High Resolution Study of Permanent Photoinduced Reflectivity Changes and Charge-Order Domain Switching in $Bi_{0.3}Ca_{0.7}MnO_3$

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We report near-field and far-field optical microscopic studies of photoinduced effects in charge-ordered $Bi_{0.3}Ca_{0.7}MnO_3$. Unlike previously reported transient photoinduced effects in manganites, we have observed permanent reflectivity changes following local sample illumination with 488 nm light. High-resolution images of exposed regions reveal optical contrast on a submicrometer scale. This observation indicates that photonic band-gap structures may be created using holographic recording in manganites. We also present images of photoinduced charge-order domain switching in $Bi_{0.3}Ca_{0.7}MnO_3$.

The perovskite-type manganese oxides $R_{1-x}A_x MnO_3$ (where R and A are trivalent rare- and divalent alkaline-earth ions, respectively) exhibit a rich variety of magnetic and electronic phenomena, such as colossal magnetoresistance (CMR), charge, and orbital ordering, etc., associated with strong coupling of lattice, charge, spin, and orbital degrees of freedom [1]. Application of modest external fields may drastically modify the state of such materials, e.g., induce an insulator to metal transition. This can be done with application of an external magnetic field as in the CMR effect [2], or with optical illumination, as was recently demonstrated [3]. Thus, a variety of new physics effects, as well as novel optoelectronic device concepts, are being constantly discovered.

A photoinduced insulator to metal transition is especially interesting from the point of view of creating photonic band-gap materials [4]. Inside a photonic band-gap region, optical modes, spontaneous emission, and zero point fluctuations are all absent, which makes such materials exhibit very unusual optical properties. A photonic band gap may appear in a three-dimensional photonic crystal (a material with periodic modulation of refractive index with a period on the order of the wavelength of light). The necessary condition for the photonic band gap to appear is high refractive index contrast (more than 2 to 1) within the photonic crystal. Creation of a photonic band-gap material is a very difficult task [5]. A three-dimensional hologram recorded in a photosensitive material (such as doped $BaTiO_3$ or $LiNbO_3$ perovskite-type oxides that exhibit a very prominent photorefractive effect) would be a very good solution, but normally the holograms have a very small refractive index contrast. Manganites may be very promising in this respect since small photoinduced variation of their properties could be "developed" by the applied magnetic field or by cooling down to low temperatures where the insulating and metallic states differ greatly in resistance and, hence, refractive index. Unfortunately, the photoinduced insulator to metal transition observed in [3] was not permanent. The lifetime of the photoinduced

metal regions in $Pr_{0.7}Ca_{0.3}MnO_3$ was of the order of a few microseconds unless the metallic state was stabilized by passing electric current (which changes the spatial distribution of photoinduced metal regions).

In this paper we report the first (to our knowledge) near-field optical microscopic studies of photoinduced effects in charge-ordered manganites. In our study we have used single crystals of $Bi_{0.3}Ca_{0.7}MnO_3$, which have a rather high temperature of charge ordering transition $T_{co} = 307$ K. Charge ordering in this and similar materials has been observed previously by neutron scattering, electron diffraction, and magnetic and transport measurements [6]. Unlike previously reported transient photoinduced effects in other manganites, we have observed permanent reflectivity changes following local sample illumination with $\lambda = 488$ nm light. High-resolution images of the exposed regions reveal fine optical contrast on a submicrometer scale. This observation opens up an exciting possibility of creating photonic band-gap structures using holographic recording in $Bi_{0.3}Ca_{0.7}MnO_3$. Such a development would lead to a material with a photonic band gap extremely sensitive to the external magnetic field and temperature.

The schematic view of our near-field optical experimental setup [7] is presented in Fig. 1. The experiments were conducted at room temperature so the $Bi_{0.3}Ca_{0.7}MnO_3$ sample was originally in the charge-ordered insulating state. The effects of local sample illumination with 488 nm light of an argon ion laser have been studied. The photon energy of such a laser is situated within a broad absorption line centered at about 3.5 eV that can be associated with charge-transfer transitions between oxygen $2p$ and manganese $3d$ states [6]. The beam from the laser was coupled into a single-mode optical fiber, which was tapered to form a 50 nm diameter uncoated tip. The microscope tip was attached to a piezotube that scanned it over the $Bi_{0.3}Ca_{0.7}MnO_3$ sample surface while keeping the tip-sample distance constant by means of shear force feedback. The sample topography was measured with nanometer
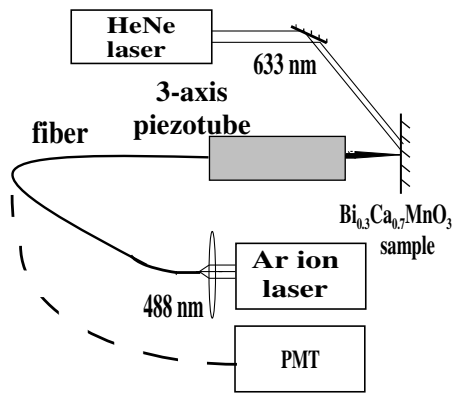
FIG. 1. Schematic view of our near-field optical experimental setup.

resolution by recording the feedback signal. The sample was illuminated from the side by weak nonresonant 633 nm light from a HeNe laser. The 633 nm light reflected by the sample surface was collected by the microscope tip and directed to a photomultiplier (PMT) by the same fiber. This was done before and after local sample exposure to 488 nm light through the microscope tip by switching the free end of the fiber from the argon ion laser to the PMT. Thus, simultaneous measurements of the sample topography and surface reflectivity at 633 nm were performed.

The results of such an experiment are presented in Fig. 2. In this experiment the microscope tip was initially positioned in the center of the field of view, and the sample was exposed for 5 s to about 30 mW of 488 nm light through the microscope tip. A substantial increase in the optical reflectivity at 633 nm has been detected within the illuminated area [compare Figs. 2(a) and 2(b)]. This is consistent with the local photoinduced insulator to metal transition, since metallic regions have higher optical reflectivity. The geometry of the produced irradiation pattern is consistent with the complicated field distribution of an uncoated fiber tip (which is caused by the interference of multiple modes at the end of the tapered region). In this experiment an uncoated tip was selected intentionally in order to produce higher illumination intensities and to study the feasibility of holographic recording in manganites. The fact that photoinduced reflectivity changes are seen in the areas far from the tip position during the illumination indicate strong interaction of $Bi_{0.3}Ca_{0.7}MnO_3$ with 488 nm light. The topography of the sample remained flat and intact after the exposure [Fig. 2(c)]. The lifetime of the photoinduced reflectivity features was surprisingly long. The reflectivity at any given point of the image changed by no more than 10% upon rescanning the same area after one hour (measurements beyond this time scale were limited by the long-term stability of our scanning microscope). Compared to the previously observed microsecond-scale lifetimes of the photoinduced effects in other manganites, the observed effect may be called
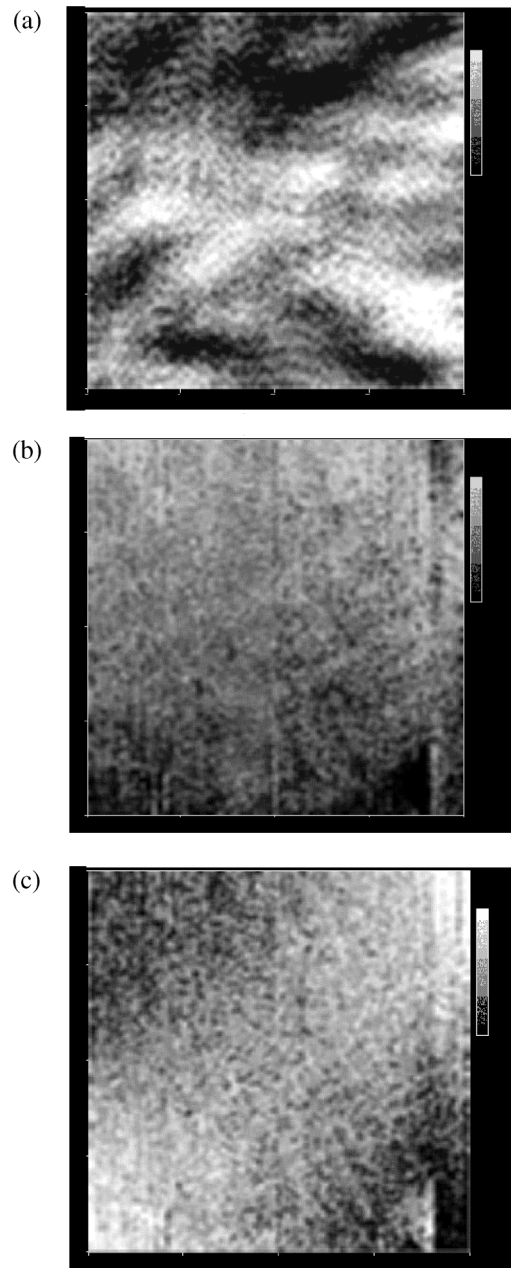

FIG. 2. 4 μm $\times$ 4 μm near-field optical microscope images of the sample topography (c) and reflectivity at 633 nm before (b) and after (a) sample exposure to 488 nm light through the tip of the microscope. A substantial increase in the local optical reflectivity after illumination is evident from the comparison of the optical images. The vertical scale in the topographical image (c) is 61 nm.

"permanent." Although the use of an uncoated tip does not guarantee the one-to-one correspondence between all the small features in the image and the actual pattern of photoinduced changes in the sample, Fig. 2(a) provides reliable evidence that features as small as fractions of a micrometer can be permanently recorded.

More regular photoinduced patterns on the surface of $Bi_{0.3}Ca_{0.7}MnO_3$ were observed after far-field illumination

through a combination of a diffraction grating and a 20× microscope objective, which produces an illumination pattern consisting of parallel interference stripes. Near-field images of such an irradiated area are presented in Fig. 3. A periodic pattern of photoinduced reflectivity changes with a ~2 μm period (which reproduces the pattern of far-field illumination) has been observed in the optical image [Fig. 3(b)], while no periodic modulation of the sample topography has been detected [Fig. 3(a)]. This result further supports the feasibility of holographic recording in manganites.

An important issue in producing volume holograms is the penetration depth of the visible light into the bulk of

(a)

(b)

FIG. 3. 4 μm × 4 μm near-field optical microscope images of the sample topography (a) and reflectivity at 633 nm (b) after sample exposure to 488 nm light through a combination of a diffraction grating and a microscope objective.

$Bi_{0.3}Ca_{0.7}MnO_3$ samples. Previous measurements of the optical constants of $Bi_{0.3}Ca_{0.7}MnO_3$ and similar materials [6,8] gave the following numbers for the real and imaginary parts of the dielectric constant at 488 nm: $\epsilon_1 \sim 8$, $\epsilon_2 \approx \sigma/\omega\epsilon_0 \sim 1.5$, where σ is the optical conductivity. Visible light penetrates into $Bi_{0.3}Ca_{0.7}MnO_3$ over a rather short distance L, given by the following expression:

$$L = 1/(\mathrm{Im}k) \approx \frac{\epsilon_1^{1/2}\lambda_0}{\pi\epsilon_2}, \qquad (1)$$

where $\mathrm{Im}k$ is the imaginary part of the wave vector in $Bi_{0.3}Ca_{0.7}MnO_3$, and λ_0 is the wavelength of light in vacuum. At 488 nm, $L \approx 300$ nm. But this distance is still substantially larger than the characteristic period of a volume hologram inside the material $\lambda/2 = \lambda_0/2\epsilon_1^{1/2} \approx$ 87 nm. In a thin film geometry when both sides of the film may be exposed through a transparent substrate, the total thickness of volume hologram may be of the order of $2L \approx 600$ nm. Thus, one may realistically expect recording of approximately ten periods of the photonic crystal structure over the depth of the material. This should be enough for the observation of photonic band-gap effects. The refractive index contrast of the volume hologram may be affected by the external magnetic field or by temperature variations. This would be very attractive in photonic device applications.

More evidence of the strong interaction of $Bi_{0.3}Ca_{0.7}$-MnO_3 with 488 nm light is the observed photoinduced charge-order domain switching discussed below. The charge-order domain structure of $Bi_{0.3}Ca_{0.7}MnO_3$ (due to the possibility of two perpendicular orientations of the Mn^{3+} and Mn^{4+} charge stripes in the lattice of $Bi_{0.3}Ca_{0.7}$-MnO_3) is easy to visualize using cross-polarized microscopy [9]. Using this technique, we were able to detect the photoinduced charge-order domain creation, and to observe real-time domain dynamics using *in situ* excitation with weakly focused 488 nm light. The results of this experiment are presented in Fig. 4.

A sample area showing enough surface topographical defects (such as a dark horizontal linear feature seen in every frame in Fig. 4, which provides a reference point) has been selected. The laser shutter has been opened and shut for about a second to provide brief local surface illumination, as seen in Fig. 4(a) (the irradiation pattern was elongated because of the small illumination angle). Immediately after the exposure, a charge-order domain wall has been created in the middle of the field of view [Fig. 4(b)]. After the laser beam was shut, the domain wall (seen as a vertical boundary of lighter and darker areas in the images) moved to the left of the field of view until it was stopped (pinned) by a large surface defect on the left side of the field of view [Figs. 4(j) and 4(k)]. The sample was placed on a hot plate which allowed us to visualize the melting of the domain structure [Fig. 4(l)] after heating the sample just above the T_{co} temperature. The described behavior was highly reproducible in any given location on

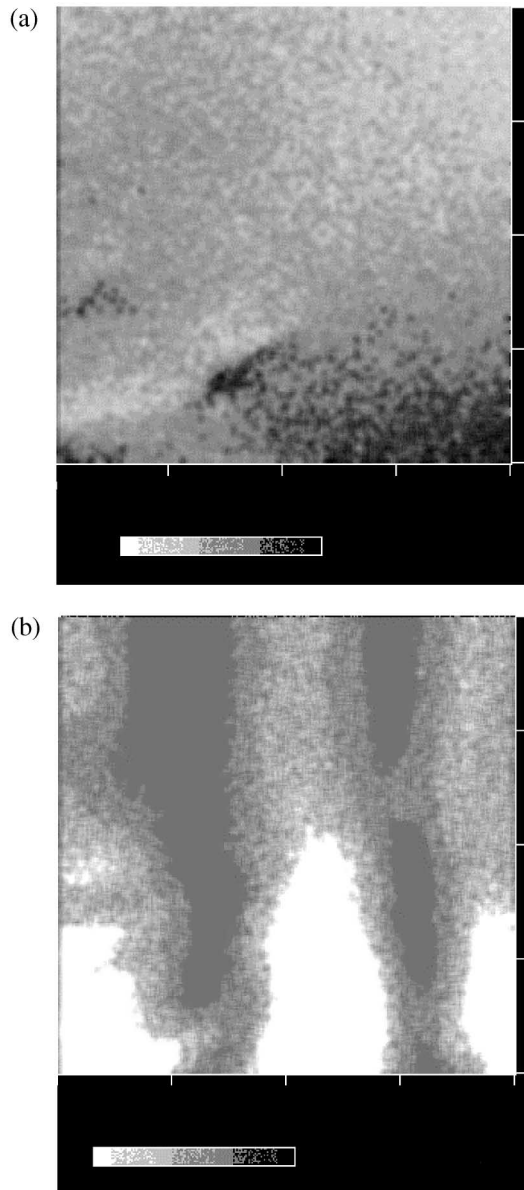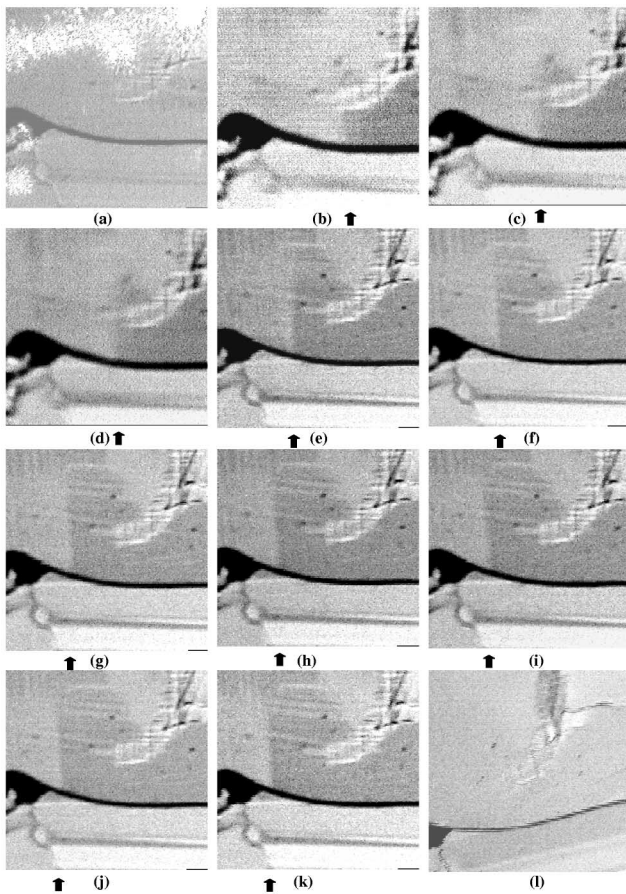FIG. 4. A series of frames captured from the movie showing photoinduced charge-order domain creation, domain wall motion and pinning by a surface defect, and melting of the charge order by heating the sample from room temperature to just above $T_{co} = 307$ K. The position of the photoinduced domain wall (seen as a vertical boundary of lighter and darker areas) is indicated by an arrow in each frame. The movie was shot at five frames per second. The size of each frame is (50×50) μm^2. The order numbers of the frames are 35 (a), 39 (b), 43 (c), 45 (d), 49 (e), 52 (f), 56 (g), 59 (h), 65 (i), 70 (j), and 93 (k). Frame (l) was taken after heating the sample above T_{co}.

the sample. A possible explanation of this effect is related to the fact that 488 nm laser light excites charge-transfer transitions between oxygen $2p$ and Mn $3d$ states. These transitions induce strong perturbations into the periodic arrangement of the Mn^{3+} and Mn^{4+} ions in the charge-ordered state. This photoinduced disorder may lead to charge-order domain switching and cause a domain wall formation. Photoinduced ferroelectric domain switching

have been observed previously in the doped $BaTiO_3$ and $LiNbO_3$ perovskite-type oxides that exhibit a pronounced photorefractive effect [10]. This is an encouraging analogy to the behavior of manganese oxides, although the charge distribution and lattice distortions in the charge-ordered state of manganites resembles an antiferroelectric state. Besides showing strong coupling of charge order with light, our images indicate a possible influence of the domain dynamics on the actively discussed fast and slow transient photoinduced reflectivity changes in manganites.

In conclusion, our high spatial resolution images of photoinduced effects in charge-ordered $Bi_{0.3}Ca_{0.7}MnO_3$ reveal fine optical contrast on a submicrometer scale. This observation opens the possibility of creating photonic band-gap structures using manganite materials. Such a development would lead to a material with a photonic band gap extremely sensitive to the external magnetic field and temperature. Microscopic images of photoinduced charge-order domain switching in $Bi_{0.3}Ca_{0.7}MnO_3$ constitute additional evidence of this material's strong interaction with light.

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