

## Elucidation of Phosphorus Co-doping Effect on Photoluminescence in Ce<sup>3+</sup>-activated SiO<sub>2</sub> Glasses: Determination of Solvation Shell Structure by Pulsed EPR

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Photoluminescence (PL) due to Ce<sup>3+</sup> in SiO<sub>2</sub> glass is strongly influenced by co-doping of phosphorus (P), whose features such as peak energy and fluorescence lifetime are very close to those in phosphate glass. The origin for this striking effect of the P co-doping has been clarified through the elucidation of the coordination structure around a Ce<sup>3+</sup> by pulsed EPR ESEEM spectroscopy. Analysis of the observed ESEEM pattern with simulation revealed that the number of P-ions in the coordination sphere is larger by an order of magnitude than that expected from the uniform distribution of P, demonstrating the formation of a solvation shell structure. It has been found that two types of the coordination manner of P–O bonds co-exist in the solvation structure, corner-sharing and edge-sharing. This solvation shell structure is almost the same as that for the calcium phosphate glass.

Silica (SiO<sub>2</sub>) glass<sup>1</sup> that is composed of a simple chemical composition has many excellent properties such as superior optical transparency down to vacuum ultraviolet region,<sup>2</sup> chemical and thermal stabilities, and the versatility in applications from vessels, optical materials for lithography to optical fibers. These properties also give SiO<sub>2</sub> glass high potential as an excellent host for optically active (OA) ions. In particular, light-emitting devices based on SiO<sub>2</sub> glass are favorable because they are compatible with the current fiber optic telecommunication system.<sup>3</sup> However, a fatal drawback of SiO<sub>2</sub> glass as the host is its poor solubility of OA ions such as a rare earth (RE) cation; doping of RE ions into SiO<sub>2</sub> glass often leads to the formation of clusters.<sup>4</sup> As a consequence, the excitation efficiency for the luminescence drastically drops due mostly to the concentration quenching.

Co-doping technique was invented to suppress the clustering of OA ions by Arai et al., which has been verified to be effective in enhancing the solubility.<sup>5,6</sup> Although numerical studies on microscopic structures around RE ions in the co-doped SiO<sub>2</sub> glasses have been reported to date, no concrete model for the coordination structure based on direct experimental evidences has been obtained.

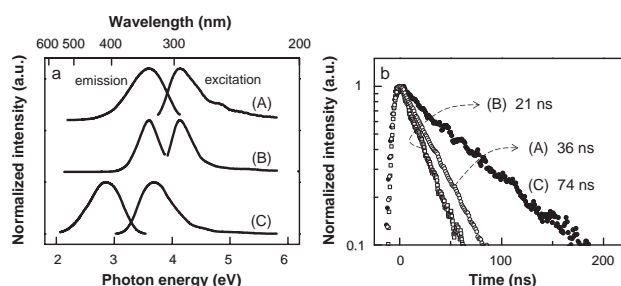
In this study, we have determined the coordination structure around Ce<sup>3+</sup> ion in phosphorus (P) co-doped SiO<sub>2</sub> glass based on simulation of pulsed EPR electron spin-echo envelope spectroscopy (ESEEM), which clarifies the co-doping effect, and further the relation between PL and the coordination structure around the RE ion. Here, Ce<sup>3+</sup> is chosen as an active ion due to the following 2 reasons: (1) The electronic transition for PL is simple (5d → 4f) and expected to be sensitive to the change

**Table 1.** Analyzed chemical compositions in Ce<sup>3+</sup>-activated glasses used in the experiments

Sample	Composition (molar %)
(A) P-doped SiO <sub>2</sub>	0.004Ce <sub>2</sub> O <sub>3</sub> –1P <sub>2</sub> O <sub>5</sub> –99SiO <sub>2</sub>
(B) Calcium phosphate	0.02Ce <sub>2</sub> O <sub>3</sub> –50P <sub>2</sub> O <sub>5</sub> –50CaO
(C) P-free SiO <sub>2</sub>	0.04Ce <sub>2</sub> O <sub>3</sub> –100SiO <sub>2</sub>

in the chemical environment. (2) PL from the Ce<sup>3+</sup> ion has a potential for the application to a UV-laser.

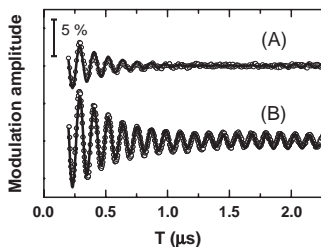
Soot preforms of SiO<sub>2</sub> doped with P were synthesized by a modified chemical vapor deposition (MCVD) method. Cerium ions were incorporated by dipping the soot to an aqueous solution of CeCl<sub>3</sub>. Then the co-doped soot was changed into glass state by thermal annealing in an inert gas atmosphere. On the other hand, calcium phosphate glasses were prepared by a conventional melt-quenching technique. The chemical compositions of the samples were analyzed by an electron probe micro-analyzer as listed in Table 1.



**Figure 1.** Emission and excitation spectra (a) and time decay curves (b) of photoluminescence (PL) intensities in the P-doped SiO<sub>2</sub> (A) and phosphate (B), and P-free SiO<sub>2</sub> (C) glasses. Time decay of PL intensity excited with 4th harmonic (266 nm) of Q-switched Nd:YAG laser was recorded with an aid of a streak camera system.

Figure 1a shows PL due to the Ce<sup>3+</sup> ion and corresponding excitation spectra of P-doped SiO<sub>2</sub> (A) and phosphate (B) glasses measured at ca. 300 K. UV emissions peaking at ca. 345 nm were observed both in the samples A and B, while blue emission peaking at ca. 435 nm was observed in P-free SiO<sub>2</sub> glass (sample C). Figure 1b shows the time decays of the PL intensities in samples A–C. Each curve was described by a single exponential decay curve with a single decay constant. The decay constants of samples A and B are almost equal to each other and they are ca. 1/2 as small as that of sample C.

Computer simulation of a three-pulse ESEEM pattern was



**Figure 2.** Observed three-pulse ESEEM spectra (open circle) for the P-doped SiO<sub>2</sub> (A) and phosphate (B) glasses. The measurement conditions were  $t = 172$  ns and  $H_0 = 500$  mT at 4 K. The best-fitted curve is also shown by solid line.

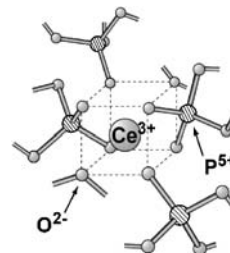
carried out using the spin Hamiltonian for the system of an electron spin  $S = 1/2$  and nuclear spins  $I = 1/2$ . A trial-and-error approach was made to obtain the best-fitted pattern by varying the values of  $N$  and  $r$ .

Open circles and solid curves in Figure 2 show respectively the observed ESEEM and best fitted calculated patterns for samples A and B. In sample A, the number  $N$  ( $=N_1 + N_2$ ) and separation  $r$  ( $r_1$  or  $r_2$ ) were obtained as  $(N_1, r_1) = (2, 0.28$  nm) and  $(N_2, r_2) = (2, 0.38$  nm) through the fitting. If we assume that the phosphorus ions are randomly distributed around a Ce<sup>3+</sup> in the range 0.3–1.2 nm, the calculated modulation amplitude was too small (ca. 0.1%) compared to the observed modulation amplitude.

There are 2 types of P-ions coordinating to a Ce<sup>3+</sup> ion through oxygens in the crystals in the Ce<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub> system, i.e., an edge-sharing and a corner-sharing type. The separation between the Ce<sup>3+</sup> and the P ion is ca. 0.3 nm for the edge-sharing or ca. 0.4 nm for the corner sharing. These two separations just correspond to the values of  $r$  obtained from the simulation, indicating that the total number of the P ions coordinating to a Ce<sup>3+</sup> through oxygens is 4. If P ions (2% of Si) are randomly distributed throughout the sample, then the expected number  $N$  should be 0.4 within the sphere of 0.6 nm around a Ce<sup>3+</sup>. It is thus clear that the doped P ions preferentially coordinate to the Ce<sup>3+</sup> ion forming a solvation shell structure. Figure 3 shows a model structure for the solvation shell in the P-doped SiO<sub>2</sub> glass.

The number and separation in the phosphate glass were also obtained by the same procedures, i.e.,  $(N_1, r_1) = (4, 0.30$  nm) and  $(N_2, r_2) = (4, 0.40$  nm). This result means 4 PO<sub>4</sub> units coordinate to a Ce<sup>3+</sup> in a bidentate manner, and 4 P-ions coordinate to a Ce<sup>3+</sup> sharing a non-bridging oxygen with a unidentate form. Such a coordination structure around a Ce<sup>3+</sup> is similar to that in the P-doped SiO<sub>2</sub> sample.

Here, the correlation between the PL properties and the coordination structure around the Ce<sup>3+</sup> ion is discussed. In the phosphorus-doped SiO<sub>2</sub> and phosphate glasses, the bidentate oxygen ions are coordinated to the Ce<sup>3+</sup> ion in an edge-sharing manner. The formal charge on the non-bridging oxygen in the P–O bond is  $-0.5$  due to the delocalization of electron over the 2 non-bridging oxygens via the  $Op\pi$ – $P3d\pi$  bond. Therefore, 4 ligands around a Ce<sup>3+</sup> belong to this type of oxygens with formal negative charge of  $-0.5$ , which is an intermediate value between a conventional non-bridging oxygen ( $-1$ ) and a bridg-



**Figure 3.** Structural model for coordination sphere around a Ce<sup>3+</sup> in P-doped SiO<sub>2</sub> glass based on the simulation of ESEEM pattern. The cubic ligand field is assumed. There are 4 phosphorus ions and 2 of them coordinate in a bidentate manner and the remaining 2 in a unidentate.

ing oxygen (0).<sup>8</sup> The energy splitting of the Ce 5d multiplets should increase with the negative charge on the ligand oxygens in the crystal field approximation. Thus, energy separation between the emitting excited state (the lowest energy state among the crystal field split Ce<sup>3+</sup> 5d multiplet) and the ground state (Ce<sup>3+</sup> 4f) increases with the reduction of the negative charge density on the ligand. This agrees with the experimental results, i.e., Ce<sup>3+</sup> coordinated by the P–O bonds gives rise to PL with larger energy or shorter wavelength (UV), while Ce<sup>3+</sup> with Si–O bonds yields blue PL (longer wavelength). The peak position of the absorption spectrum (not shown in the figure) agreed with that of the excitation spectrum for each sample. That is, the observed blue shift of the PL band upon P-doping is due to up-shift of the center of Ce 5d levels as well as reduction in the Ce 5d multiplet splitting, both of which were caused by weak ligand field nature of P–O bonds.

The present result demonstrates that the doped phosphorus coordinates to a Ce<sup>3+</sup> with a high preferentiality, forming a solvation structure which is close to that in phosphate glasses. Although phosphate glasses provide weak ligand field for an OA ion, their physical properties are much inferior to those of SiO<sub>2</sub> glass, in particular, in terms of solarization toughness and chemical durability.<sup>9</sup> However, the phosphorus-doped SiO<sub>2</sub> glasses having the solvation shell structure enjoy both merits of SiO<sub>2</sub> and phosphate glasses, and thus it is a potential material for a UV glass laser.

## References

- 1 L. Skuja, *J. Non-Cryst. Solids*, **239**, 16 (2000).
- 2 H. Hosono, Y. Ikuta, T. Kinoshita, K. Kajihara, and M. Hirano, *Phys. Rev. Lett.*, **87**, 175501 (2001).
- 3 S. Tanabe, *C. R. Chimie*, **5**, 815 (2002).
- 4 J. Lægsgaard, *Phys. Rev. B*, **65**, 174114 (2002).
- 5 K. Arai, H. Namikawa, K. Kumata, T. Honda, Y. Ishii, and T. Handa, *J. Appl. Phys.*, **59**, 3430 (1986).
- 6 K. Arai, H. Namikawa, Y. Ishii, H. Imai, H. Hosono, and Y. Abe, *J. Non-Cryst. Solids*, **95&96**, 609 (1987).
- 7 W. B. Mims, *Phys. Rev. B*, **5**, 2409 (1972).
- 8 R. Brückner, H. U. Chun, and H. Goretzki, *Glastech. Ber.*, **49**, 211 (1976).
- 9 D. T. Bowron, G. A. Saunders, R. J. Newport, B. D. Rainford, and H. B. Senin, *Phys. Rev. B*, **53**, 5268 (1996).