Wavelength- and Angle-Selective Optical Memory Effect by Interference of Multiple-Scattered Light

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(Received 10 May 1999)

We report observations of a new optical memory effect in Sm-doped ZnS nanocrystals and elucidate its mechanism. One of the salient properties of this effect is that the incident angle as well as the wavelength of incoming light is memorized with high resolution. We show that this effect is not based upon spectral selection of homogeneous absorption lines as in the persistent spectral hole-burning effect but upon recording of interference patterns of multiple-scattered light in disordered media.

PACS numbers: 42.25.Hz, 42.25.Dd, 78.90.+t

In strongly scattering media, various remarkable phenomena related to multiple scattering of light, such as coherent backscattering [1–3], memory effects [4], laser action without an external cavity [5], and Anderson localization of light [6], have been observed. To this list we add here a novel effect observed in Sm-doped ZnS nanocrystals, in which both the wavelength and the incident angle of incoming light is memorized with high resolution. Its appearance as the wavelength memory resembles that of the persistent spectral hole-burning effect [7]. However, we show that the mechanism is entirely different, and the effect is due to interference of multiple-scattered light in the medium. It is closely related to weak localization of light and expected to find application in high-density optical data storage.

Sm-doped ZnS nanocrystals were prepared by the same procedure as that for CdS nanocrystals [8] with Zn-$(CH_3COO)_2$ and $Sm(CH_3COO)_3$ (molar ratio 100:1) as the starting materials. The diameter of the nanocrystal was estimated to be about 3 nm from the width of the x-ray diffraction peaks of ZnS. The sample was obtained as powder of particles with the size ranging from 100 to 300 μm, and each particle is made up of many nanocrystals. All the spectral measurement was done at room temperature. An attenuated light beam from a tunable cw dye laser was used to measure the excitation spectra for fluorescence around 15 900 cm^{-1}. The excitation spectra have a peak at 17 500 cm^{-1}, which is ascribed to transitions in the Sm ion.

Figure 1 shows how the wavelength of irradiating light is memorized in the medium. Experimental procedure is the same as that for persistent spectral hole burning [7]. After the measurement of the excitation spectrum shown in Fig. 1(a), the sample was irradiated at the wave number indicated by the arrow with the same laser beam as that for the spectral measurement, but with an intensity about 10^4 times higher. As shown in Fig. 1(b), a narrow hole was observed in the spectrum measured after the irradiation. The width of the hole was 2.3 cm^{-1}. The observed decrease of the emission intensity is tentatively ascribed to photoionization of Sm^{2+} ions. The depth of the hole fell off gradually with time after the burning, but as much as half of the initial hole was found to remain after 24 h. Similar hole burning was observed all over the tunable range of the employed dye laser from 16 500 to 17 500 cm^{-1}, and was always accompanied by an almost uniform decrease of the whole band in the excitation spectrum, as is shown in Fig. 1.

In the conventional spectral hole burning, the presence of a rather narrow resonance line of localized optical centers, such as dye molecules or ions, dispersed in a host matrix is essential; the center frequency of the line is distributed owing to inhomogeneity of the host, and a broad absorption band is formed; when the medium is irradiated by monochromatic light with a certain frequency within the absorption band, centers that are resonant to the light are removed from the absorption band by some photoreaction, and a hole is observed in the absorption band [7]. The effect observed in Fig. 1 is quite similar to the conventional hole-burning effect in appearance, and therefore we are using the same terms, hole and hole burning, for this effect. However, a remarkable difference arises from the measurement of the angular dependence of

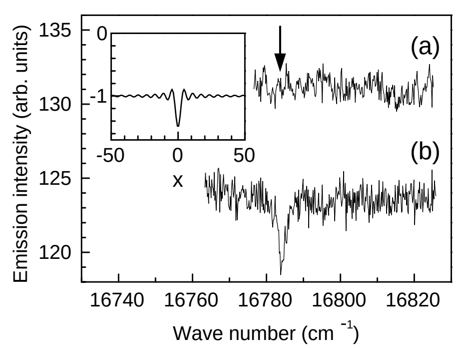

FIG. 1. Excitation spectra of Sm-doped ZnS nanocrystals before (a) and after (b) laser-light irradiation. Irradiation time and power were 5 s and 1 mW/mm^2, respectively. Inset shows the function $-[1 + \sin(x)/2x]$.

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holes shown in Fig. 2. In the measurement, the sample was rotated around an axis lying in the surface of the stage that holds the sample powder, and the angle of the incident beam relative to the surface normal was changed. First, we burned a hole at an angle of 0°. A hole was clearly observed as shown in spectrum 1 in Fig. 2. However, when the sample was rotated by only 0.162°, the first hole vanished completely. Then, at the same angle, the second hole was burned at a different wave number, and the result is shown as spectrum 3. The first hole was not erased, although it vanished at 0.162°; it reappeared and the second hole disappeared when the angle was turned back to 0°. When the sample was gradually rotated to the angle of 0.162° again, the first hole faded out, and the second hole was restored. In brief, the hole was observed when not only the wave number but also the incident angle of the measuring light coincided with those of the burning light. This angle dependence cannot be understood by considering a removal of a resonance line. Moreover, any resonance line in any host would not have such properties that the resonance width is as narrow as 2 cm^{-1} at room temperature and simultaneously the resonance frequency is distributed over 1000 cm^{-1}. Therefore, the present hole burning calls for an explanation by some novel mechanism.

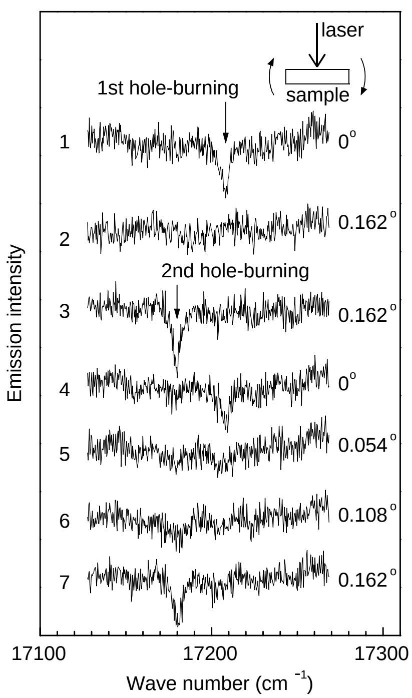

FIG. 2. Spectra of holes burned and measured at different incident angles. The numeral on the left side of each spectrum indicates the order of the measurement, while the value on the right side indicates the incident angle. The first hole was burned at 0° before the measurement of spectrum 1, and the second hole was burned at 0.162° between the measurements of spectra 2 and 3.

The fact that the hole depends on the incident angle suggests that this hole is related to some interference effect. Even if a medium cannot directly record the wavelength of the incident light, the wavelength can be registered if an interference fringe is formed in the medium and the medium can record the spatial distribution of the light intensity. This kind of process causes the spatial hole-burning effect in standing-wave lasers and is utilized in the Lippmann color holography [9]. Suppose that a mirror placed at the back of a recording medium reflects the transmitted light, which has the wave number k_w along the z axis in the medium, back to the medium and creates a standing wave. If the fringe pattern of the standing wave is expressed as $1 - \cos(2k_w z)$, and some photoreaction decreases the absorption coefficient in proportion to the light intensity, then the change in the absorption coefficient is proportional to $-[1 - \cos(2k_w z)]$. A reading light beam with the wave number k_r creates another standing wave, and the change in the total amount of the absorbed light due to the photoreaction is given by the overlap integral, or the intensity-intensity correlation function, of the two standing waves. In a medium with the length L, it is proportional to

$$C(k_r) = -\int_0^L [1 - \cos(2k_w z)][1 - \cos(2k_r z)]\,dz$$

$$\simeq -L\left(1 + \frac{\sin[2(k_w - k_r)L]}{4(k_w - k_r)L}\right), \tag{1}$$

when k_r is close to k_w, and $Lk_r \gg 1$. If the medium is fluorescent, also the change in the excitation spectrum of the fluorescence is proportional to $C(k_r)$. The first and the second term in Eq. (1), which is plotted in the inset of Fig. 1, correspond to the uniform decrease and the hole in the excitation spectrum shown in Fig. 1(b), respectively. In the absence of the interference effect, only a change corresponding to the first term, which directly reflects the change in the absorption spectrum, would be observed. If Eq. (1) is applied to the hole of Fig. 1(b) with a FWHM of 2.3 cm^{-1} in a medium with the refractive index 2.37 (of ZnS), the path length L is estimated to be 0.6 mm. However, the powder sample does not have this long linear optical path, nor has it a mirror. Since the sample is an aggregate of nanocrystals, it can be regarded as a multiple-scattering medium. A light path in such a medium is folded many times. Hence we infer that superposition of light waves that arrive at each position within the scattering medium along various paths creates a speckle-like interference pattern in the medium and produces a similar effect as the fringe in a uniform medium. The interference pattern changes according to both the wavelength and the angle of the incident light. Therefore the wavelength and the angle are registered if the interference pattern is burned in the medium. By analogy with Eq. (1) for a standing wave, the hole shape is presumably equivalent to the intensity correlation function of light waves within the scattering medium. This is contrasted to the conventional measurement of the intensity correlations, in which transmitted or reflected light is measured outside the scattering medium and the correlation function is obtained by numerical calculation [4,10].

Wavelength resolution of the hole burning that is due to interference of multiple-scattered light, or the correlation frequency of the scattered light within the medium, is considered to be determined by the total length of the folded path in a scattering medium, which corresponds to the length $2L$ in a uniform medium. This relation is parallel to that between the correlation frequency of fluctuating transmitted light and the travel time through a scattering medium [10]. On the other hand, angular resolution is determined by the coherence length l of the multiple-scattered light in the direction perpendicular to the incident light beam, and is approximately given by λ/l, where λ is the light wavelength. It is expected that wavelength and angular resolution of the hole are dependent on the particle size because the spread of the scattered light is probably bordered by the particle surface, and that wavelength and angular resolution are reduced in smaller particles. Thus we measured particle-size dependence of the holes in three samples: (1) a heap of particles with a diameter of 100–300 μm; (2) a heap of particles ground and sieved through 74 μm mesh; and (3) sparsely dispersed particles ground and sieved through 74 μm mesh. The reason sample 3 was adopted is that scattered light possibly itinerates over many particles in the heaped sample, and l might be different if the particles are separated. In sample 3, the particle density is so low that the particles do not touch one another, and the interference is closed in a single particle. As is expected, the hole width shown in Fig. 3(a) is larger in sample 2 than 1. The hole of sample 3 is even broader than sample 2, which indicates that interfering light in the heaped sample spreads over many particles. Angular dependence of the hole depth shown in Fig. 3(b) is almost the same for samples 1 and 2, but becomes broader for sample 3. Angular resolution λ/l of sample 3 is calculated with $l = 74$ μm and $\lambda = 0.58$ μm to be about 0.45°. This value agrees well with the experimental result of 0.4°, which supports the inference that each particle in sample 3 independently contributes to the hole burning.

In a scattering medium, a constructive interference of time-reversed counterpropagating waves is known to cause weak localization of light and coherent backscattering [11], which is observed as a narrow cone of scattered light around the exact backward direction [1–3]. The size of the coherent backscattering cone also is inversely proportional to the lateral spread of the scattered light in the medium, or l, and is given by λ/l [11]. In Fig. 3(c), the coherent backscattering peak is clearly observed for the three samples. The presence of the coherent backscattering peak implies the presence of interference between time-reversed counterpropagating waves, even in a single particle in the sparse sample 3. The angular dependence of the coherent backscattering in Fig. 3(c) resembles that of the hole in Fig. 3(b) well for the three samples. This result gives evidence that, in this material, the hole-burning effect and the coherent backscattering are caused by interference of the same multiple-scattered light.

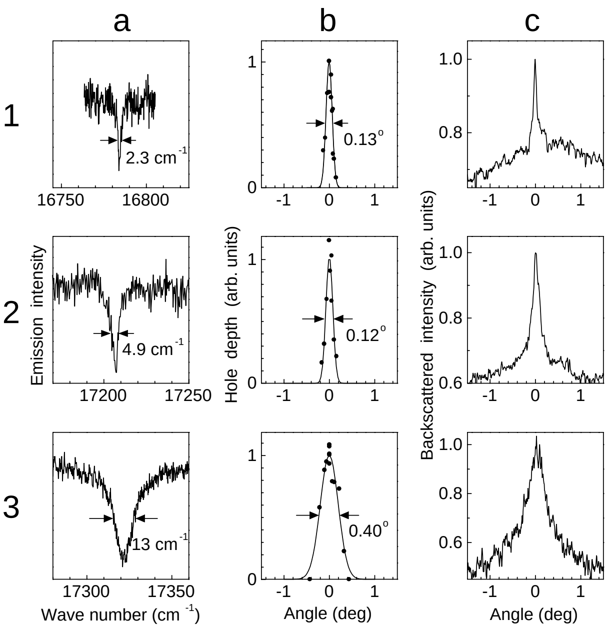

FIG. 3. Hole spectrum (column a), angular dependence of the hole depth (column b), and coherent backscattering cone (column c) of three forms of Sm-doped ZnS nanocrystals. Samples are, a heap of particles with a diameter of 100–300 μm (row 1), a heap of particles sieved through 74 μm mesh (row 2), and sparsely dispersed particles on a glass plate sieved through 74 μm mesh (row 3). In column b, closed circles are experimental data, and lines are Gaussian profile to fit the data. FWHM's of the hole spectrum and the angular dependence are indicated in columns a and b.

In conclusion, we have shown that the wavelength and angle selective optical memory effect observed in Sm-doped ZnS nanocrystals is caused by interference of multiple-scattered light. Although it is similar to the persistent spectral hole-burning effect, the wavelength selectivity of the present effect stems from the nonlocal interference process and is closely related to the Lippmann color holography and the wavelength multiplexed holography [9,12]. It will give a unique means for the direct measurement of the intensity correlation function of multiple-scattered light within the medium. Quantitative description of the linewidth and lineshape of holes and the relation with the backscattering cone will require detailed information on the spatial distribution and correlations of light field in the multiple-scattering medium. Since a nanocrystal with a diameter of 3 nm is possibly too small to be an effective scatterer, some inhomogeneity with a larger scale might act as a strong scatterer. This effect will be observed in other combinations of multiple-scattering media and photoreactive materials. Experiments with more controlled scatterers are being carried out.

When this effect is viewed from the standpoint of optical data storage, information is stored and retrieved in the three-dimensional space of the medium by a simple way of changing the wavelength and the incident angle of light. High density optical data storage which exceeds the diffraction-limited surface density of the order of λ^{-2}, has long been sought. Three-dimensional data storage using a crossing beam pair and two-photon excitation has been devised [13]. Thick holograms also store data in three dimensions [12,14]. These methods, however, require two beams and rather complicated optical setup. Near-field scanning optical microscopy can be applied to data storage to circumvent the diffraction limit [15], but the storage is in two dimensions and uses even more sophisticated setup. Storage density of persistent spectral hole burning is not restricted by the light wavelength and can be very high [7], but few materials are practical at room temperature. Then the effect reported here can be an alternative to these methods. One might point out that the angular selectivity is lost if the recording beam is focused tightly, but the frequency multiplicity remains and will bring a significant advantage over conventional two-dimensional optical memories.

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