Scattering-based hole burning through volume speckles in a random medium with tunable diffusion constant

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A photoreactive random medium with tunable diffusion constant D is fabricated by infiltrating Sm^{2+}-doped macroporous aluminosilicate glass with liquid crystal (LC). Time-resolved transmission experiment reveals that D in the LC-infiltrated sample changes abruptly at around 35 °C due to the phase transition of LC between nematic and isotropic. The hole burning effect based on the interference of multiply scattered light is investigated with a particular motivation of controlling hole burning properties externally via temperature. We demonstrate that the holes are separately registered in each LC phase and can be detected selectively depending on the temperature. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2955830]

In random media where the dielectric constant varies randomly on the optical length scale, light waves undergo multiple scattering and interference. Light transport in random media is described by two crucial parameters, i.e., transport mean free path l^* (the distance through which the light travels before the direction of light propagation is randomized) and diffusion constant $D=v_E l^*/3$, where v_E is the energy velocity of light.[1] In strongly scattering media having small l^* and D, interference effects influence the light transport. Constructive interference on counterpropagating paths, for instance, leads to enhanced backscattering, known as weak localization.[2–4] In case of extremely strong scattering where l^* multiplied by wave vector k approaches unity,[5] it is predicted that light transport comes to a halt due to interference, which is referred to as Anderson, or strong, localization of light. Addition of optically active species into such media provides particularly intriguing systems since the photon localization can enhance the interaction between photons and medium. One fascinating example is a random laser, in which the combination of optical gain with multiple scattering gives a mirrorless laser action.[6–8]

Another interesting phenomenon is a "hole-burning effect" observed in photoreactive random media.[9–11] This effect is based on the fact that the interference patterns created inside the random medium, i.e., volume speckles, are very sensitive to the frequency and wave vector of the incident light. When the photoreactive random medium is exposed to an intense "writing" beam having frequency ω_w and wave vector k_w, the volume speckle is registered as the three-dimensional gradation of photobleaching because the rate of photoreaction is a function of light intensity. If the medium shows both the photobleaching and fluorescence, one can access to the registered pattern by exciting the medium with a "reading" beam having frequency ω_r and wave vector k_r and monitoring the emission intensity as a function of $\Delta\omega$ $(=\omega_r-\omega_w)$ or Δk $(=k_r-k_w)$. When $\Delta\omega=\Delta k=0$, the reading beam creates the interference pattern that matches the preregistered pattern, and selectively excites the photobleached part of the medium. Therefore, a dip is observed in the plot of emission intensity versus $\Delta\omega$ or Δk, and is recognized as a "hole."

A typical example of hole burning in the Δk domain is given in Fig. 1(a). As a specimen, we used Sm^{2+}-doped macroporous aluminosilicate glass with dimensions of $10\times10\times5$ mm^3. The sample was prepared via sol-gel route accompanied by phase separation.[12] Aluminosilicate glass was selected as a host of Sm^{2+} ions because Al^{3+} ions help the homogeneous dispersion of samarium ions, and facilitate the reduction of Sm^{3+} to Sm^{2+} ions during heating in reducing atmosphere.[13,14] The micrometer-scale structure is displayed in Fig. 1(b), where bicontinuous morphology of gel skeletons and pores can be observed. These pores act as scattering elements to incoming light waves so that the sample looks opaque. An Ar^+ laser beam ($\lambda=488$ nm) was used as the light source to induce the photoreaction and fluorescence. As schematically illustrated in Fig. 1(c), the excitation of the $4f^6\rightarrow4f^5 5d^1$ transition of Sm^{2+} with the 488 nm light causes intense fluorescence at around 683 nm, corresponding to the radiative relaxation to the ground $4f^6$ state. The irradiation with the 488 nm light also brings about photobleaching of Sm^{2+}; a part of the excited electrons is captured by some trapping sites to ionize Sm^{2+} to Sm^{3+}.[15] During the irradiation, therefore, the emission intensity of Sm^{2+} decreases as time elapses [Fig. 1(d)]. Utilizing these properties, five holes shown in Fig. 1(a) were burned and detected in the following sequence. First, the sample was placed on a rotation stage and irradiated with a writing beam (30 mW) for 10 min to burn the first hole. Then, the sample was rotated by 9 mrad around an axis perpendicular to the incident plane, and the spot irradiated beforehand was again exposed to the beam for 10 min to burn the second hole. Accordingly, the third, fourth, and fifth holes were also burned at different incident

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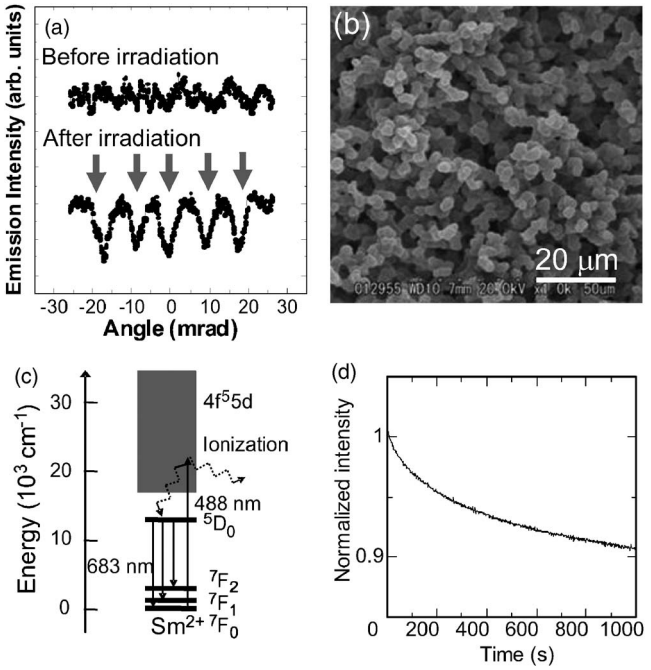

FIG. 1. (a) Emission intensity as a function of incident angle of reading beam for the Sm^{2+}-doped macroporous aluminosilicate glass. Upper signal: before irradiation with writing beams. Lower signal: after irradiation with writing beams. Arrows indicate the incident angles of writing beams. (b) SEM image of specimen used for the hole burning experiments. (c) Energy levels of Sm^{2+} in aluminosilicate glass. (d) Time evolution of the Sm^{2+} emission intensity under irradiation with a 488 nm laser light at 30 mW. The emission was collected with a photomultiplier tube combined with glass filters.

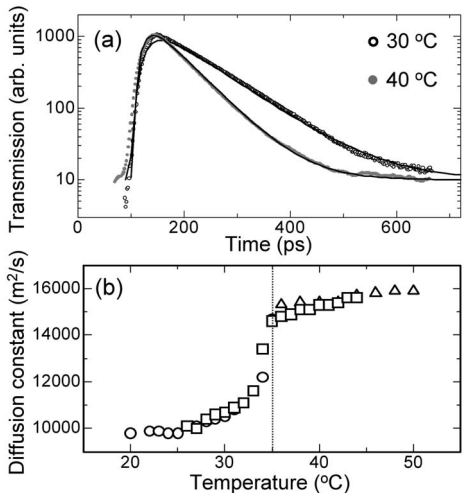

FIG. 2. (a) Temporal intensity profiles of the light pulse transmitted through the sample at 30 °C (represented by open black circles) and 40 °C (closed gray circles) after deconvolution with the profile of incident pulse. Solid curves are the theoretical fits of Eq. (1) to the profile after deconvolution. (b) Temperature dependence of the diffusion constant for the macroporous glass sample infiltrated with 5CB. Different symbols (○, □, △) correspond to different experimental runs. The transition temperature of 5CB between nematic and isotropic phases is indicated by a vertical dotted line.

angles or different $k_w = 2\pi \sin\theta/\lambda$, where θ is the incident angle. After the hole burning, the laser beam was attenuated by a factor of 500 (0.06 mW) and used as the reading beam to probe the holes without causing additional photoreactions. The irradiated spot was excited by the reading beam, and the emission intensity from Sm^{2+} was plotted as a function of incident angle of the reading beam. The appearance of distinct holes in the Δk domain clearly indicates that multiple data about the wave vector of writing beam are registered inside the medium. If a tunable laser is utilized as the light source, holes can be created and detected in the $\Delta\omega$ domain as well. Thus, this phenomenon is potentially applicable to high-density optical storage since a huge number of data can be stored in a volume medium by altering ω_w and k_w.

Because the scattering-based hole burning memorizes ω_w and k_w in the form of volume speckles, if the spatial structure of speckle pattern is tunable via temperature or electric field, one can control the hole burning properties externally. Liquid crystals (LCs) are very suitable for this purpose due to their strong temperature dependence of refractive index and coupling with electric field. Among various phases of LC, the nematic phase is characterized by an alignment of molecules along a common axis called a nematic director.[16] The partial ordering leads to a birefringence, which disappears when LC is heated into the isotropic phase. Owing to these properties, infiltration of random media with nematic LCs gives systems where scattering strength can be modulated through the control over external fields.[17] Based on this concept, Wiersma and Cavalieri reported random laser systems with temperature[18,19] or electric field[20] tunable emission properties. These results motivate us to infiltrate photoreactive random media with LC in order to explore the possibility of external control over the scattering-based hole burning.

In this study, we demonstrate the temperature control over scattering-based hole-burning effect for Sm^{2+}-doped macroporous aluminosilicates glasses infiltrated with LC. 4-cyano-4′-n-pentylbiphenyl (5CB) was selected as LC because the phase transition between nematic and isotropic phases takes place at relatively low temperature (~35 °C). Utilizing an abrupt change in refractive index with the phase transition of LC, the appearance of holes can be switched externally via the environmental temperature. In other words, whether holes are observed or not is controllable by the change in scattering strength with temperature. This property would be advantageous from a technological aspect of increasing the recording density in optical storage.

The Sm^{2+}-doped macroporous aluminosilicates glass was prepared as described elsewhere.[12] The prepared macroporous aluminosilicate glass has a sharp pore size distribution centered at around 3.1 μm, and the volume fraction of pores is 0.72. The presence of Sm^{2+} can be confirmed by the emission spectrum for the sample heat treated at 800 °C in reducing atmosphere. The Sm^{2+}-doped porous glass was infiltrated with 5CB in isotropic phase at 60 °C, and the diffusion constant D of light was evaluated by means of time-resolved transmission experiments. Examples of time-resolved diffusion profile are displayed in Fig. 2(a). As the light source, a mode-locked Ti:sapphire laser operating at 82 MHz with a pulse duration of 130 fs and a wavelength of 810 nm was used. The selection of wavelength comes from the fact that the absorption of Sm^{2+} is negligibly small around this wavelength range.[21] A short pulse was incident on the front sample surface and the diffuse transmission light was monitored by a streak camera. The as-measured profile was deconvoluted using the reference one measured without sample to obtain the data for a delta pulse. In Fig. 2(a), the open and closed circles show the deconvoluted profiles of the diffuse transmission at 30 and 40 °C, respectively. The longer tail of intensity for the profile taken at 30 °C indicates

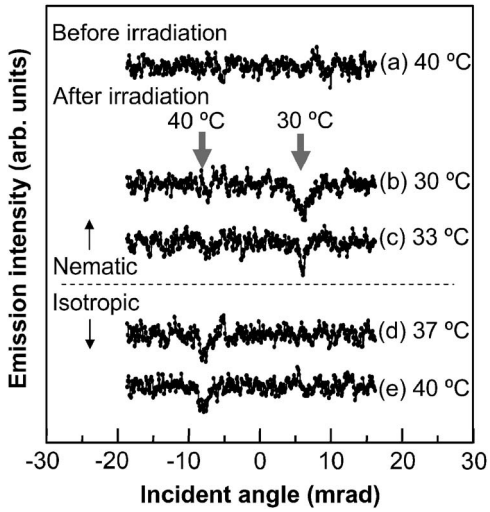

FIG. 3. Angular profiles of emission intensity before and after burning of holes for the Sm^{2+}-doped macroporous glass infiltrated with 5CB. The hole burning is carried out at +7 and −7 mrad under irradiation with a writing laser beam at 30 and 40 °C, respectively, as indicated by arrows. (a) shows the emission intensity vs incident angle of reading beam at 40 °C before hole burning, and (b)–(e) exhibit those at 30, 33, 37, and 40 °C, respectively, after hole burning. A horizontal dotted line separates the different LC phases; the profiles (b), (c) (nematic phase), and (d), (e) (isotropic phase).

that D is smaller, or scattering is stronger at 30 °C. The diffusion of a delta pulse through a slab of thickness L is given by[22,23]

$$T(t) \propto e^{-ct/l_a} \sum_n (-1)^n n^2 e^{-n^2 \pi^2 Dt/L^2}, \tag{1}$$

where c is the velocity of light and l_a is the absorption length. We assume that l_a is infinitely large at $\lambda = 810$ nm, and fitted Eq. (1) to the deconvoluted data by taking $L = 2.94 \times 10^{-3}$ m and using D as a fitting parameter. The solid curves correspond to the calculated ones with $D = 10\,500$ m^2/s (30 °C) and 15 300 m^2/s (40 °C). The correspondence between data and theory is good. The temperature dependence of D between 20 and 50 °C is displayed in Fig. 2(b). In the plot, different symbols mean different experimental runs. An abrupt change in D at around 35 °C can be ascribed to the large variation in refractive index coincident with the transition between the nematic and isotropic phases.

Scattering-based hole burning effect was measured for Sm^{2+}-doped macroporous glass infiltrated with 5CB by using an Ar^+ laser ($\lambda = 488$ nm) as the writing and reading beams. Two holes were burned and detected in the Δk domain as follows. First, the sample temperature was set to 40 °C where 5CB is in the isotropic phase, and the first hole was burned at the incident angle of −7 mrad. Then, the sample was cooled to 30 °C where 5CB is in the nematic phase, and the second hole was burned at the incident angle of +7 mrad. After the burning of two holes, the emission intensity was measured as a function of Δk at 30, 33, 37, and 40 °C using the reading beam. Figure 3 summarizes the overall results before and after hole burning. Despite the hole burning at two different incident angles, two holes do not appear simultaneously in each angular profile of emission intensity; the hole burned at 30 °C is detected at 30 and 33 °C but not at 37 and 40 °C, while the hole burned at 40 °C is observed at 37 and 40 °C but not at 30 and 33 °C. Considering the phase transition of 5CB at around 35 °C, the observed results indicate that information about the wave vector of writing beam is registered separately at 30 and 40 °C, depending on whether 5CB is in nematic or isotropic phase. As seen in Fig. 2(b), the phase transition causes the large difference in refractive index contrast, or scattering strength, at 30 and 40 °C, and modulates the spatial structure of the volume speckle pattern. Therefore, the hole burned in one phase of LC cannot be accessed when LC is in the other phase. When both the writing and reading procedures are performed in the same LC phase, holes are accessible even at temperatures different from the writing temperature. This is presumably due to an indistinguishable change in interference pattern with temperature variation, which is caused by too small change in D, or refractive index, as indicated in Fig. 2(b).

In summary, we have prepared a macroporous alumonosilicate glass doped with Sm^{2+} using the sol-gel method accompanied by the phase separation, and infiltrated the pores with 5CB which undergoes a nematic-isotropic phase transition at 35 °C. The diffusion constant in the 5CB-infiltrated macroporous glass shows an abrupt change at around 35 °C due to the phase transition of 5CB. The scattering-based hole burning effects can be controlled externally via the environment temperature, indicating that the interference patterns can be separately registered in each LC phase through photoionization of Sm^{2+}. This phenomenon is interesting from a viewpoint of application to optical storage, since the independent hole production at different temperatures enhances the data multiplicity.

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