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Rare earths in nanocrystalline glass–ceramics

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Abstract

The optical spectroscopic analysis of rare earth ions in transparent oxyfluoride glass–ceramics obtained from SiO_2–Al_2O_3–PbF_2–CdF_2 based precursor glasses is presented. The oscillator strengths of the optical transitions were measured from the absorption spectra of glasses and glass–ceramics doped with rare earth ions. The results were analysed in the framework of the Judd–Ofelt theory giving the values of the three Ω_2, Ω_4 and Ω_6 intensity parameters over the rare earth series. On the other hand, high efficient infrared-to-blue upconversion has been observed in Tm^{3+}–Yb^{3+} codoped glass and glass–ceramic compared to the Tm^{3+} single doped matrices. The contributions to the upconversion process of the rare earth ions in the nanocrystalline and in the vitreous phase of the glass–ceramics have been distinguished. Finally, laser action in Nd^{3+}-doped glass–ceramic has been studied. Losses due to UV and visible upconverted emissions inside the laser cavity have been also estimated.

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1. Introduction

Nowadays, one of the most interesting fields of research is focused on the development of optical devices based on rare earth (RE) ions doped materials for their use in telecommunication systems, such as upconversion fibers, optical amplifiers, solid-state lasers and 3D displays [1–3]. Efforts have been focus on finding materials with low-energy phonons, in order to reduce the multiphonon non-radiative de-excitation and improve cross-sections of the rare earth ions, being the fluoride and chalcogenide based matrices the common choices.

However, in 1993 Wang and Ohwaki [4] found a new kind of suitable matrices, i.e. the transparent oxyfluoride glass–ceramics doped with RE ions. These matrices take advantage of combining various remarkable properties in one material, since the oxyfluoride glass–ceramic is a multiphase material that consists of one aluminosilicate glassy phase and a fluoride nanocrystalline phase. The combination of its ease of fabrication and manipulation in air-atmosphere, its large transparency and the ability to incorporate RE ions in fluoride type nanocrystals make this material unique in the field of optical material engineering [1–3].

The RE-doped oxyfluoride glasses with composition (in mol%) of 30 SiO_2, 15 Al_2O_3, 29 CdF_2, 22 PbF_2, $(4 - x)$ YF_3 and x REF_3 (RE = rare earth) used in this work were prepared by melting and processing the thor-

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oughly mixed composition in a platinum crucible at 1050 °C for 2 h in air and then poured on a stainless steel plate at room temperature (RT). Although no controlled atmosphere is necessary and only conventional manipulation cautions are needed, there are some problems that must be taken into account during the precursor glass preparation such as spontaneous devitrification, rare-earth clustering or inhomogeneous dopant distribution [5,6].

Nanocrystalline structures are obtained after a thermally controlled growth of the crystal phase directly in the glass [1–10]. The transparent oxyfluoride glass–ceramic under study was obtained after a thermal treatment of the precursor glass at 470 °C at the onset of the crystallization peak for 36 h. Both the precursor glass and the subsequently obtained glass–ceramic show good optical quality and a large transparency. Two possibilities exist for producing a transparent glass–ceramic system [1,3]. The crystals must be sufficiently small to produce no effective scattering in the visible range or optical isotropy must be achieved within the glass–ceramic. Tick et al. [7] have analysed the scattering losses of a Tm^{3+}-doped glass–ceramic optical fiber and concluded that, although a relatively large refractive index mismatch of about 0.06 exists between glassy and crystalline phases, its transparency is because there is less than 10 vol% of crystals in the matrix with sizes of the order of 10 nm or less. Thus the condition for high transparency is achieved by the existence of uniformly dispersed nanocrystals with interparticle spacing of dimensions comparable to the particle size.

The structural transition expected after a thermal treatment of the precursor glass can be monitored by X-ray diffraction. As shown in Fig. 1, along with two broad curves, typical of structures without long-range order like glasses, there is a number of narrow and relatively intense peaks that reveals a diffraction pattern of a crystalline phase. From the analysis of these peaks it has been concluded that this partially crystallized sample contains cubic fluoride nanocrystallites of the β-PbF_2 phase. This result is in agreement with that found by Silva et al. in SiO_2–PbF_2–CdF_2 matrices [8], although Tick et al. [7] have suggested that the crystal phase in the glass–ceramic under study comprises PbF_2, YF_3 and CdF_2. From the X-ray diffraction peak width and using the Scherrer formula, an average size of the crystals ranging from 15 to 25 nm has been found [5,9,10].

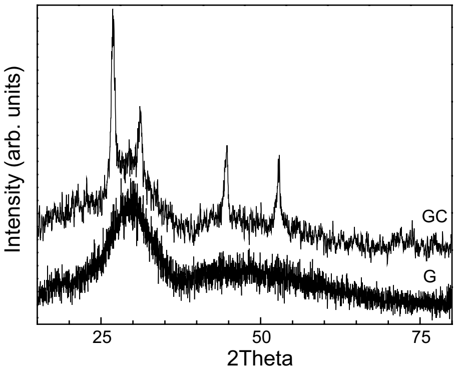

Fig. 1. X-ray diffraction patterns of oxyfluoride glass (G) and glass–ceramic (GC).

On the other hand, Méndez-Ramos et al. [5] and Silva et al. [8] have demonstrated that in the glass–ceramic the formation of the β-PbF_2 phase is favoured by the incorporation of RE ions in the crystalline phase, playing the role of heterogeneous nucleating agents and partially replacing the Pb^{2+} ions. Changes introduced in the RE local structure by the thermal treatment can be monitored by optical spectroscopic studies, showing properties that are mainly due to low-energy phonon environments with higher quantum efficiencies than in the precursor glass. In the β-PbF_2 nanocrystals the lanthanide ions enter in two sites of low symmetry with similar distribution profiles [5], but unfortunately detailed information about the exact low point symmetry of the immediate environment is not available. For higher doped glass–ceramics, in addition to diluted ions it has been observed the presence of EuF_3 clusters that favour the energy transfer processes due to the shortening of distances between RE ions [5].

2. Results and discussion

2.1. Spectral intensities over the rare earth series

The intensities of bands in the absorption and luminescence spectra of matrices doped with trivalent RE elements have been successfully characterized by the Judd–Ofelt theory [11]. The main goal is that the absorption and emission probabilities between any two states are given as a function of three intensity, or Judd–Ofelt, parameters (Ω_2, Ω_4 and Ω_6) that characterize a given RE–matrix combination.

The theory considers that the intra-configurational transitions between 4f states of the RE ions are mainly electric-dipole in nature and are forced by inter-configurational opposite-parity wave function mixing. However, the physical meaning of the Judd–Ofelt para- meters and the mechanisms that rule their behaviour is still a matter of discussion. In general, the Ω_2 parameter, that describes the hypersensitive transitions, depends on short-range effects, such as covalency and/or local structural changes, whereas the Ω_4 and Ω_6 are long-range parameters that can be related to the bulk properties of the glass, such as the viscosity or the basicity of the matrix [12–14]. Since the f orbitals are shielded from the environment, correlations of the intensity parameters with the chemical nature of the