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Multilayer optical memory using femtosecond-laser induced fluorescence in rare-earth ion doped glass

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Abstract We report three-dimensional fluorescent memory by recording optical bits with irradiation of femtosecond laser pulses at 800 nm and by reading photoluminescence change in Eu^{3+} doped glass. We produced multi-layered micro-bit patterns and read the blue emission from the 405 and 325 nm excitations due to permanent reduction of Eu^{3+} to Eu^{2+} in sodium borate glass by scanning the irradiated region in multilayers.

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1 Introduction

Three-dimensional optical storage has drawn considerable interest recently to improve storage capacity. In this scheme, the data are stored at different levels within a volume recording medium. For that purpose, change of optical properties in glasses or polymers using femtosecond laser irradiation is very attractive in both the scientific and technological aspects [1]. Another prospective advantage of optical bit recording using femtosecond laser lies in surpassing of the diffraction limit in recording by using nonlinear optical properties. Also, the size of a photo-modified region is well defined, since the build up of stress is not much expected even with high power due to nonthermal character of the interaction.

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The detection of stored bits is usually done by means of a refractive index change or a fluorescent signal. Fluorescent memory has much better signal-to-noise ratio than refractive index memory. An example of the fluorescent memory is to utilize the valence state change of rare-earth ions. A feasible three-dimensional memory has been already demonstrated by utilizing the photoluminescence spectrum change of space-selective spots by femtosecond laser irradiation in Sm-doped glasses [2, 3]. The change of the valence state of Eu ions caused by femtosecond laser irradiation was also confirmed [4]. In this report, we present a multi-layered pattern of 3D fluorescence bits by utilizing the valence state change of europium ions in sodium borate reduced by femtosecond laser irradiation with indicating its potential application to high-density optical memory. We used two different methods to read the stored data. One was to read the fluorescent spots by scanning the sample directly, and the other was to read data from the fluorescence image from a confocal microscope.

2 Experiment

The glass samples were prepared using melt and quenching technique. The composition of the glass host used in this study was $85B_2O_3$–$15Na_2O$, and we added 0.1 mol% Eu_2O_3 as dopants. Powders of reagent grade were mixed together and melted in a platinum crucible for 30 min at 1300°C. Then, the melt was poured to a stainless plate and pressed to a thickness of about 2 mm by another plate. The glasses were annealed for 3 h at 300°C and mechanically polished. After the glass samples were cut and polished, their optical properties were measured. A regeneratively amplified 800-nm Ti:sapphire laser system with a 1-kHz repetition rate and a 100-fs pulse duration was employed as the

irradiation source. A laser beam was focused by a micro-objective with NA 0.42 inside the sample on a motorized xyz stage, and the spot interval was controlled by the programmed scan speed.

The absorption, excitation, and fluorescence spectra of the irradiated area were measured by a spectro-photometer and a fluorescence spectrometer. To measure the absorption spectrum of the glass sample after the laser irradiation, we made an irradiated area of 3×3 mm inside the glass sample that consisted of lines by scanning the laser beam at a rate of 0.5 mm/s. The multilayer fluorescent bit pattern formed by femtosecond laser irradiation was read out by scanning the sample during a laser-diode excitation at 405 nm and a HeCd laser excitation at 325 nm. We also used a reflection-type fluorescent confocal microscope which detected the 410–490 nm emission as a signal.

3 Results and discussion

Femtosecond laser irradiation on Eu^{3+} ion doped glass changed absorption and photoluminescence spectra. Figure 1a shows the change in absorption spectra before and after irradiation. In the visible range, the absorption coefficient of the unirradiated sample was negligible. The wavelength of the incident laser was 800 nm, and the Eu-doped glass does not have any absorption at the wavelength. Thus, single-photon absorption cannot create any spectral change, and nonlinear absorption such as multiphoton absorption is required to provide electrons to the conduction band. The irradiated glass shows a broad induced absorption in the ultraviolet region which has a band peaking at approximately 300 nm. The band can be ascribed to the absorption due to the $4f$–$5d$ transition of Eu^{2+} [5]. The photoluminescence spectra of the 0.1 mol% Eu^{3+} doped glass under excitation at 325 nm before and after the 400 mW irradiation also support the valence state change of Eu ions as shown in Fig. 1b. The shorter wavelength side of the emission band under the 325 nm excitation is suppressed because of a cut-off filter used to block the excitation light. The emissions from the unirradiated sample in between 550 and 750 nm can be attributed to the well-known transitions from $^5D_0$ to ^7F_J ($J = 0$–4) levels of Eu^{3+} ions [6]. It can be seen that the concentration of Eu^{2+} ions is negligible in the unirradiated sample, because there is no blue emission. A new broad emission band at 400 nm formed after laser irradiation in the spectrum can be assigned to the lowest $5d$–$4f$ transition of Eu^{2+} in the host. In contrast, the intensity of Eu^{3+} slightly decreased with increased irradiation intensity and exposure time. Thus, it indicates that a part of the Eu^{3+} ions are photoreduced to Eu^{2+} as a result of the femtosecond laser irradiation. The strong photoluminescence band

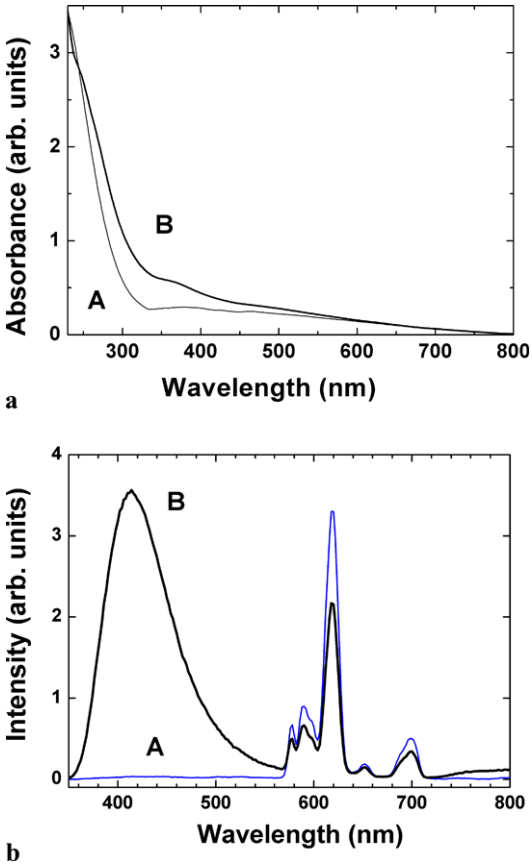

Fig. 1 Absorption and photoluminescence spectra before and after femtosecond laser irradiation: **a** absorption change; **b** photoluminescence change. *Curve* A is before irradiation, and *curve* B is after irradiation

appearing as a result of the photoreduction has better contrast compared with the results reported recently for Sm-doped glasses [2, 3]. The emission due to the d–f transitions is broadened because of the large spatial extension of the $5d$ wave function and the lattice vibration of the surroundings. The detailed mechanism of the photo-reduction was explained elsewhere [4].

The multilayer patterns were formed with various femtosecond laser irradiation conditions and read out by two different methods. At first, we read the fluorescent bit signals at 450 nm from the multilayer by scanning the recorded area in the x, y, and z directions during excitation at 325 nm. Scanned signal from five layers after irradiation are shown in Fig. 2. The signal from a spot irradiated with five pulses of 1 μJ energy has a width of 3 μm. The femtosecond-laser beam diameter at the focused spot was also estimated as 3 μm. However, the real size inside the glass is not easily determined because of nonlinear optical process. We used a zigzag pattern to record information from a spot and the layer separation of 50 μm to reduce the signal from the other layers. The lateral separation of bits was also 50 μm. The number of layers which we can record and read could be

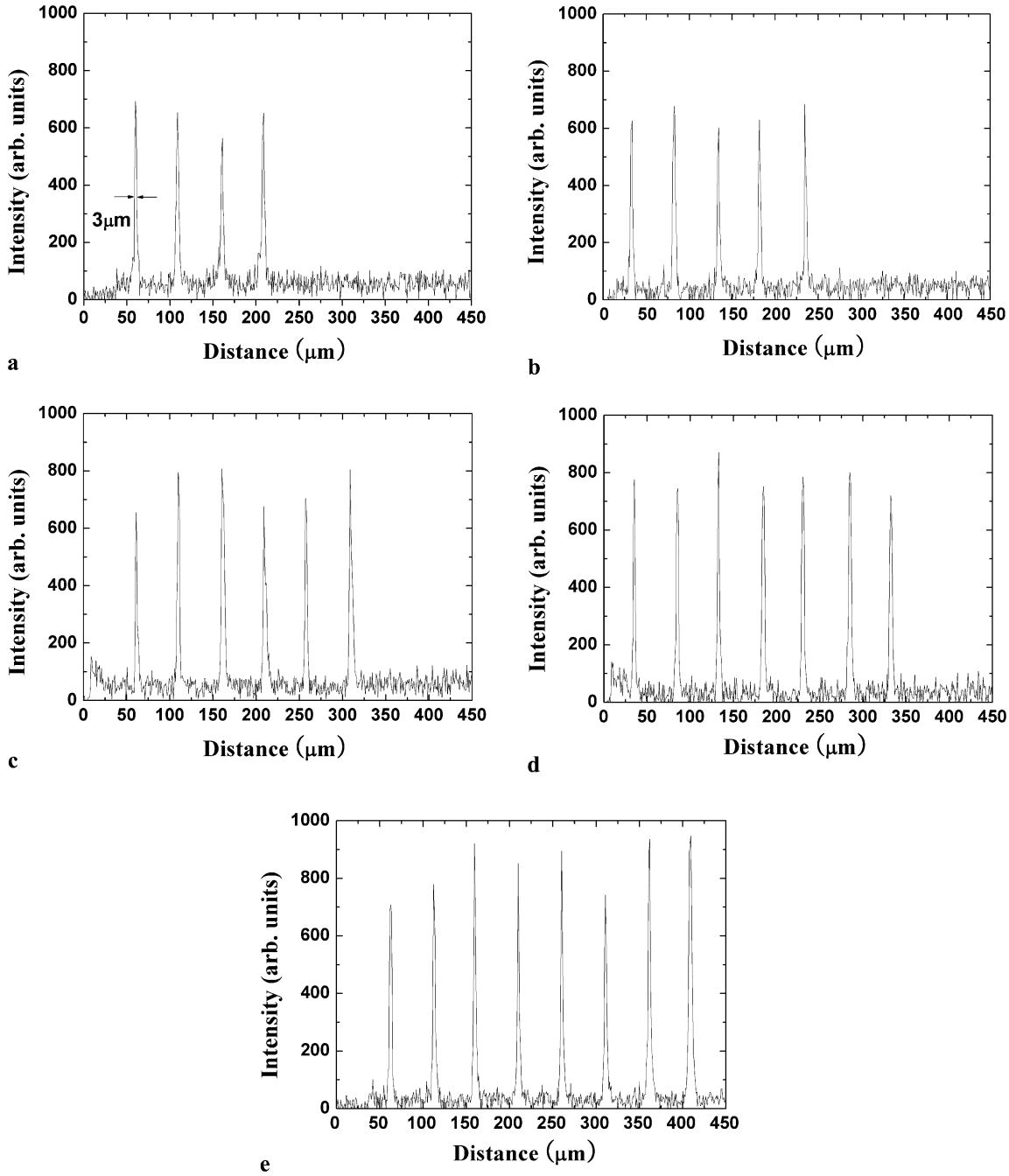

Fig. 2 Multilayer fluorescent bits obtained with excitation at 325 nm by scanning in five layers. **a** First layer, **b** second layer, **c** third layer, **d** fourth layer, and **e** fifth layer

extended to much more than five layers. However, it is impractical to use a bulky HeCd laser at 325 nm to read the recorded bit information. The other method was to use a reflection-type fluorescent confocal microscope to improve the lateral and longitudinal resolutions. In this case, we detected a blue emission from the recorded bits with excitation at 405 nm although the signal is much weaker. Figure 3 shows the scanned signals of the images from a few selected layers among 20 recorded layers. The lateral separation of bits and the layer separation was 9 and 10 μm, respectively. Each spot was obtained with ten pulses of 2 μJ energy. The average fluorescence bit size was estimated as 2.5 μm. It is slightly smaller than the value obtained with higher energy pulses in Fig. 2, because the confocal microscopic method has the better spatial resolution.

The contrast remained relatively low and noisy background may be originated from the limitation of excitation wavelength and power in the confocal microscope which has

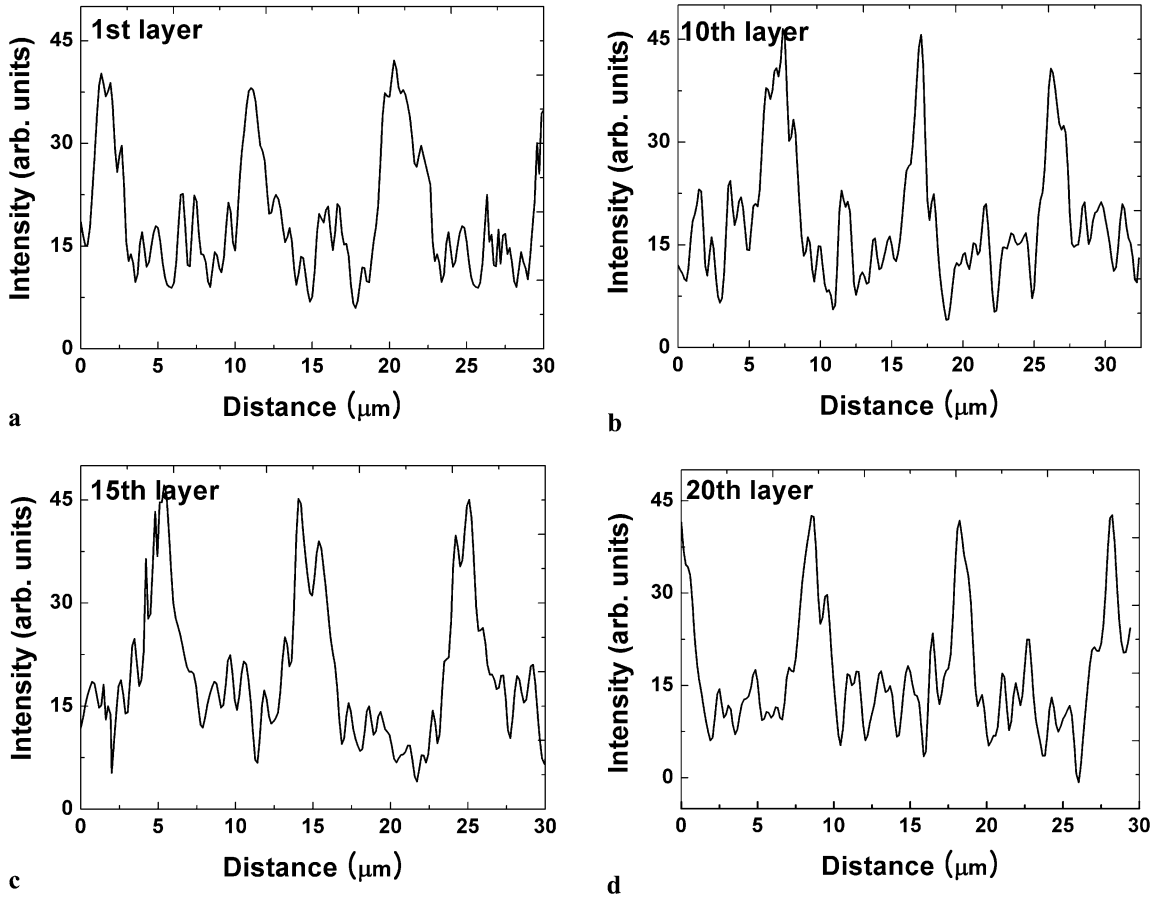

Fig. 3 Multilayers showing fluorescent bits obtained with excitation at 405 nm using a confocal microscope. **a** First layer, **b** tenth layer, **c** fifteenth layer, and **d** twentieth layer

an LD at 405 nm. The 325 nm excitation produced a better signal-to-noise ratio than the 405 nm, because the absorption cross-sections of Eu^{2+} ions at 325 nm has several times larger than at 405 nm. The mechanical damage threshold of the material was determined to be about 1 J/cm^2 by observing the optical image after the irradiation. However, the fluorescence bit can be observed in a sample irradiated with much lower than the threshold if the fluorescence detection system has better sensitivity. The increase of numerical aperture of a micro-objective is also an efficient way to gain storage capacity. More work will be necessary to improve signal-to-noise ratio by optimizing the reduction conditions.

4 Conclusions

We showed the feasibility of three-dimensional fluorescent memory in 0.1% Eu-doped sodium borate glass. By using photo-reduction of Eu^{3+} ions we obtained strong emission in the blue. We obtained fluorescent bits of 3 μm lateral size in a five-layer pattern by scanning the sample in different layers during excitation at 325 nm. We also used a confocal microscope to get fluorescent bits of 2.5 μm lateral size in a twenty-layer pattern during excitation at 405 nm. Eu-doped sodium borate glass can be a potential medium for realizing a high-density 3D fluorescent memory. However, it is necessary to improve the signal-to-noise ratio by controlling dopant concentration and laser exposure.

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