Luminescence and variation of valent state for cerium within pores of mesoporous silica

LETTER TO THE EDITOR

Luminescence and variation of valent state for cerium within pores of mesoporous silica

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Abstract. Photoluminescence of cerium (Ce) in silica was investigated by putting Ce ion into pores of mesoporous silica by soaking the silica in solutions of trivalent or tetravalent Ce ion followed by drying. It has been shown that no luminescence was observed for Ce^{3+}-soaked samples. But for Ce^{4+}-soaked samples without any reduction treatment, very strong luminescence was unexpectedly observed. There are two luminescence peaks at around 345 and 665 nm. The intensities at the peaks increase with rise of Ce^{4+} ion concentration in soaking solution up to 0.15 M beyond which higher concentration leads to decrease of the intensity. These facts were explained in terms of ion exchange between Ce^{4+} ion and silicon in the silica network on pore walls and valence variation of Ce in the silica network during drying.

Within the last three decades, the research on trivalent-cerium-ion- (Ce^{3+}-) doped materials has been stimulated by phosphors and scintillator applications [1]. It is well known that almost every element in the periodic table can be 'stuffed' into glasses, which makes it easier to control the quantities and energy levels of electron and hole traps than in crystals. There is no luminescence in tetravalent-cerium-ion- (Ce^{4+}-) doped glasses due to the lack of 4f electron transition. Ce^{4+}-doped glasses should be subjected to reduction treatment so that luminescence occurs. Only when the Ce^{3+} ion is doped into a silica network does the effect of the crystal field on cerium lead to luminescence [2, 3]. In this study, however, instead of directly doping cerium into a silica network, we put the Ce^{4+} and Ce^{3+} ions into pores of mesoporous silica by soaking and investigate their luminescence and variation of valent state. What is unexpected is that very strong luminescence was observed for Ce^{4+}-soaked samples without any reduction treatment, but no luminescence observed for Ce^{3+}-soaked samples. The details are reported in this letter.

The monolithic mesoporous silica host was first prepared by the sol–gel technique, as previously described [4], with tetraethyl oryhosilicate, water and alcohol (catalysed by nitric acid), followed by aging, drying and finally annealing at 973 K for 1 hour. The thermal treatment was stopped at 973 K to prevent pore collapse occurring at higher temperature. The sample fired at this temperature is strong enough not to break when in contact with a liquid. The porosity of the monolithic silica host obtained in this way was estimated to be about 50% by the weighing method (assuming the skeleton density of silica to be 2.2 g cm^{-3}). The pores of silica are sharply distributed at around 3.5 nm in diameter by the isothermal N_2 sorption technique and pore diameter analysis [4], and the specific surface area is evaluated to be about 650 m^2 g^{-1} using the Brunauer–Emmett–Teller equation [5]. The pre-formed silica was then soaked in $Ce(SO_4)_2$ or $Ce(NO_3)_3$ solution with different

concentrations at room temperature for about 10 days, which is long enough to soak the samples [6], followed by drying in air at up to 150 °C (the decomposition temperatures for $Ce(SO_4)_2$ and $Ce(NO_3)_3$ are higher than 190 and 200 °C respectively). No reduction treatment was performed. X-ray diffraction shows the existence of $Ce(SO_4)_2$ or $Ce(NO_3)_3$ crystal in the corresponding dried soaked samples. Corresponding N_2 sorption isotherms confirmed that $Ce(SO_4)_2$ or $Ce(NO_3)_3$ is located within pores of silica, as previously reported [4]. Luminescence was measured on an F-3010 fluorescence spectrophotometer (Hitachi) at room temperature (excitation wavelength: 250 nm) for all samples. Optical diffusion reflectance was measured on a Cary 5E UV–VisNir spectrophotometer over the wavelength range from 200 to 1000 nm (optical scanning starts from long wavelength, 1000 nm, to short wavelength, 200 nm).
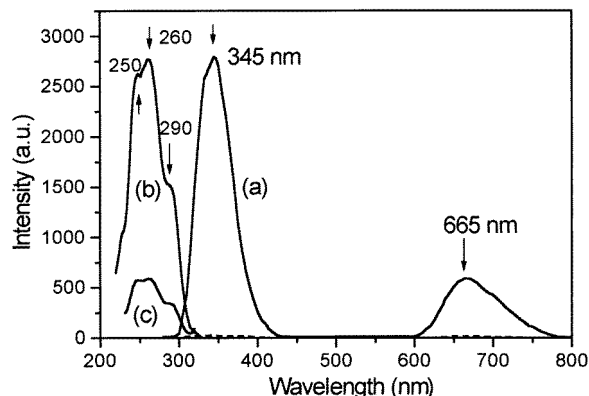

Figure 1. Emission and excitation spectra (Ex = 250 nm). Solid lines: Ce^{4+}-soaked sample (0.15 M), (a) emission spectrum, (b) and (c) excitation spectra monitoring at 345 and 665 nm respectively; dashed line: emission spectrum of Ce^{3+}-soaked sample (0.15 M).

Figure 1 indicates typical emission and excitation spectra for Ce^{4+}- and Ce^{3+}-soaked samples. No luminescence was observed for all Ce^{3+}-soaked samples. Unlike our usual expectation, however, it has been shown that the Ce^{4+}-soaked samples assume strong luminescence. There are two emission peaks at around 345 nm and about 665 nm, and the former is about 4 times higher than the latter for all Ce^{4+}-soaked samples. There are the same excitation spectra for these two emission peaks, which means the same emitting mechanism. The variation of luminescence intensity at about 345 nm with the change of Ce^{4+} ion concentration in soaking solution is shown in figure 2. The intensity increases with rise in soaking concentration up to 0.15 M at which maximum intensity was reached and a higher concentration results in decrease of the luminescence intensity.

It is well known that Ce^{3+} ion in glass matrix (lattice sites) can emit fluorescence due to the 5d to 4f transition, and luminescence will not be observed in the Ce^{4+}-ion-doped glasses because of the lack of 4f electrons [7]. So there must exist trivalent cerium in the Ce^{4+}-soaked samples in addition to $Ce(SO_4)_2$ within pores although no reduction treatment was conducted. For verification of the existence of trivalent cerium, infrared measurement was performed. But no Ce^{3+}-related signal was detected, mainly due to too small an amount. However, in optical absorption spectra (diffusion reflectance), there exists an obvious absorption peak, as shown in figure 3. As references, the spectra of CeO_2, $Ce(SO_4)_2$ and $Ce(NO_3)_3$ were also taken. For the reference samples containing Ce^{4+} ions, no absorption peak but the absorption edge was observed. In contrast, for the Ce^{3+}-soaked
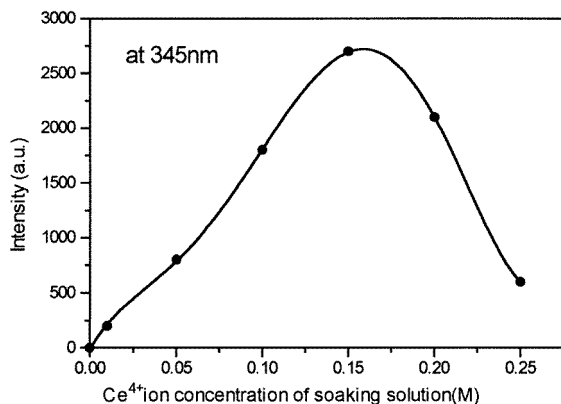
Figure 2. The intensity at 345 nm versus Ce^{4+} ion concentration of soaking solution for the Ce^{4+}-soaked sample.
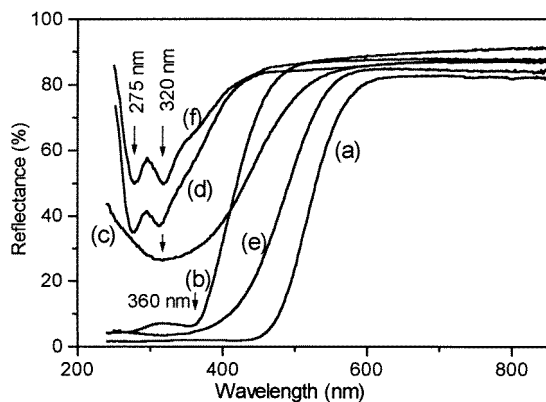
**Figure 3.** Diffusion reflection spectra. (a) $Ce(SO_4)_2$ (reference), (b) CeO_2 (reference), (c) Ce^{4+}-soaked silica (dried at 150 °C), (d) Ce^{3+}-soaked silica (dried at 150 °C), (e) sample (d) followed by oxidation treatment, (f) $Ce(NO_3)_3$ (reference).

sample, there are two absorption peaks at around 275 and 320 nm, which correspond to the 4f to 5d transition [8, 9] and are the same as the corresponding reference sample in this study (see curves (d) and (f) in figure 3). After oxidation treatment, the white transparent sample becomes yellow in colour, indicating the variation from Ce^{3+} to Ce^{4+}. The absorption peaks disappear and the spectrum assumes only an absorption edge (see curve (e) in figure 3). So the Ce in the Ce^{3+}-soaked sample is still trivalent before oxidation treatment. For Ce^{4+}-soaked samples, there is only one wide absorption peak, which should correspond to overlapping of the two peaks on curve (d) or (f). The coexistence of tri- and tetravalent cerium in the Ce^{4+}-soaked samples has also been shown by x-ray photoelectron spectroscopy (which is not shown here due to space limitation and will be reported in detail elsewhere). We suggest that, for the Ce^{4+}-soaked samples, there exist not only Ce^{4+} ions in the form of $Ce(SO_4)_2$ but also Ce^{3+} ions which must be in the pore wall.

Now we make a brief discussion. When Ce^{4+} ion goes into pores of silica during soaking, Ce^{4+} ions partially substitute the silicon sites (Si) on the pore wall, and hence enter the silica network or tetrahedron (SiO_4), as previously described [6]. No charge

compensation is needed. Si on the pore wall bonds with hydroxyl (–OH) due to the existence of an unsaturated bond, i.e. $\equiv$Si–OH. When the pore wall is in contact with Ce^{4+} ion in the solution within the pore, some Si ions in $\equiv$Si–OH are substituted by Ce^{4+} ions or ion exchange occurs, namely:

$$\equiv Si-OH + Ce^{4+} \rightarrow \equiv Ce-OH + Si^{4+}. \qquad (1)$$
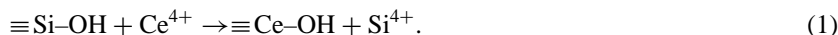
During subsequent drying, the charge transfer will occur between Ce^{4+} and the oxygen ion O^{2-} in the OH group, leading to the reduction of Ce^{4+} in the network to Ce^{3+} or the reaction

$$2(\equiv Ce-OH) \rightarrow 2(\equiv Ce) + H_2O + 1/2O_2 \uparrow \qquad (2)$$
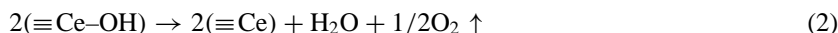
occurs, accompanied by dehydration. The 5d levels of Ce^{3+} ions are highly affected by the ligand field of the first coordinating sphere [10]. Obviously, the crystal field surrounding Ce^{3+} ion on the pore wall is strongly asymmetric, which results in significant splitting of the 5d level. Referring to that previously reported [11], this splitting is schematically shown in figure 4 and indicates the emission mechanism of two luminescence peaks. The number of reduced Ce^{3+} ions in the silica network on the pore wall increases with rise in Ce^{4+} concentration of the soaking solution, leading to increasing luminescence intensity for the Ce^{4+}-soaked samples. When the soaking concentration is more than 0.15 M, the distance between Ce^{3+} ions in the pore wall is small enough for them to interact with each other, resulting in a decrease of luminescence intensity [12].
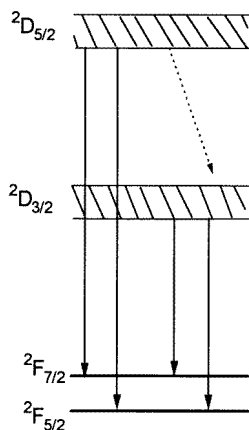
Figure 4. Schematic diagram for emission mechanism of Ce in silica.

In contrast, for the Ce^{3+}-soaked samples, the Ce^{3+} ion in solution within pores is difficult to ion exchange with Si in the pore wall because of the valence difference. After drying, only very few Ce^{3+} ions (if any) are located in the silica network, most Ce^{3+} ions still exist in the form of crystal $Ce(NO_3)_3$ within pores, leading to no luminescence observed although Ce in the sample is in the trivalent state. Further study is in progress.

In summary, as an alternative technique to manufactured Ce-doped silica, we put Ce ion into pores of mesoporous silica by soaking the silica in Ce ion solution and subsequent drying without reduction treatment. Ce^{4+}-soaked silica assumes strong luminescence. It is suggested that it results from ion exchange between Si in the silica network on pore walls and Ce^{4+} ion in solution within the pores, and reduction of Ce^{4+} by oxygen ions in hydroxyl during drying (dehydration). But it is difficult to ion exchange between Ce^{3+} ion and Si

on pore walls due to the valence difference, leading to no luminescence being observed for the Ce^{3+}-soaked silica.

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