

Spatial manipulation of the valence state of rare-earth ions in macroporous media prepared by a sol-gel method

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Abstract: Sm²⁺-doped Al₂O₃-SiO₂ glasses with three-dimensionally interconnected macroporous morphology have been prepared via an alkoxy-derived sol-gel process containing poly (ethylene oxide) and SmCl₃·6H₂O. The macroporous structure is obtained by concurrently inducing the phase separation and sol-gel transition. Using a visible laser with the wavelength of 590 nm, the valence state of Sm²⁺ has been manipulated spatially. When the photoionization of Sm²⁺ is combined with multiple light scattering in the porous glasses, holes are burned in wave-vector domain. The hole profile can be controlled by the macroporous morphology.

1. Introduction

The transport of light waves in spatially-disordered media is strongly modified by multiple scattering. In strongly scattering media, interference of multiple-scattered light brings about various interesting phenomena such as photon localization [1].

Recently, a novel optical memory effect was observed in strongly scattering media doped with Sm²⁺ [2,3]. Irradiation of the scattering medium with a monochromatic light creates a three dimensional interference pattern of multiple-scattered light within the medium. By recording the interference pattern through photobleaching of Sm²⁺, the information about wavelength and incident angle of light is stored because the interference effect depends on the wavelength and incident angle of the incoming light. This effect results from interference of scattered light, so the scattering-strength control of host materials is very important. So far, multiple-scattering hosts offered for this optical memory effect have been limited to compacted powders, including aggregates of semiconductor nanoparticles, and ground glasses.

In order to obtain spatially-disordered dielectrics with tunable scattering strength, we have focused on macroporous monoliths instead of conventional powder-based disordered systems [4,5]. The sol-gel derived macroporous structure is formed when the transient structure of phase separation developed during hydrolysis and condensation of metal alkoxide is frozen by the sol-gel transition [6,7]. The sizes of pores and skeletons can be tuned by the relative rate of phase separation to that of sol-gel transition, which allows us to tune the scattering strength systematically. The sol-gel-derived macroporous monoliths, if combined with photoreactive ions such as Sm²⁺, would be regarded as new materials for the scattering-based optical memory effect.

In this study, we report the occurrence of hole-burning effect based on the interference of multiple-scattered light in macroporous Sm²⁺-doped Al₂O₃-SiO₂ glasses, where the photoionization of Sm²⁺ is used as the photobleaching process to produce the hole. The choice of the Al₂O₃-SiO₂ glass system comes from the fact that Sm²⁺ can be homogeneously incorporated into SiO₂ glass codoped with Al₂O₃, in contrast to the case of pure SiO₂ glass [8-10].

2. Experimental

A sol-gel method including phase separation was used to fabricate macroporous 5AlO_{3/2}·95SiO₂ (in mol%) glasses containing nominally 3 wt% Sm₂O₃. Tetramethoxysilane, Si(OCH₃)₄, and aluminum *sec*-butoxide, Al(OC₄H₉)₃, and SmCl₃·6H₂O were used as the sources of inorganic components without further purification. Al(OC₄H₉)₃ was mixed with *sec*-butanol with a volume ratio of 1 : 2 to lower the viscosity. Poly(ethylene oxide) (PEO) with an average molecular weight of 10,000 was used as the polymer component to induce the phase separation. The starting compositions of the samples are listed on Table 1. Nitric acid was utilized as the catalyst for the hydrolysis and condensation.

Gel samples were prepared by mixing 2M nitric acid aqueous solution containing PEO and SmCl₃·6H₂O with a mixture of Si(OCH₃)₄, Al(OC₄H₉)₃, and *sec*-butanol in an ice bath, as we reported previously [8]. After stirring vigorously for 30 min, the resultant transparent 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. Heat treatment was performed at 800 or 1000 °C for 2 h in air. To reduce Sm³⁺ into Sm²⁺, the sintered gel heat-treated at 800 °C in air were further reheated at 1000°C for 30 min under the flowing of a reducing gas of 50 vol% N₂, 47.5 vol% Ar, and 2.5 vol% H₂.

Table 1. Typical starting compositions of samples. (unit: g)

sample	Si(OCH ₃) ₄	Al(OC ₄ H ₉) ₃	sec-butanol	60% HNO ₃ aq	H ₂ O	PEO	SmCl ₃ ·6H ₂ O
P085	4.90	0.42	0.70	2.10	8.48	0.85	0.13
P090	4.90	0.42	0.70	2.10	8.48	0.90	0.13
P095	4.90	0.42	0.70	2.10	8.48	0.95	0.13
P100	4.90	0.42	0.70	2.10	8.48	1.00	0.13

3. Results and discussion

Figure 1 depicts SEM photographs of samples heat-treated at 800°C in air and reheated at 1000°C under reducing atmosphere. All the samples exhibit the bicontinuous morphology of gel skeletons and pores. Also, it is found that the size of pores and skeleton becomes smaller as the PEO content increases. In the reaction solution, the phase separation is induced by the repulsive interaction between the PEO adsorbed on alkoxy-derived oligomers and the solvent; the former is hydrophobic and the latter is hydrophilic. As a result, initially homogeneous reaction solution separates into two phases; one rich in PEO and oligomers, and the other in solvent. Freezing of the transient bicontinuous structure of phase separation by sol-gel transition followed by the evaporation of the solvent yields the macroporous structure. The sizes of pores and skeletons is determined by the relative rate of phase separation to that of sol-gel transition. The phase-separation rate varies with the PEO concentration, resulting in the successive variation of macroporous morphology with PEO content as shown in Fig. 1.

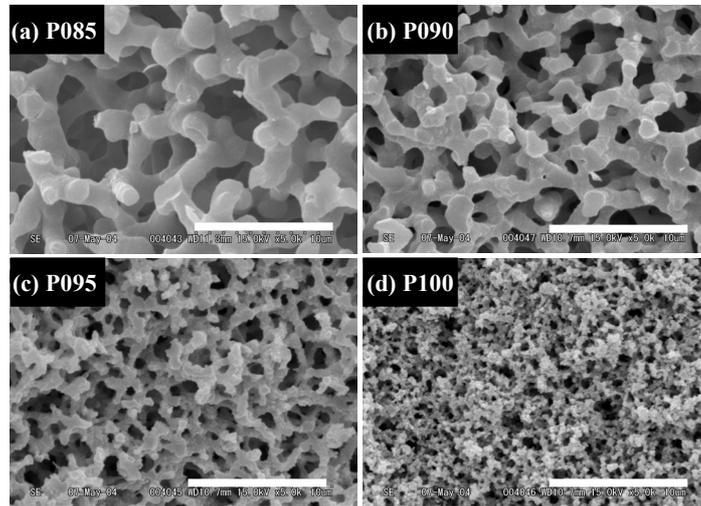


Fig.1. SEM photographs of 5AlO₃/2-95SiO₂ gels heat-treated at 800°C in air and reheated at 1000°C under reducing atmosphere: (a) P085, (b) P090, (c) P095, and (d) P100. Bars = 10 μm.

Typical fluorescence spectra are shown in Fig. 2 for P085. When the dried gel is heat-treated only at 1000 °C in air, the emission peaks ascribed to the 4f-4f transitions of Sm³⁺ are observed as shown in Fig. 2 (a); the emission lines at around 565, 603, and 649 nm are assigned to the ⁴G_{5/2} → ⁶H_{5/2, 7/2, 9/2} transitions of Sm³⁺, respectively. As shown in Fig. 2 (b), on the other hand, new emission peaks appear for the glass heat-treated at 800 °C in air and then reheated at 1000 °C in reducing atmosphere. These peaks observed at around 684, 700, and 728 nm are assigned to the 4f-4f transitions of Sm²⁺, corresponding to the Sm²⁺: ⁵D₀ → ⁷F_{0, 1, 2} transitions, respectively. It is evident that Sm³⁺ is reduced to Sm²⁺ in the Al₂O₃-SiO₂ glass during the heat treatment in the

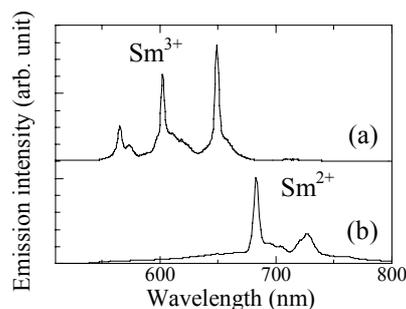


Fig. 2. Fluorescence spectra for 5AlO₃/2-95SiO₂ glass (P085) heat-treated at 1000°C (a) and that heat-treated at 800°C in air and reheated at 1000°C in reducing atmosphere (b).

reducing condition.

If the photoionization of Sm^{2+} occurs in macroporous glasses that strongly scatter light, holes may be burned through the interference of multiple-scattered light. Direct evidence for the occurrence of hole burning based on this mechanism is given by the hole production against the incident angle of laser beam i.e., in the wave-vector domain [2,3,11,12]. In Fig. 3 is shown the fluorescence intensity for P080, P085, P090, and P100 as a function of the incident angle of laser beam. In the measurements, the sample was rotated around an axis perpendicular to the incident plane (see the left side of Fig. 3), so that the angle of incidence, θ was varied. After holes were burned at $\theta = 0^\circ$ using a laser beam with the wavelength of 590 nm, the incident angle of the attenuated laser beam was scanned while monitoring the Sm^{2+} fluorescence. One can see from Fig. 3 that holes are observed in all the samples and that the hole width increases in the order of P085 < P090 < P095 < P100.

To characterize the scattering strength of our samples, coherent backscattering (CBS) experiments were carried out for macroporous glasses without Sm^{2+} . CBS appears as a distinct peak in the plot of the backscattering intensity versus the scattering angle. The peak known as CBS cone originates from the constructive interference of time-reversed counterpropagating waves in the exact backscattering direction [13-15]. In nonabsorbing media, the width of cone reflects the lateral spread of light in a disordered medium and is

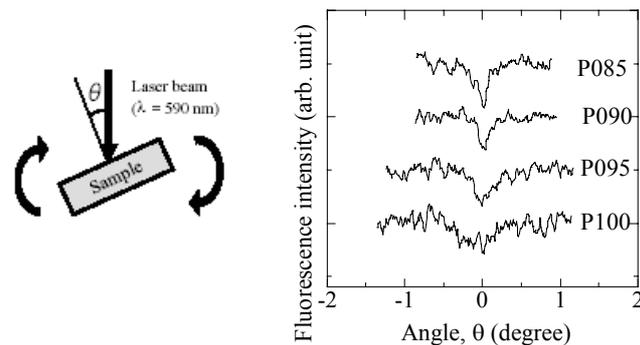


Fig. 3. Hole profiles for P085, P090, P095, and P100 as a function of the incident angle of laser light. The writing wavelength was 590 nm. Left side: the schematic illustration of the experimental setup.

inversely proportional to l , where l is the transport mean free path, or the average distance required to randomize the propagation direction of light [16]. The smaller l means the stronger scattering strength of the medium. We evaluated from the angular width of CBS cones that $l = 5.6, 4.0, 3.1,$ and $2.5 \mu\text{m}$ for P085, P090, P095, P100, respectively. The sample dependence of l indicates that the scattering strength is stronger in the sample with the finer macroporous morphology. Similarly to the case of CBS cone, it is anticipated that the angular width of the hole profile is inversely proportional to the lateral spread of light in the medium, because light waves injected at different points on the incident plane interfere inside the medium. The behavior of light diffusion is affected by the strength of optical scattering and also by the amount of optical absorption in the scattering medium. Since the concentration of Sm^{2+} in the present samples is assumed to be almost the same as one another, the variation of hole width shown in Fig. 3 is ascribed to the sample dependence of scattering strength. The stronger scattering in the sample with finer morphology suppresses the diffusion of scattered lights inside the medium, resulting in the broader hole width.

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