Formation of Interconnected Macropores in Sm^{2+}-doped Silicate Glasses through Phase Separation: Fabrication of Photosensitive and Dielectrically Disordered Materials

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Fabrication of Sm^{2+}-doped silicate glasses possessing interconnected macropores has been attempted via two different procedures utilizing a phase-separation phenomenon; one includes liquid–liquid phase separation of macroscopically uniform melt-quenched glasses under heat treatment, and the other polymerization-induced phase separation in alkoxy-derived sol-gel systems. Macroporous silicate glasses doped with Sm^{2+} can be successfully prepared via the sol-gel method.

Various interesting effects based on the interference of multiply scattered light have been observed in dielectrically disordered materials, where the indices of refraction vary on length scales of the order of the wavelength of light. For instance, the interference between counterpropagating waves in the disordered structures gives rise to enhanced backscattering, often called coherent backscattering or weak localization.[1]

Recently, it has been reported that a novel optical memory effect appears in dielectrically disordered media combined with photoreactive ions or molecules such as Sm^{2+} or fulgide.[2] When such materials are irradiated with a visible laser, the interference of multiply scattered light causes the spatial modulation of the optical absorbance through photobleaching. A dip or hole is burned in the frequency and wave-vector domains, since the interference effect depends on the wavelength and incident angle of the laser beam. The formation of micrometer-sized grating by a single laser beam is obviously responsible for the appearance of the hole-burning effect and makes it possible to manipulate the chemical and/or physical state of ions or molecules inside the corresponding spatial volume. This phenomenon is thus applicable to high-density optical storage, in which the data information is recorded as three-dimensional random interference patterns.

So far, the hole-burning effect based on the interference of multiply scattered light has been examined for fine particles or fine powders.[2] However, monolithic structures are rather favorable for the practical use. Pore formation is a promising technique for obtaining monolithic scattering media. Especially the pores of the size lying in the range of submicron to several microns scatter strongly visible light, and the interference effect is also anticipated. In this study, we attempt to form well-defined submicrometer- or micrometer-sized pores in silicate glasses and also to incorporate Sm^{2+} into the skeleton for the purpose of fabricating photosensitive and dielectrically disordered materials. Porous glasses have been extensively investigated from the technological and basic research standpoint, but few studies were focused on the macroporous glasses as the matrices of rare-earth ions, to our knowledge. Here, we present two approaches to introduce Sm^{2+} into monolithic silicate glasses possessing interconnected macropores through phase separation; one is a conventional technique that involves liquid–liquid phase separation of macroscopically uniform melt-quenched glass under heat treatment, and the other a novel sol-gel process that includes the phase separation induced by the hydrolysis and polymerization of alkoxides.

A porous glass known as Shirasu Porous Glass (SPG)[3] was prepared from a $CaO–Al_2O_3–B_2O_3–SiO_2$ system using the procedure similar to that of porous VYCOR glasses. The choice of SPG system comes from the fact that the pore size is relatively large compared to that of the VYCOR family and lies in the range of 0.1 to 10 µm.[3] Reagent-grade $CaCO_3$, Al_2O_3, B_2O_3, SiO_2, and Sm_2O_3 were used as the starting materials for glass preparation. These raw materials were weighed to make $9.2CaO\cdot 8.0Al_2O_3\cdot 27.6B_2O_3\cdot 55.2SiO_2\cdot 1.0SmO$ composition (in molar ratio) and mixed thoroughly. The mixture was melted in a platinum crucible at 1500 °C for 2 h in air. The resultant Sm^{3+}-doped glass was remelted in a glassy carbon crucible under a nitrogen atmosphere at 1500 °C for 1 h to reduce Sm^{3+} to Sm^{2+}. The glass thus obtained was heat-treated at 830 °C for 25 h in order to induce the phase separation, and immersed in a 0.2 M HCl solution at 80 °C for 10 h so as to form pores.

Another porous glass having the nominal composition of $5AlO_{3/2}\cdot 95SiO_2\cdot 1.0SmO$ (in molar ratio) was prepared via the sol-gel process including phase separation.[4] The alumina–silica system was selected in this study because samarium ions could be homogeneously incorporated as Sm^{2+} into aluminosilicate glasses, in contrast to pure silica glass.[5] $SmCl_3\cdot 6H_2O$ was used as the source for samarium ions, and poly(ethylene oxide) (PEO) with an average molecular weight of 10000 as the polymer to induce the phase separation. The sample was prepared as follows. First, 4.90 g of tetramethoxysilane, 0.42 g of aluminum *sec*-butoxide, and 0.70 g of *sec*-butanol were mixed at room temperature. Then, the alkoxide mixture was added to a solution of $SmCl_3\cdot 6H_2O$ (0.13 g) and PEO (0.95 g) in 2 M nitric acid (10 mL) and stirred vigorously at 0 °C for 30 min. The resultant homogeneous solution was poured into a glass container. Gelation was carried out at 40 °C in the sealed container. The wet gel thus obtained was aged for 24 h and dried at 60 °C for the solvent evaporation. Heat treatment at 800 °C for 2 h in air was performed to completely remove PEO and also to obtain the sintered gel. To reduce Sm^{3+} to Sm^{2+}, the heat-treated gel was further reheated at 1000 °C for 30 min in a reducing gas of 50% N_2, 47.5% Ar, and 2.5% H_2.

A scanning electron microscope (SEM) was used to observe the macroscopic morphology. Fluorescence spectra were measured with a fluorescence spectrophotometer (Hitachi, 850) using an Ar^+ laser (488 nm) as the excitation source.

It is well known that bicontinuous structures can be obtained as a result of the phase separation of $9.2CaO\cdot 8.0Al_2O_3\cdot 27.6B_2O_3\cdot 55.2SiO_2$ glass (referred to as original glass) under appropriate heat-treatment conditions; the two phases turn out to be a CaO–B_2O_3-rich phase and an Al_2O_3–SiO_2-rich phase.[3] Subsequent acid treatment dissolves out the continuous calcium borate phase, leaving the continuous aluminosilicate phase. The inset of Figure 1 depicts a SEM image of the specimen after the acid treatment. The bicontinuous morphology of skeleton and pores with the average size of approximately 1 µm is clearly observed. The analysis with an energy-dispersive X-ray (EDX) spectrometer confirmed that the elemental ratios of Al/B and Si/B (or Al/Ca and Si/Ca) were much larger in the macroporous glass than in the original glass. Fluorescence spectra are shown in Figure 1 for the original glass, the phase-separated glass, and the macroporous glass. For the original and phase-separated glasses, the emission peaks due to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1, and 2) transitions of Sm^{2+} are observed at around 684, 700, and 728 nm, respectively [see Figures 1a and 1b].[5,6] Unfortunately, the macroporous glass exhibits no emission lines of Sm^{2+} [Figure 1c], indicating that almost all of Sm^{2+} ions in the phase-separated glass are partitioned into the calcium borate-rich phase which is leached out with the acid. From a point of view of glass formation, divalent rare-earth ions like Sm^{2+} are believed to have chemical properties similar to Ca^{2+}, Sr^{2+}, and Ba^{2+}. Namely, it is conceivable that the local environments of Sm^{2+} and Ca^{2+} are very similar to each other in the original glass, resulting in the preferential distribution of Sm^{2+} in the calcium borate phase after phase separation.

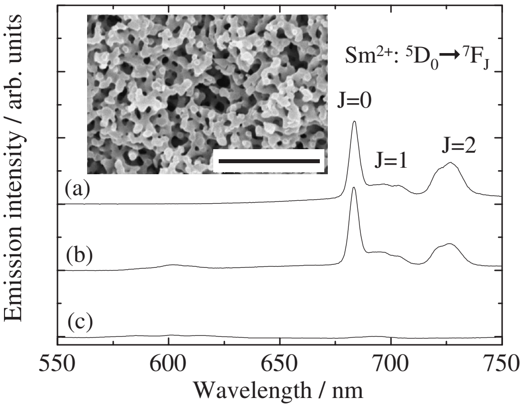

Figure 1. Fluorescence spectra of Sm^{2+} in the original glass (a), the phase-separated glass (b), and the macroporous glass (c). The inset shows the SEM photograph of the sample (c). Bar = 10 µm.

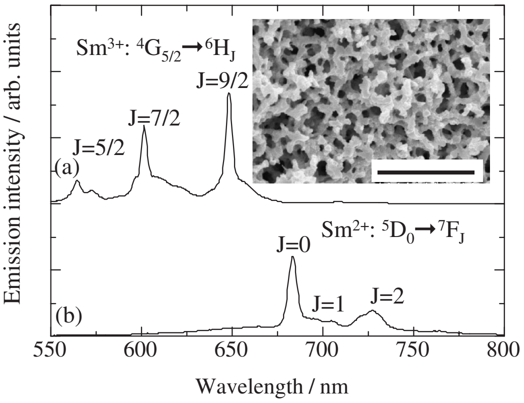

Figure 2. Fluorescence spectra for the sol-gel-derived $5AlO_{3/2}\cdot 95SiO_2$ glass heat-treated at 1000 °C in air (a) and that heat-treated at 800 °C in air and reheated at 1000 °C in reducing atmosphere (b). The inset shows the SEM photograph of the sample (b). Bar = 10 µm.

On the other hand, the sol-gel process including phase separation is found to be effective in incorporating Sm^{2+} into the skeleton of macroporous glasses. The bicontinuous structure is formed when the transient structure of phase separation induced by the hydrolysis and polycondensation of alkoxides is frozen by the sol-gel transition.[4] In the present system containing PEO, the phase separation is driven by a repulsion interaction between solvent mixtures and PEO adsorbed on alkoxy-derived oligomers. Upon drying the wet gel, the phase with PEO and inorganic components becomes the gel skeleton, and the phase composed mainly of solvents turns into macropores. Figure 2 shows fluorescence spectra of the sintered $5AlO_{3/2}\cdot 95SiO_2$ glasses. For the sample heat-treated at 1000 °C in air, the emission peaks ascribed to the $^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2, 7/2$, and $9/2$) transitions of Sm^{3+} are observed at around 565, 603, and 649 nm, respectively [see Figure 2a],[5,6] whereas the sample heat-treated at 800 °C in air and reheated at 1000 °C under reducing atmosphere manifests the emission spectrum characteristic of Sm^{2+} [Figure 2b]. The SEM image of the sample containing Sm^{2+}, which is displayed in the inset of Figure 2, confirms that the interconnected morphology is maintained after the heat treatment at 1000 °C.

In conclusion, we have shown that Sm^{2+}-doped macroporous monoliths can be successfully prepared using the sol-gel method including phase separation, although heat-induced phase separation of the CaO–Al_2O_3–B_2O_3–SiO_2 system and the subsequent acid treatment yield macroporous glasses without Sm^{2+} or with undetectable Sm^{2+}. The excitation into the $4f^6 \rightarrow 4f^55d$ transition of Sm^{2+} brings about the photobleaching attributable to the photoionization of Sm^{2+} to Sm^{3+} as well as the Sm^{2+} fluorescence as shown in Figures 1 and 2. Very recently, we have observed the hole-burning effect by combining the photoionization of Sm^{2+} with multiple light scattering in the sol-gel derived porous glasses. The macroporous morphology can be precisely controlled by the compositional parameters such as PEO content.[4] We expect that this capability to tailor the morphology extends the possibility of photonic applications.

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