Quasinondestructive Holographic Recording in Photochromic $LiNbO_3$

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We have observed quasinondestructive holographic storage with a continuous-wave laser at $\lambda = 532$ nm in near-stoichiometric $LiNbO_3$ doped with Tb and Fe. This crystal showed an exceptionally long grating decay time and also exhibited a fast color change upon exposure to ultraviolet (UV) light. It was demonstrated that the grating recorded from the UV-exposed, colored state can be continuously read out over 9 h at a reading intensity as high as 8 mW/cm^2. In addition, the written grating could be easily erased with UV illumination which returned the crystal back to the original colored state.

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Photorefractive materials have been extensively investigated as potential media for holographic data storage (HDS) since the discovery of photorefractivity in lithium niobate ($LiNbO_3$) [1]. Holographic data storage with photorefractive materials has held the promise of high storage densities, short access times, and high transfer rates [2,3]. Material requirements generally include high dynamic range and sensitivity, long dark storage time, resistance to erasure during readout, and so on. For practical read-write memory, the fast erasure of stored information is also to be considered. One of the most important problems in the implementation of holographic information storage is the gradual erasure of information during readout, i.e., the destructive or volatile readout. Several techniques have been developed to overcome this problem, which include thermal fixing [4,5] and electrical fixing [6,7]. Heating or application of high electric field, however, is not practical. Another path to nonvolatile readout is the use of photon-gated or two-color recording [8,9], in which a gating light (usually of higher photon energy than the recording beams) is present during recording for sensitizing the medium. This light just aids the recording process but is not at the recording wavelength, thereby making the readout at a longer wavelength nonvolatile. This all-optical process is more attractive, and substantial progress has recently been made on this and similar approaches [10–12]. However, the sensitivities obtained by this process still remain very low.

Other processes that have achieved either quasinondestructive readout or grating formation with extended lifetime have also been reported in many photorefractive materials using a variety of techniques [13–16]. Many of those involve the formation of complementary gratings. Taking advantage of the different time constants between the two or more competing gratings, the overall lifetime of information during readout can be much prolonged. Because of the difficulty in fast erasing, these processes have been investigated mainly for read-only holographic storage. We have found that some near-stoichiometric $LiNbO_3$ crystals exhibit an exceptionally long grating decay as well as a photochromic effect, which are very obvious in crystals doubly doped with Tb and Fe. By combining these two features, we were able to achieve highly sensitive and quasinondestructive holographic recording while maintaining the recording reversibility, i.e., the capability of fast erasure.

Near-stoichiometric $LiNbO_3$ crystals have been grown by the top-seeded solution method using the melt containing 59 mol% Li_2O and 41 mol% Nb_2O_5 with 200 ppm Tb_2O_7 and 100 ppm Fe_2O_3. The crystal composition was estimated from the Curie temperature measured by differential thermal analysis and found to be $Li/Nb \approx 49.7/50.3$ [17]. Details on the crystal growth will be reported at a later time. A sample ($a \times b \times c = 8 \times 3.1 \times 10\ mm^3$) investigated here was cut from the boule, oriented, and optically polished. The absorption spectrum of a Tb,Fe-doped crystal was similar to that of an ordinary Fe-doped crystal, as shown in Fig. 1(a). However, this double-doped crystal exhibited a strong and thermally stable induced absorption band in the visible range when exposed to ultraviolet (UV) light, as shown in Fig. 1(b). It is accepted that in $LiNbO_3$ containing Fe, the photochromic effect arises from the change in valence state from Fe^{3+} to Fe^{2+}, caused by the photoinduced charge transfer via the conduction band [18]. This seems obvious because we have also observed the same but weaker photochromic effect in Tb-doped $LiNbO_3$ crystals, which were found to contain a small amount of natural Fe impurities. However, the UV-sensitive sites have yet to be identified. It is unlikely that these are Tb ions themselves, because little optical absorption change associated with Tb was observed. One possibility is that these sites are increased in concentration and become more stable by introducing Tb. The UV-induced absorption band of Tb,Fe-doped $LiNbO_3$ was very stable against thermal decay at room temperature

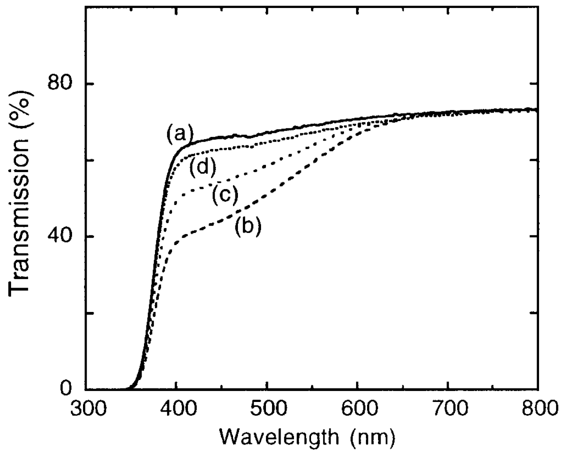

FIG. 1. Transmission spectra of Tb,Fe-doped $LiNbO_3$ (sample thickness is 3.1 mm). (a) Before UV exposure; (b) after UV exposure ($I_{UV} = 0.7$ W/cm^2) for 4 sec; (c) after bleaching for 40 sec at $\lambda = 532$ nm and $I = 400$ mW/cm^2; (d) after bleaching for 360 sec at $\lambda = 532$ nm and $I = 400$ mW/cm^2.

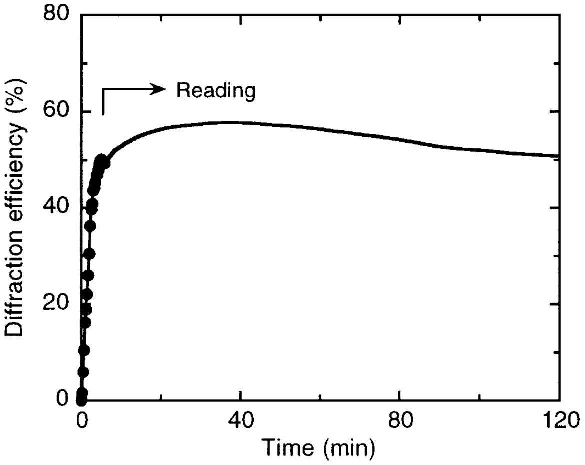

FIG. 2. Grating buildup and decay in the uncolored state. Total writing intensity is 800 mW/cm^2 at $\lambda = 532$ nm and $\Lambda = 0.936$ μm.

but could be optically bleached with visible lights. The response to UV light was very fast, and the induced absorption was saturated in a few seconds at each UV intensity. A Hg-Xe lamp was used as the UV source, which has several characteristic peaks in the range of 300–400 nm. In this work, the intensity of UV light was fixed at the maximum output intensity of this lamp, about 0.7 W/cm^2. Figures 1(c) and 1(d) show the bleaching processes with visible light at $\lambda = 532$ nm. Our interest in this reversible photochromic effect is to use it in fast hologram erasure, not to record permanent absorption holograms as often done in other photochromic materials. Thus, the fast coloration upon UV exposure can be effectively used for erasing the stored information if holograms are recorded from the colored state.

The photorefractive properties of Tb,Fe-doped $LiNbO_3$ were characterized by the conventional two-wave-mixing technique. A continuous-wave green laser at $\lambda = 532$ nm was split into two beams of equal intensity, with each being in the intensity range of 8–800 mW/cm^2. These two beams (5 mm in spot diameter) were extraordinarily polarized and made to intersect symmetrically inside the crystal of 3.1 mm thickness so that the grating vector is parallel to the crystal's c axis. The external crossing angle between the two beams was 30°–55°. In the recording process, both beams were incident on the crystal, with one of them blocked from time to time in order to measure the diffraction efficiency. During readout, one of the recording beams was completely shut off. The diffracted signal was monitored by a photodiode which was connected to either a digital oscilloscope or a chart recorder, depending on the time scale. The diffraction efficiency is here defined as the intensity ratio between the incident and diffracted beams. At first, the grating was recorded from the uncolored state [Fig. 1(a)]. Figure 2 shows the buildup and decay characteristics of grating written from this state. The grating during readout decayed very slowly following the initial increase in diffraction efficiency. This initial increase is not unusual and is often observed in many cases due to the beam coupling and other effects. In fact, when the c axis of the crystal was rotated by 180°, the grating decayed a little faster without revealing this phenomenon, but the decay time was still very long in comparison to the buildup time, with a time constant ratio over 30. Since no appreciable change in absorption spectrum was observed in association with the recording from this uncolored state, the UV-sensitive sites are unlikely to be involved in this grating formation.

It is more interesting to investigate the grating formation from the colored state [Fig. 1(b)], in which the bleaching process will take place together with the hologram recording. Before recording, the crystal was exposed to UV light for about 5 sec, and then the grating was recorded with two green writing beams ($I_{tot} = 800$ mW/cm^2, equally divided into two beams) in the absence of UV light. The result is shown in Fig. 3. The measured photorefractive sensitivity was ~0.1 cm/J, in which the sensitivity was defined as the initial time derivative of the square root of diffraction efficiency divided by the total recording intensity and the crystal thickness. In readout, the diffraction efficiency initially decreased. Then it began to slowly increase, ultimately decaying to zero after a few hours, as observed in the uncolored case. The grating could be easily erased by UV illumination at anytime during readout. These behaviors can be tentatively explained in the following way. During the recording process, an additional grating is written to UV-sensitive deep sites. This grating will be washed out gradually even under the nonuniform writing beams because all these UV-sensitive sites will ultimately be occupied through the bleaching process. If the recording process is finished before complete bleaching, however, a part of this additional grating still exists. This remaining grating will be erased during subsequent

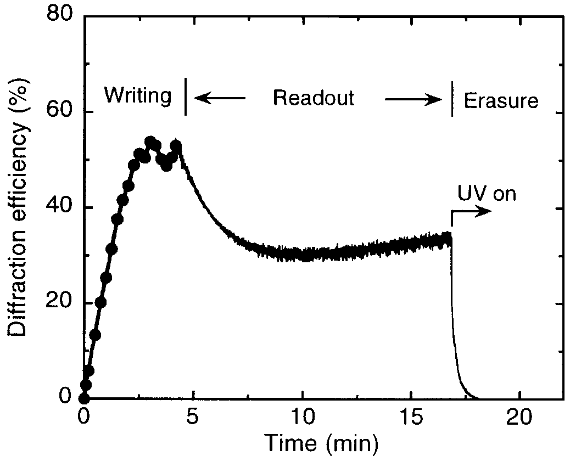

FIG. 3. Recording from the UV-exposed state (colored state). The grating is fast erased in the initial stage of readout because of the bleaching. After the bleaching is finished, the grating is decayed in a similar way to that observed in the uncolored case. Irradiation with UV can erase the grating fast by returning the crystal back to the original colored state. Total writing intensity is 800 mW/cm^2 at $\lambda = 532$ nm and $\Lambda = 0.936$ μm.

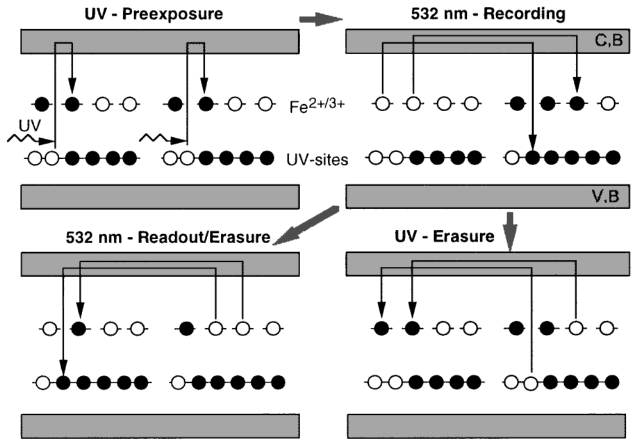

FIG. 5. A charge transfer model in codoped LiNbO$_3$.

readout, as shown in Fig. 3. Figure 4 shows the normalized decay characteristics during readout, measured after recording for different times. As the grating is recorded for a longer time, the initial decrease in diffraction efficiency becomes less and also the complete bleaching is finished in a shorter time. The grating written to the UV-sensitive sites decays faster than the other grating (or multiple gratings). Therefore, the decay behavior after complete bleaching will be similar to that observed from the uncolored state; i.e., it rises slightly at first and then decays ultimately to zero. Meanwhile, the crystal quickly responds to UV light and all trapped charges can be accessed by UV photon. Therefore, UV irradiation can erase all gratings fast at anytime during recording or readout, returning the crystal back to the original colored state. Figure 5 is the energy band diagram representing the expected charge transfer processes during preexposure, recording, readout, and erasure.

The dependencies of grating buildup and erasure on the total writing intensity are shown in Fig. 6. As the intensity decreased, the maximum efficiency obtained also decreased. This may be because the average trap concentrations in different sites are intensity dependent. As the bleaching rate is strongly dependent on the light intensity, it may also be partly responsible. Figure 6 also illustrates that the overall decay lifetime is greatly extended by decreasing the intensity. Recording at a high intensity and readout at a lower intensity can meet both of the desired characteristics, high diffraction efficiency and long decay time. Figure 7 shows the evolutions of diffraction efficiency during readout measured for two different reading intensities of $I_{\text{ref}} = 400$ mW/cm^2 (open circles) and 8 mW/cm^2 (filled circles), in both of which

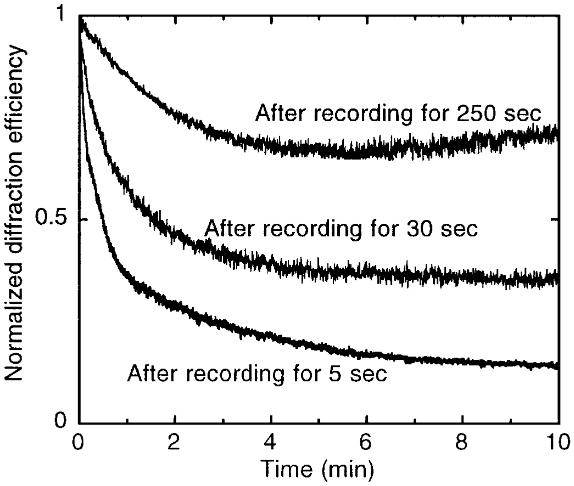

FIG. 4. Decay characteristics measured after recording for different times. Total recording intensity is 800 mW/cm^2.

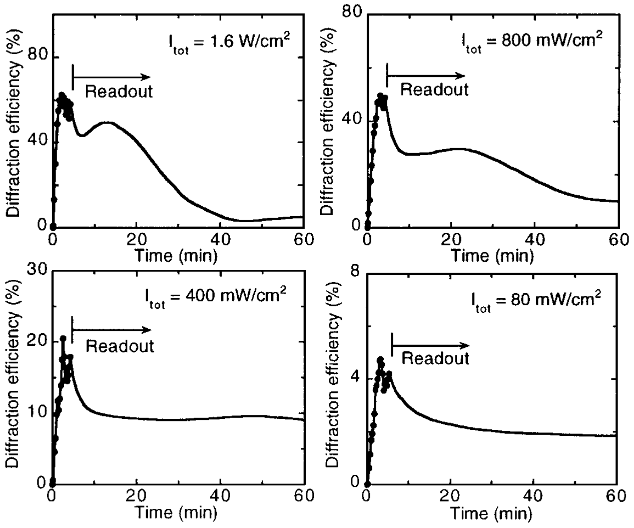

FIG. 6. The dependencies of grating buildup and erasure on the total writing intensity. In all cases, the crystal was preexposed to UV for 5 sec before recording. $\Lambda = 0.936$ μm.

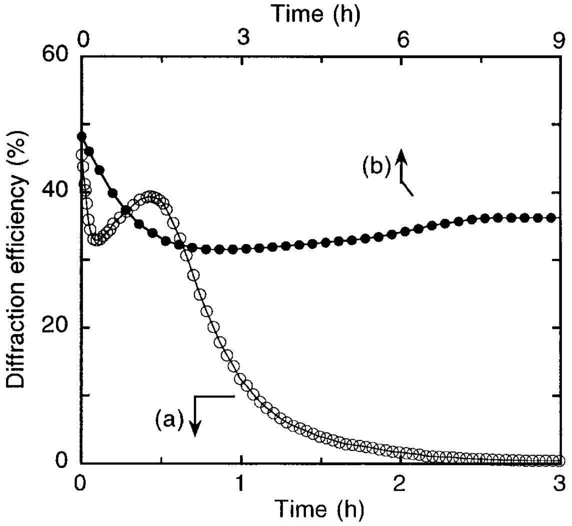

FIG. 7. Decay of grating vs reading intensity. (a) Measured with the reading intensity = 400 mW/cm^2; (b) measured with the reading intensity of 8 mW/cm^2. In both cases, the grating was recorded for 90 sec with a total writing intensity of $I_{\mathrm{ref}} = I_{\mathrm{obj}} = 400$ mW/cm^2.

the grating was recorded for 90 sec at the writing intensity of $I_{\mathrm{ref}} = I_{\mathrm{obj}} = 400$ mW/cm^2. While the grating decayed almost to zero in 2 h with a reading intensity of 400 mW/cm^2, it remained over a diffraction efficiency of 30% during 9 h of continuous readout when the reading intensity was reduced to 8 mW/cm^2. From the practical point of view, there is a low limit to the reading intensity which will depend on the number of bits per hologram, the number of holograms to be stored, and so on. At the reading intensity of 0.5 mW/cm^2 which is still sufficiently high, a continuous readout over a week is expected. This is very encouraging. In two-color recording, the gating beam not only aids the recording process but also plays a partial role in erasing the written grating. In the process described here, however, UV light is used for preexposure and erasure only. The absence of it during recording can thus give rise to a higher M number. In addition, all results presented here were obtained in an as-grown crystal without any reduction heat treatment. Therefore, holograms can be stored for quite a long time in the dark. The dark storage time was estimated to be over 2 yr at room temperature.

$LiNbO_3$ doped with Fe only, which was grown under the same conditions, showed similar behaviors to those observed in a codoped crystal. One fundamental difference is, however, that this Fe-doped $LiNbO_3$ did not reveal any noticeable photochromic effect, thereby lacking the capability of fast erasure by UV illumination. Our preliminary electron paramagnetic resonance studies of codoped $LiNbO_3$ were not successful in identifying the UV-sensitive absorption centers so far. More detailed optical and analytical analyses will be required. Nonetheless, the currently obtained results suggest that this photochromic double-doped $LiNbO_3$ might provide a significant breakthrough to the current material bottleneck of HDS.

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