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Crystal-field spectroscopy of Eu^{3+} doped silica glasses

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ABSTRACT

Fourier transform absorption spectroscopy in the 500–6000 cm^{-1} and 9–300 K ranges is applied to monitor the effects produced by Eu^{3+} incorporation into sol–gel silica samples doped with concentration increasing from 0.001 to 10 mol%. The aim is to investigate the formation of aggregates by exploiting the Eu^{3+} crystal-field transitions. Complementary microreflectance and Raman spectra are also measured in the range of silica intrinsic vibrational modes to confirm the hypothesis of matrix modification induced by increasing doping levels. Evidences of clustering are found for high Eu^{3+} concentrations. Up to 3 mol% the crystal-field line intensities gradually increase and the OH^- content smoothly decreases. A further increase to 10 mol% causes drastic, remarkable changes, i.e. sharp crystal-field lines appear which narrow by lowering the temperature. Furthermore, the OH^- related bands are no longer detectable. For concentrations up to 3 mol% the aggregates are amorphous as the silica matrix, while for the Eu^{3+} 10 mol% sample they show a rather ordered structure.

1. Introduction

Scintillating materials find applications in several fields as medicine [1], high energy physics [2], and security controls [3]. In alternative to the currently employed crystalline scintillators, glasses were recently considered due to their good mechanical properties, chemical stability, easy shape modeling [4], and compatibility with silica based photonics. Recent studies on rare earth (RE) doped glasses evidenced a poor luminescence efficiency due to low energy transfer between the glass matrix and the active ions and to the presence of non-radiative decay channels [2,3]. Among the latter, OH^- deserves particular attention because it is present in the samples as a consequence of the preparation process [5] and cannot be completely removed even by subsequent thermal treatments [6]. To improve the luminescence properties, the research is moving towards sol–gel nano-composite materials, where the active phase is composed of RE-rich aggregates [7]. The real application of such materials requires further investigations about the mechanisms driving the cluster formation and the possible non-radiative decay channels.

In the present work the crystal-field transitions of Eu^{3+} in sol–gel SiO_2 glasses are exploited to probe clustering phenomena, originated by gradually increasing the dopant concentration in a wide range (0.001–10 mol%). In addition to the crystal-field analysis, vibrational spectroscopies (infrared absorption, microreflectance, and Raman) were applied to monitor the OH^- content and the matrix modifications induced by Eu^{3+} incorporation.

2. Experimental procedures

The glass samples were prepared by the sol–gel method, as described in Ref. 8. The Eu^{3+} concentrations, expressed in molar fraction, varied in the 0.001–10 mol% range. Pure SiO_2 samples were also prepared and submitted to the same thermal treatments as the samples doped with Eu^{3+}. Most of the samples are transparent, but a few of them show “foggy” or partially “milky” regions. The 10 mol% sample is almost completely milky. CsI based pellets were prepared to measure the absorption spectra of powdered Eu^{3+}-compounds (as oxyorthosilicates or oxides) used as references. The weight ratio was, e.g. for the Eu_2SiO_5 pellet, about 20 mg sample over 100 mg CsI. Optical absorption spectra were monitored at room temperature (RT) by means of a Bomem DA8 Fourier transform spectrophotometer in the wave number range 500–6000 cm^{-1} with a resolution of 1 cm^{-1}. A few samples were also measured in the temperature range 9–300 K, thanks to a 22 model Cryodine Refrigerator of CTI Cryogenics equipped with KRS-5 windows, to make evident possible sharp lines due to Eu^{3+} in ordered phases. Microreflectance measurements were performed at RT by exploiting an IR PLAN microscope from Spectra Tech (Stamford, CT) coupled to the spectrometer by means of a mirror system; the reflectance standard was a gold mirror.

Raman spectra were obtained at RT by a micro-Raman spectrometer (Labram, Jobin-Yvon). The excitation sources were either the 488 nm line of an Ar laser or the 632.8 nm line of a He–Ne laser. Unpolarized

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Raman spectra were collected in a backscattering configuration through a CCD detector.

3. Results

Due to Eu^{3+} $4f^6$ configuration, the fundamental manifold is the J-singlet $^7F_0$, thus all the crystal-field (CF) absorption transitions should start from a unique sublevel. The first excited manifolds ($^7F_{1,2,3}$) lie at energies lower than 2000 cm^{-1}, thus the transitions having as final states such manifolds should not be detected in silica glasses due to the fundamental vibrational absorption overlapping [9]. Fig. 1A portrays the RT absorption spectra of a few samples doped with different amounts of Eu^{3+} (0, 3, and 10 mol%): bands due to $^7F_0 \rightarrow {}^7F_{4,5,6}$ transitions can be detected at 3 mol% (curve b). In the investigated range, in addition to the CF absorptions of Eu^{3+}, there are the peaks related to Si–OH stretching and combination modes (at about 3670 and 4520 cm^{-1}, respectively [10]) and the O–Si–O asymmetric stretching overtone at ~2260 cm^{-1} [11]. The spectra modifications induced by the gradual Eu^{3+} increase up to 3 mol% can be summarized as follows:

1. broad and weak bands grow, as due to the presence of Eu^{3+}, at ~2670, 2826, 3020, 3900, 4526, and 4760 cm^{-1}, see dashed rectangles in Fig. 1A;
2. the Si–OH stretching mode absorption at about 3670 cm^{-1} smoothly decreases;
3. a shoulder at about 3600 cm^{-1} overlaps the Si–OH stretching peak, being quite evident in the 3 mol% sample (compare curves a and b in panel C).

In the 10 mol% doped sample remarkable changes occur (curve c, panel A) with respect to the lower concentration ones. The Eu^{3+} related absorptions are characterized by rather sharp lines, even in the RT spectra. The Si–OH peaks are no longer detected and the bump at 3600 cm^{-1} disappears. The O–Si–O asymmetric stretching overtone, at 2260 cm^{-1}, is heavily modified and a shoulder due to Eu^{3+} appears at 2238 cm^{-1}. The milky texture of the sample causes light scattering and consequently the background grows by increasing the wave number.

The spectra of the pure and Eu^{3+} doped (3 and 10 mol%) samples were measured at low temperature to better understand the origin of the unusual (for a glass) narrow peaks shown by Eu^{3+} 10 mol% sample. The spectra were compared with those measured at 9 K on two CsI pellets of Eu_2SiO_5 and Eu_2O_3. The absorptions in the Eu^{3+} 3 mol% doped sample remain broad even at 9 K, while the 10 mol% doped sample shows a line-rich spectrum: by lowering the temperature the lines become narrower and narrower and their number increases.

To investigate the changes induced by Eu^{3+} doping on the SiO_2 intrinsic vibrational modes, microreflectance measurements on all the Eu^{3+} doped samples were performed: Fig. 2 displays the spectra (normalized to the reflectivity maximum at 1123 cm^{-1} to emphasize the differences) of the pure sample and two doped ones (3 and 10 mol%). The spectra of lower Eu^{3+} concentration samples are not reported for clarity, since they practically coincide with that of the pure one (curve a). The main features are the peaks at 780 and 1123 cm^{-1} (with a shoulder at 1230 cm^{-1}) related to the bending and asymmetric stretching modes of O–Si–O groups, respectively [11]. By increasing the doping level up to 3 mol% (e.g. curve b) the reflectivity maximum slightly shifts towards low wave numbers. Furthermore, the dip at 1200 cm^{-1} becomes more marked, new bands appear in the 860–950 cm^{-1} region, and the peak at about 780 cm^{-1} increases. Similar effects were recently observed in silica glasses doped with other rare earths, as Ce^{3+}, Tb^{3+}, Gd^{3+}, and Yb^{3+}

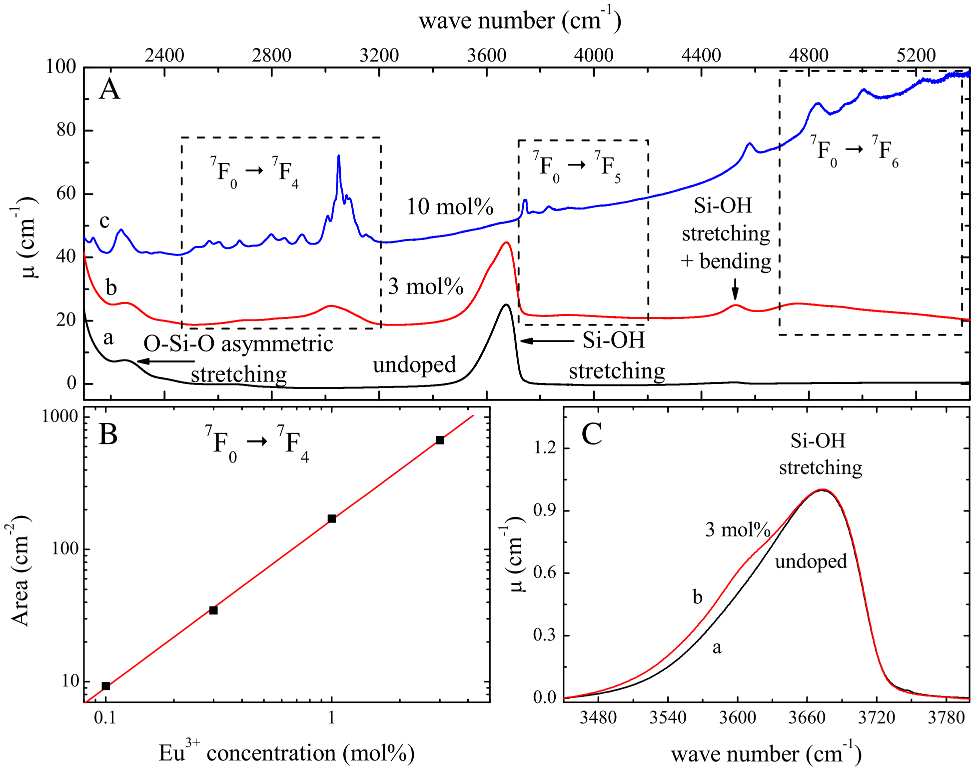

Fig. 1. Panel A. Room temperature optical absorption spectra measured on SiO_2 samples doped with different amounts of Eu^{3+} in the region of the $^7F_0 \rightarrow {}^7F_{4,5,6}$ transitions. Curve a: undoped sample; curve b: Eu^{3+} 3 mol%; curve c: Eu^{3+} 10 mol%. The spectra are vertically shifted for clarity. Panel B. Log–log plot of the area subtended to the Eu^{3+} peaks, related to $^7F_0 \rightarrow {}^7F_4$ transition, as a function of the Eu^{3+} concentration. The solid curve is the linear fit of the experimental data. Panel C. Normalized absorption spectra measured in the region of the OH^- stretching mode (~3670 cm^{-1}) on an undoped (curve a) and on an Eu^{3+} 3 mol% doped (curve b) sample.