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Investigation of the local environment of Eu^{3+} in a silicophosphate glass using site-selective spectroscopy and Molecular Dynamics simulations

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ABSTRACT

Silicophosphate glasses (SiO_2-P_2O_5) doped with Eu^{3+} ions were synthesized by the sol-gel process. Optical properties of these glasses were investigated by means of emission spectra and lifetime measurements. The Fluorescence Line Narrowing (FLN) technique was also used to explore the local structure around the Eu^{3+} ions in this host and to understand the role of phosphate as a codopant. As it is the case for aluminum, the ability of phosphate to avoid the rare earth clustering was investigated, and the role of this codopant in modifying the local order around the rare earth ion was evidenced. The analysis of the FLN spectra and lifetime measurements is consistent with this interpretation. Molecular Dynamics simulations were performed to evaluate and confirm these structural features. Two classes of europium sites were distinguished in agreement with the experimental characterization.

1. Introduction

Rare Earth (RE) doped glasses are well known as potential materials for optical devices in laser and telecommunication technologies. Among these materials, the silicate glasses are still promising host materials for successful applications in photonics materials [1–3]. But in such materials, a good efficiency is generally achieved with a high doping level, and the conventional melt-quench technique to obtain a glass does not allow high enough RE concentration. Alternatively, the sol-gel route is attractive because, proceeding at lower temperature, the RE concentration can be increased up to 10%. However, even at lower concentrations and whatever the synthesis route, the RE emission properties are subject to the so-called concentration quenching. This limitation is generally attributed to the RE ions clustering which leads to energy transfers between clustered ions by cross-relaxation or phonon-assisted mechanisms [4].

To avoid RE clustering and concentration quenching, an efficient solution is to codope the silica matrix with chosen cations [5]. It has been shown that using Al^{3+} and/or P^{5+} as codoping cations is remarkably effective [6]. In a previous work [2], we could explained this efficiency in analyzing the medium range structure around Eu^{3+} in a Al^{3+}-codoped silicate glass. Using photoluminescence measurements and Molecular Dynamics simulations, we have shown that the RE ions are preferentially located in aluminum-rich domains and that their local structure is strongly affected by the presence of aluminum. It was also demonstrated that Al^{3+} codoping delays the dehydroxylation mechanism during the densification process from the initial gel to the final glass. Consequently, the efficiency of the aluminum anti-quenching effect has to be balanced by a challenging removal of the residual OH^- ions which are responsible for a fast non-radiative relaxation process.

This work is an attempt to better understand the phosphorus effect on the RE-doped silica glass and to compare it with the one of aluminum from the structural and spectroscopic points of view. Even if both cations are known to allow a solubility enhancement of the RE in the silica glass, there is still no clear evidence for a distinct or similar role. Using electron spin-echo envelope modulation spectroscopy, Saitoh et al. [6] have obtained information on Er^{3+} coordination structures of Al-codoped and (Al + P)-codoped silica glasses. They could conclude that there is a striking structural

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difference explaining the difference in the inhomogeneous broadening of the photoluminescence band of Er^{3+}. Here, we propose to further analyze the role of P^{5+} in using Eu^{3+} as a structural probe. This luminescent ion is of interest because its optical properties are well known to be highly sensitive to the local environment and have proved to be efficient in the study of disordered materials. Consequently, we report photoluminescence results on the first stages of the drying and densification processes for a Eu^{3+}/P^{5+}-codoped sol-gel SiO_2 glass. A detailed analysis of the luminescent sites in the densified glass is performed by means of the Fluorescence Line Narrowing (FLN) technique. Numerical simulations using the Molecular Dynamics (MD) technique are also performed to support the experimental analysis. We finally propose an interpretation on the phosphorus role in the structuring of the RE environment, explaining the origin of the two kinds of sites which were distinguished by FLN measurements and by MD modeling.

2. Experimental

2.1. Samples preparation

Silicophosphate gels were prepared *via* hydrolysis and condensation of tetraethoxysilane(TEOS), triethylphosphate (TEP) in the presence of ethanol (C_2H_5—OH), distilled water (H_20), and hydrochloric acid (HCl) as catalyst. Europium was introduced in the initial stage of the process, by dissolving hydrated europium nitrate $Eu(NO_3)_3,5H_2O$ in the mixture of HCl and water. The molar ratio in the initial solution was 1:0.1:4:3:0.2 for TEOS:TEP:C_2H_5—OH:H_2O:HCl [7,8]. The solution of all ingredients was stirred for 2 h and transferred into plastic beakers for which the covers were unscrewed to allow vaporization of the residual solvents, and the samples were dried for five weeks at room temperature. Gelation and aging of the samples took place within this period. Next, the samples were transferred into an oven and sintered in air using a heating rate of 0.1 °C/min up to the desired final temperature. In this work, we have studied the influence of the annealing temperature on the glass structure. Therefore, we will focus our analysis on the sample with molar ratio Si/P/Eu = 1/0.1/0.01, heated at different temperatures between 150 °C and 900 °C.

2.2. Experimental set-up

For lifetime and photoluminescence measurements, a Nd:YAG laser was used for excitation at 355 nm. Spectra were recorded using a Jobin-Yvon THR 1500 spectrometer and a cooled R943602 Hamamatsu photomultiplier tube (PMT). A multichannel analyzer Standford SR430 and a fast amplifier discriminator (Standford 445) were used to perform lifetime measurements. Fluorescence Line Narrowing (FLN) spectra were measured at 77 K using the 532 nm line of the Nd:YAG laser pumping a rhodamine 6G dye laser setup (Quanta Ray).

3. Numerical simulations

The numerical simulations were performed using classical Molecular Dynamics (MD) modeling. Two systems have been modeled with the following compositions: $24Eu_2O_3\cdot 4800SiO_2$ (silica doped with 1 mol% Eu^{3+}) and $24Eu_2O_3\cdot 240P_2O_5\cdot 4800SiO_2$ (silica doped with 1 mol% Eu^{3+} and codoped with 10 mol% of P_2O_5). In such a way, each modeled structure has about 16 000 atoms in a cubic box with length of about 63 Å. The simulations have been performed using LAMMPS [9], with periodic boundary conditions, and with a Buckingham-based rigid ionic potential. As developed by Mountjoy et al. [10], this potential is composed of two parts: the two-body term describes the interaction between atomic pairs while the three-body term is employed to take into account some effects of covalence in the O-P-O and P-O-P interactions. The two parts are computed according to these expressions:

$$V_{ij}\,(r) = \frac{q_i q_j}{4\pi\varepsilon_0 r} + A_{ij}\exp\left(\frac{-r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6} \tag{1}$$

$$V_{iji}(\theta) = \frac{1}{2}K_{iji}\left(\theta_{iji} - \theta\right)^2 \tag{2}$$

where i and j are atom types, r is the distance between two atoms, θ is the bond angle for O-P-O and P-O-P interactions, q_i is charge, and A_{ij}, ρ_{ij}, C_{ij} and K_{iji} are potential parameters listed in Table 1 and already published in Ref. [10–12]. The Coulomb part of the two-body potential (Eq. (1)) is evaluated using the Wolf method [13], consisting in a spherically-truncated, charge-neutralized, shifted, pairwise 1/r summation. Some authors [14,15] have recently developed core-shell potentials with the aim to better reproduce the medium-range features of silicate glasses. But, as it was demonstrated by Du et al. [11,16], a rigid ionic potential such as the one used in our simulations is also relevant to model short- and medium-range structures of RE-doped silicate or phosphate glasses. The choice of this potential, for which parameters were previously published, is therefore rational to model the glass structures of interest.

The following common process has been used to produce the modeled glass structures: an initial configuration is firstly melted at 5000 K for 40 ps to ensure a perfect mixing of the system. Melts are then cooled to room temperature (300 K) with a quenching rate of 4.7 K/ps. The glassy structures are finally relaxed at room temperature for 40 ps. During the latter stage, the structural parameters are sampled for further analysis.

4. Results

4.1. Spectroscopic characterization

4.1.1. Sintering effect on PL spectra

Several multiplet transitions $^5D_0 \rightarrow {}^7F_{J=0,1,\ldots,6}$ compose the Eu^{3+} emission spectrum. The highest energy one, $^5D_0 \rightarrow {}^7F_0$, is only allowed by *J*-mixing effects. The electrostatic local field of the luminescent site influences strongly the shape and the position of this spectral band. The second transition, $^5D_0 \rightarrow {}^7F_1$, is mainly magnetic dipolar and its intensity does not depend on the local field. However, the splitting feature of this band directly depends on the crystal field experienced by the luminescent site. For this reason, the analysis of the $^5D_0 \rightarrow {}^7F_1$ band shape can provide very useful information on the local structure around the rare earth ion.

The different densification stages of a gel to a glass have been investigated using europium emission as a probe. Fig. 1 shows the evolution of the emission spectrum during the transition from the gel to the glass for the Eu^{3+}-P^{5+}-codoped silica sample. An

Table 1
Potential parameters used in Eqs. (1) and (2).

i-j	q_i (e)	A_{ij} (eV)	ρ_{ij} (Å)	C_{ij} (eV.Å^6)
Si-O	2.4	13,702.905	0.1938	54.681
P-O	3.0	26,655.472	0.1819	86.856
Eu-O	1.8	5,950.5287	0.2537	27.818
O-O	−1.2	2,029.2204	0.3436	192.58
i-j-i		K_{iji} (eV)		θ_{iji} (°)
P-O-P		3.0		135.5
O-P-O		3.5		109.47