtained from the powder mixture of wollastonite (CS) and tricalcium phosphate (TPC) in the eutectic 80% CaSiO_3 , 20% $\text{Ca}_3(\text{PO}_4)_2$ mol% composition. Furthermore, 1 and 2 wt% of Nd_2O_3 were added to the eutectic composite to obtain the doped samples. The resulting powders were isostatically pressed at 200 MPa for 2 minutes giving ceramic rods which were sintered at 1200°C for 10 hours.

Glass and glass-ceramic eutectic rods were obtained by the laser floating zone technique (LFZ), which has been described elsewhere in detail [1,13]. This technique permits to control the solidification rate, providing high axial and radial thermal gradients in the liquid-solid interface, of a great importance in the microstructure domain, and opens up the possibility of fabricating eutectic glasses and glass-ceramics [1,14]. The diameter of the rods and the growth rates were varied in order to modify the crystalline character of the samples. In the first place, keeping constant the diameter length around 2.5 mm, the samples were grown at rates of 50, 100, 250 and 500 mm/h. Secondly, while keeping the growth rate at 100 mm/h, the feed rate was modified to obtain final diameters between 2.5 and 4.5 mm. Samples were grown in air, and after growth they were annealed at 650°C for 5 h to relieve inner stresses. Table 1 shows the processing features of the glass-ceramic samples used in this work and the amount of Nd_2O_3 present in each sample.

Table 1. Eutectic glass-ceramic samples used in this work together with the growth rate (V), diameter (D), and Nd_2O_3 concentration.

	V (mm/h)	D (mm)	Nd_2O_3 (wt%)
Sample 1	50	2.50	1
Sample 2	100	2.30	1
Sample 3	250	2.60	1
Sample 4	500	2.45	1
Sample 5	100	2.45	2
Sample 6	100	4.50	2

2.2 Experimental techniques

The microstructure, composition, and crystalline features of the phases present in the samples were determined by means of scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy analysis (EDX), and Electron backscatter diffraction (EBSD), with a field emission JEOL JSM-7000F microscope.

The samples temperature was varied between 10 and 300 K in a continuous flow cryostat. Site-selective steady-state emission and excitation spectra were obtained by exciting the samples with a 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 Triax 190 monochromator, and the signal was detected by a Hamamatsu H10330A-75 photomultiplier and finally amplified by a standard lock-in technique.

3. RESULTS AND DISCUSSION

3.1 Microstructural characterization

In order to analyse the influence of the processing conditions on the microstructure of the glass-ceramic samples, a microstructural analysis was carried out by means of scanning electron microscopy (SEM). The growth rate, rod diameter, and amount of doping material present in the sample are the key factors involved in the arrangement of the microstructure, i.e., in their size, number of phases, and alignment with respect to the growing direction. It is worth noticing that the axial and radial temperature gradients in the solidification interface are related to the cooling rate in such a way that the crystalline nature of the sample increases with diameter and decreases with growth rate [1,14]. As an example, Figs. 1(a) and 1(b) show the longitudinal-section micrographs of samples doped with 1 wt% of Nd_2O_3 with diameters around 2.5 mm, and grown at 50 mm/h (a) and 500 mm/h (b) respectively, whereas Figs. 1(c) and 1(d) show the longitudinal-section of samples doped with 2 wt% of Nd_2O_3 grown at 100 mm/h with diameters of 2.45 mm (c), and 4.5 mm (d) respectively. The inset in each micrograph shows the details of the microstructure in a cross-section view. The microstructure is made up of fibers with an irregular shape, (clear phase), embedded in a greyish matrix, (dark and black phases). These figures show how the variation in growth rate or diameter can modify the size as well as the number of phases present in the samples. A growth rate increase or a diameter decrease leads the system to a structural arrangement from three to two phases. Furthermore, the parallel alignment of the phases with respect to the growing direction can be lost as the growth rate is diminished or the diameter increased as a consequence of the loss of flatness in the solidification front.

Fig. 1. Longitudinal-section micrographs of samples doped with 1 wt% of Nd_2O_3 with a diameter of 2.5 mm and grown at 50 mm/h (a) and 500 mm/h (b) and samples doped with 2 wt% of Nd_2O_3 grown at 100 mm/h with diameters 2.45 mm (c), and 4.5 mm (d). The inset shows the details of the microstructure in a cross-section view.

The increase of the amount of doping material leads to a diminution in the number of phases formed, which goes from three to two phases, and furthermore, the dark phase turns from crystalline into amorphous. Moreover, if the occupation areas of this phase were compared, around a 50% had been increased in the sample doped with a 2 wt% of Nd₂O₃ with respect to the one doped with 1 wt% of Nd₂O₃. In either case, the increase of doping material did not affect the alignment of the phases with respect to the growing direction.

The composition of the phases was determined by means of an energy dispersive X-ray (EDX) analysis. In the case of samples with three phases, (samples 1, 2, and 6 from Table 1), the clear phase was rich in CaO and P₂O₅ with a low content of SiO₂. The dark phase was rich in SiO₂ and CaO with a very low content of P₂O₅, and in the black phase there was a high amount of CaO and SiO₂ and a low content of P₂O₅. Regarding Nd₂O₃, though a similar content was found in the three phases, both in the clear and dark ones, it was mainly placed in the black phase. In the case of samples with two phases, (samples 3, 4, and 5 from Table 1), the composition of the clear and dark phases was similar to the previous case. As an example, Table 2 shows the compositional analysis in wt% of samples grown at 50 mm/h and 500 mm/h with a diameter around 2.5 mm and doped with 1wt% of Nd₂O₃.

Table 2. Compositional analysis in wt% of the phases present in the eutectic glass-ceramic samples grown at 50 mm/h and 500 mm/h and doped with 1wt% of Nd₂O₃.

	V (mm/h)	SiO ₂	P ₂ O ₅	CaO	Nd ₂ O ₃
Clear phase	50	15.54	31.67	52.17	0.61
Dark phase	50	50.18	3.18	46.11	0.53
Black phase	50	42.02	18.17	38.21	1.60
Clear phase	500	15.38	32.82	51.1	0.69
Dark phase	500	46.2	11.57	41.56	0.68

The crystalline nature of the phases was determined by an electron backscatter diffraction (EBSD) analysis. In the case of samples with three phases, the clear phase had an apatite-like structure, which could be apatite, oxyapatite or hydroxyapatite, whereas the dark phase had a Ca₂SiO₄ structure and the black one was amorphous. In the case of samples with two phases, the clear phase, as in the previous case, had an apatite-like structure but in this case the dark one was amorphous [13]. Therefore, the clear phase was crystalline in any case but the dark one turned from crystalline into amorphous as the growth rate was increased or the diameter decreased.

3.2 Site-selective laser spectroscopy

The influence of the growth rate and diameter on the spectroscopic properties of Nd³⁺ ions in the eutectic glass-ceramics has been studied by using site-selective laser spectroscopy in the ⁴I_{9/2}→⁴F_{3/2,5/2} transitions. The excitation spectra of the ⁴I_{9/2}→⁴F_{3/2,5/2} transitions obtained by collecting the luminescence at different emission wavelengths along the ⁴F_{3/2}→⁴I_{11/2} laser transition for the glass-ceramic samples suggest that Nd³⁺ ions are incorporated in a crystalline phase in these glass-ceramics. As an example, Fig. 2 shows the low temperature excitation spectra corresponding to the ⁴I_{9/2}→⁴F_{3/2,5/2} transitions obtained at 1066 nm for the glass-ceramic samples doped with 1 wt% of Nd₂O₃ grown at 50, 100, 250, and 500 mm/h together with the excitation spectrum of the glass sample for comparison. As can be seen, the spectra corresponding to the ⁴I_{9/2}→⁴F_{3/2} transition in the glass-ceramic samples show at least four main bands instead of the two expected Stark components of the ⁴F_{3/2} doublet in a low crystal field symmetry, which indicates the presence of different environments for Nd³⁺ ions in these matrices. By comparison with the excitation spectrum of the glass sample the spectra of this transition show two new peaks at around 859 and 886 nm. The spectra corresponding to the ⁴I_{9/2}→⁴F_{5/2} transition also show a new sharp peak at around 810 nm, not observed in the excitation spectrum of the glass sample, which indicates that Nd³⁺ ions are in a crystalline environment. The position of these new peaks is almost independent of the growth rate. However, as growth rate decreases the spectrum becomes more defined with narrower peaks.

Fig. 2. Excitation spectra of the $^4I_{9/2} \rightarrow ^4F_{5/2}$ transitions obtained by collecting the luminescence at 1066 nm in the glass and glass-ceramic samples obtained at different growth rates and doped with 1 wt% of Nd_2O_3 .

A similar behaviour is obtained when the ceramic/glassy character of the sample is modified by the variations of the rod diameter. As in the previous case, the position of the bands corresponding to the $^4I_{9/2} \rightarrow ^4F_{3/2,5/2}$ transitions is independent on the diameter of the rod but the spectrum is more defined with narrower peaks for the wider diameter, i.e., the more crystalline sample. Figure 3 shows the excitation spectra corresponding to the glass-ceramic samples doped with 2 wt% of Nd_2O_3 grown at 100 mm/h with 2.45 and 4.5 mm diameters.

Fig. 3. Excitation spectra of the $^4I_{9/2} \rightarrow ^4F_{5/2,3/2}$ transitions obtained by collecting the luminescence at 1066 nm in the glass-ceramic samples doped with 2 wt% of Nd_2O_3 grown at 100 mm/h with diameters 2.45 and 4.5 mm.

To obtain information about the different environments for Nd^{3+} ions in these glass-ceramic samples, excitation spectra at different emission wavelengths along the laser transition were performed. Figure 4(a) shows the excitation spectra obtained by collecting the luminescence at 1050, 1066, and 1080 nm of a glass-ceramic sample grown at 100 mm/h and doped with 1 wt% of Nd_2O_3 . The spectra are very different depending on the emission wavelength which indicates that Nd^{3+} ions are in different crystal field sites. The spectrum obtained at 1050 nm shows, for the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}$ transition, sharp and well-resolved peaks with the most intense one located at around 802.2 nm which indicates a crystalline environment for Nd^{3+} ions. This intense peak disappears and the spectrum becomes an unstructured broad band for the samples grown at 250 and 500 mm/h (see Fig. 4(b) as an example). The low energy band corresponding to the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$ doublet narrows into one single component as expected for one well defined crystal field site. The high energy component of the doublet, which is more tightly coupled to the host vibrations, shows a more complex structure, probably due to the accidental mixing of emissions coming from different crystal field sites. According with the previous microstructural analysis these results suggest that this spectrum at 1050 nm corresponds to Nd^{3+} ions in a crystalline phase corresponding to Ca_2SiO_4 which is only present for samples grown at low rates (50 and 100 mm/h). However, the spectrum obtained at 1080 nm shows broad bands similar to those found in the glass sample. The spectrum corresponding to the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$ transition shows at least two components in the low energy band. This behaviour has been also found in the glass sample being a consequence of contributions from Nd^{3+} ions in a multiplicity of environments (see Fig. 4(c)). In the case of the excitation spectrum collected at 1066 nm, as seen before, in addition to the broad bands, sharp peaks at around 810.8, 859, and 886 nm appear which according to the EBSD analysis, could correspond to Nd^{3+} ions in the apatite-like crystalline phase which is present in all glass-ceramics samples.

Fig. 4. Excitation spectra obtained at different emission wavelengths for the glass-ceramic samples doped with 1 wt% of Nd_2O_3 grown at 100 mm/h (a) and 250 mm/h (b) and for the glass sample (c).

The effect of the crystallization stage of the samples is also reflected in the emission spectra. Figure 5 shows the emission spectra at 10 K obtained under excitation at 802.2 and 810.8 nm respectively for the samples grown at 50 and 500 mm/h together with the spectra of the glass sample. As can be seen, different emission spectra are obtained depending on the excitation wavelength. The spectrum obtained for the glass-ceramic sample grown at 50 mm/h under excitation at 802.2 nm shows a complex structure with a sharp peak at 1050 nm together with other components. This peak disappears and the spectrum becomes broader and similar to the one found in the glass sample for the glass-ceramic sample grown at 500 mm/h. This indicates that at this wavelength, in the glass-ceramic samples grown at low rates (50 and 100 mm/h), we simultaneously excite Nd^{3+} ions in dicalcium silicate crystalline and in amorphous phases making it difficult to isolate the emission corresponding only to the crystalline phase. As we have mentioned before, this crystalline phase becomes amorphous for the samples prepared with high growth rates which is confirmed by the

features observed in the emission spectra of the samples grown at 250 and 500 mm/h. However, the spectrum obtained at 810.8 nm shows, in all glass-ceramic samples, a sharp line with an effective linewidth of about 3.1 nm centered at around 1067 nm together with other much lower Stark components, which suggests that at this wavelength we are exciting Nd^{3+} ions in the apatite-like crystalline phase which is present in all glass-ceramic samples.

Fig. 5. Steady-state emission spectra of the ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ transition obtained under excitation at 802.2 nm and 810.8 nm for the glass-ceramic samples grown at 50 mm/h and 500 mm/h and for the glass sample.

4. CONCLUSIONS

Eutectic glass-ceramics of composition $0.8\text{CaSiO}_3\text{-}0.2\text{Ca}_3(\text{PO}_4)_2$ doped with 1 and 2 wt% of Nd_2O_3 were fabricated by the laser floating zone technique. The growth rate and rod diameter are the key factors involved in the crystallization process and hence in the size, number of phases present in the glass-ceramic samples, and in their alignment with respect to the growing direction. In particular, the glassy character of the glass-ceramic samples increases with the increase of the growth rate or the decrease of the rod diameter.

The microstructural analysis shows the existence of three (two crystalline and one amorphous) or two phases (one crystalline and one amorphous) depending on the growth rate. The crystalline phases correspond to Ca_2SiO_4 and apatite-like structures, being the dicalcium silicate (Ca_2SiO_4) crystalline phase only present in the glass-ceramic samples grown at low rates (50 and 100 mm/h).

The differences among the spectral features of the site-selective excitation and emission spectra of Nd^{3+} ions allow to distinguish between crystalline and amorphous environments for the rare-earth ions and to correlate the spectroscopic properties with the microstructure of these eutectics. The presence of dicalcium silicate (Ca_2SiO_4) crystalline phase in the samples grown at low rates can be unambiguously identified from the excitation spectra of the ${}^4\text{F}_{3/2}$ state of Nd^{3+} ions. These results show the potentialities of rare-earth-doped eutectic glass-ceramics obtained from the LFZ technique as luminescence probes for in vitro applications based in their bioactive and luminescent properties.

ACKNOWLEDGMENTS

This work was supported by the Spanish Government MEC under Projects No. MAT2009-14282-C02-02, FIS2011-27968, Consolider SAUUL CSD2007-00013, and Basque Country Government IT-659-13 and SAIOTEK S-PE12UN016. Daniel Sola thanks the JAE-DOC program and the Science and Technology Inter-Ministry commission of Spain and FEDER funds of the EC under project MAT2009-13979-C03-03 for the financial support of his contract.

REFERENCES

- [1] J. Llorca and V. M. Orera, "Directionally solidified eutectic ceramic oxides," *Prog. Mater. Sci.* 51, 711-809 (2006). (and references therein)
- [2] R. I. Merino, J. A. Pardo, J. I. Peña, G. F. de la Fuente, A. Larrea, and V. M. Orera, "Luminescence properties of ZrO_2 -CaO eutectic crystals with ordered lamellar microstructure activated with Er^{3+} ions," *Phys. Rev. B* 56, 10907-10915 (1997).
- [3] R. Balda, S. Garcia-Revilla, J. Fernández, R. I. Merino, J. I. Peña, and V. M. Orera, "Near infrared to visible upconversion of Er^{3+} in $\text{CaZrO}_3/\text{CaSZ}$ eutectic crystals with ordered lamellar microstructure," *J. Lumin.* 129, 1422-1427 (2009).
- [4] P. N. de Aza, F. Guitian, and S. de Aza, "Phase diagram of wollastonite-tricalcium phosphate," *J. Am. Ceram. Soc.* 78, 1653-1656 (1995).
- [5] P. N. de Aza, F. Guitian, and S. de Aza, "Bioeutectic: a new ceramic material for human bone replacement," *Biomaterials* 18, 1285-1291 (1997).
- [6] P. N. de Aza, F. Guitian, and S. de Aza, "A new bioactive material which transforms *in situ* into hydroxyapatite," *Acta Mater.* 46, 2541-2549 (1998).
- [7] M. Magallanes-Perdomo, P. Pena, P. N. de Aza, R. G. Carrodeaguas, M. A. Rodríguez, X. Turrillas, S. de Aza, and A. H. de Aza, "Devitrification studies of wollastonite-tricalcium phosphate eutectic glass," *Acta Biomater.* 5, 3057-3066 (2009).
- [8] M. Magallanes-Perdomo, Z. B. Luklinska, A. H. de Aza, R. G. Carrodeaguas, S. de Aza, and P. Pena, "Bone-like forming ability of apatite-wollastonite glass ceramic," *J. Eur. Ceram. Soc.* 31, 1549-1561 (2011).
- [9] C. Wang, Y. Xue, K. Lin, J. Lu, J. Chang, and J. Sun, "The enhancement of bone regeneration by a combination of osteoconductivity and osteostimulation using β - CaSiO_3/β - $\text{Ca}_3(\text{PO}_4)_2$," *Acta Biomater.* 8, 350-360 (2012).
- [10] J. A. Pardo, J. I. Peña, R. I. Merino, R. Cases, A. Larrea, and V. M. Orera, "Spectroscopic properties of Er^{3+} and Nd^{3+} doped glasses with 0.8CaSiO_3 - $0.2\text{Ca}_3(\text{PO}_4)_2$ eutectic composition," *J. Non-Cryst. Solids* 298, 23-31 (2002).
- [11] R. Balda, J. Fernández, I. Iparraguirre, J. Azkargorta, S. García-Revilla, J. I. Peña, R. I. Merino, and V. M. Orera, "Broadband laser tunability of Nd^{3+} ions in 0.8CaSiO_3 - $0.2\text{Ca}_3(\text{PO}_4)_2$ eutectic glass," *Opt. Express* 17, 4382-4387 (2009).
- [12] R. Balda, R. I. Merino, J. I. Peña, V. M. Orera, and J. Fernández, "Laser spectroscopy of Nd^{3+} ions in glasses with the 0.8CaSiO_3 - $0.2\text{Ca}_3(\text{PO}_4)_2$ eutectic composition," *Opt. Mater.* 31, 1319-1322 (2009).
- [13] D. Sola, R. Balda, J. I. Peña, and J. Fernandez, "Site-selective laser spectroscopy of Nd^{3+} ions in 0.8CaSiO_3 - $0.2\text{Ca}_3(\text{PO}_4)_2$ biocompatible eutectic glass-ceramics," *Opt. Express* 20, 10701-10711 (2012).
- [14] D. Sola, F. J. Ester, P. B. Oliete, and J. I. Peña, "Study of the stability of the molten zone and the stresses induced during the growth of Al_2O_3 - $\text{Y}_3\text{Al}_5\text{O}_{12}$ eutectic composite by the laser floating zone technique," *J. Eur. Ceram. Soc.* 31, 1211-1218 (2011).