

Photoinduced resistivity changes in $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ thin films

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We report charge-ordered $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ thin films with charge-ordering temperature near room temperature, and observation of large photoinduced resistivity changes in these films associated with melting of the charge ordering by visible light. Films grown under small compressive strain exhibit the largest photoinduced resistivity changes. The lifetime of the photoinduced low-resistance state is on the order of half a minute. These photoinduced resistivity changes in thin films of $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ make them very promising for photonic device application. © 2005 American Institute of Physics. [DOI: 10.1063/1.1868869]

Doped rare-earth manganites $R_{1-x}A_x\text{MnO}_3$ (R being a trivalent rare-earth and A being a divalent alkaline-earth ion) exhibit a large diversity in electronic, magnetic, and orbital states due to the complex interplay of the corresponding degrees of freedom. One of the most intriguing properties of manganites is charge ordering (CO), wherein holes are localized at fixed positions of the Mn^{4+} ions.¹⁻⁴ Application of magnetic field, electric field, or electromagnetic wave irradiation drastically modifies the charge-ordered state, inducing an insulator-to-metal transition.^{2,5-7} A photoinduced insulator-to-metal transition in manganese oxides is especially interesting from the point of view of creating photonic band-gap materials,^{8,9} which allow control of dispersion and propagation of light. One can anticipate that a high refractive index contrast between the photoinduced conducting and insulating phases of CO manganites would be sufficient for development of a photonic crystal material. Once created, such a material would be quite unusual, since its properties could be easily tuned by application of a modest electric or magnetic field. In addition, since conductive properties, and therefore optical contrast, of the CO manganites are very sensitive to temperature, one could expect the development of rewritable photonic devices.

Recently, we observed permanent photoinduced reflectivity changes in a charge-ordered $\text{Bi}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$ single crystal,¹⁰ and demonstrated that this phenomenon can be potentially used for creation of various photonic crystal materials. However, since visible light penetrates into the bulk of this material only to a depth of about 300 nm,¹⁰ thin films of $\text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3$ with CO at room temperature are necessary for photonics applications. Preparation of such thin films presents quite a few challenges, since as a rule, thin-film properties differ from the properties of bulk material due to strain effects, changes in the magnetic and electron transport properties, etc.

The main results of this work is the first preparation of charge-ordered $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ thin films with CO tempera-

ture near room temperature, and observation of large photoinduced resistivity changes in these films. This development became possible due to the key role of strain on the photo-sensitivity of thin $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ films. It opens real possibilities for photonics device applications of these materials.

Thin films were grown by the pulsed-laser deposition technique from a polycrystalline target with nominal composition of $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$. The substrates used were [100] LaAlO_3 (LAO), which has a pseudocubic crystallographic structure with $a=3.79$ Å, and [100] SrTiO_3 (STO) with $a=3.905$ Å of a cubic structure. The laser energy density on the target was about 1.7 J/cm², and the deposition rate was 10 Hz. The LAO and STO substrates were kept at a constant temperature of 800 °C during the deposition. The deposition was carried out at a pressure of 400 mTorr of flowing oxygen. After deposition, the samples were slowly cooled to room temperature at a pressure of 400 Torr of oxygen. $\theta/2\theta$ scans show that films are epitaxial and single phase. The width of rocking curves, 0.04° for films grown on LAO and 0.3° for films grown on STO, shows good crystallinity of these films. Direct current resistivity was measured by a four-probe method. For sample illumination we used a continuous argon laser with 514, 488, 476, and 457 nm wavelengths, which has power of 150 mW in multiline mode.

Bulk $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ has a CO temperature of 330 K.¹¹ At the CO transition, the temperature dependence of the resistivity has a kink (a change in derivative) accompanied by a peak in the temperature dependence of magnetization.¹¹ Our target material has similar properties: the CO temperature (T_{CO}) is 333 K, as indicated by the temperature dependence of the resistivity (Fig. 1) and by a peak in the temperature dependence of magnetization (not shown).

The rise in resistivity at the CO temperature in thin films is not as sharp as observed in the bulk material, as was noted previously for the charge-ordered thin films of a different composition.¹² The CO temperature for thin films on LAO is lower than for the bulk: $T_{\text{CO}}=274$ K for 120-nm-thick film and 256 K for 40 nm. On the contrary, the films grown on STO have CO temperature $T_{\text{CO}}=347$ K, which is higher than

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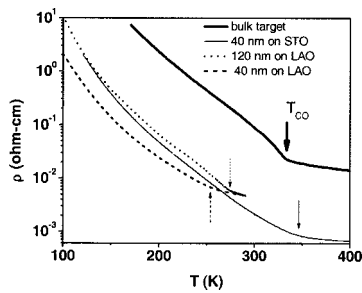


FIG. 1. Temperature dependence of resistivity of $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ polycrystalline target and thin films of different thicknesses grown on LAO and STO substrates. The CO temperatures are indicated with the arrows.

the T_{CO} of the bulk material. Our preliminary resonant and nonresonant x-ray scattering measurements on these films detected peaks associated with charge ordering below CO temperatures, consistent with the resistivity measurements.¹³ Such significant difference in CO temperatures for thin films grown on different substrates indicates the large effect of substrate-induced strain in thin films of $\text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3$. The lattice parameters of LAO and STO are 3.79 and 3.905 Å respectively, while corresponding lattice parameter for $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ is $V^{1/3} = 3.81$ Å.¹⁴ Therefore, films grown on LAO have small compressive strain, while films grown on STO are under tensile strain. Previously reported studies of charge-ordered $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ thin films of different thicknesses on STO and LAO do not show any significant difference in T_{CO} for films of different thicknesses or grown on different substrates.^{12,15} A detailed study of strain effects on CO in $\text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3$ films will be published elsewhere.¹⁶

Light-induced resistivity changes in $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ thin films are shown in Fig. 2. For this experiment we used a four-in-line electrical contact configuration, as shown in [Fig. 2(a) inset]. The distance between voltage contacts was approximately 0.3 mm. The space between voltage contacts was illuminated with full power (150 mW) multiwavelength (514, 488, 476, and 457 nm) argon laser light. The laser beam was slightly focused with a 100 mm focal length lens, producing an illuminated region on the sample of approximate diameter of 0.05 mm and power density at the illuminated region of approximately 5×10^4 W/cm².

When the 40 nm film grown on STO was illuminated with argon laser light, its resistivity decreased approximately by a factor of 2 [Fig. 2(a)]. This change persisted up to 295 K with laser light on. The photoinduced resistivity change was not studied at higher temperature, since we do not have an optical access in the high temperature setup. When the illumination was switched off, the resistivity of the sample returned to its previous value [Fig. 2(a)]. A much more striking effect was observed for the 40 nm film grown on LAO. When this film was illuminated, its resistivity decreased by about one order of magnitude, almost returning to the value of resistivity for temperatures above the CO transition [Fig. 2(b)]. These data were taken while the sample temperature was ramped up at a rate of 2 K/min. This allows us to notice that the resistivity decreases rather slowly under illumination, and also returns slowly to its higher value, when the light is switched off [Fig. 2(b)]. This photoinduced change persists up to the CO temperature (256 K). This indicates that the observed photoinduced resistivity change is associated with melting of the CO.

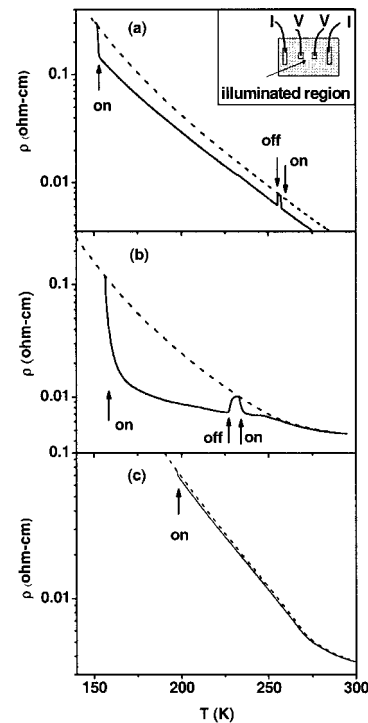


FIG. 2. Photoinduced resistivity changes for $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ thin films: (a) 40 nm on STO, (b) 40 nm on LAO, and (c) 120 nm on LAO. Inset shows experimental current and voltage contact configuration with respect to the illuminated region. All temperature dependencies are taken on warming. Temperature dependencies of resistivity without illumination are shown with the dashed line. Solid line represents temperature dependencies of resistivity of illuminated samples. Arrows indicate the temperatures at which laser light was switched on or off.

Thicker films (120 nm on LAO and STO) exhibit a much smaller photoinduced effect. The result for a 120 nm on LAO is shown in Fig. 2(c). Such a remarkable change in the photoinduced effect for films of different thicknesses suggests that the substrate induced strain plays a significant role in properties of the charge-ordered thin films of $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$. It appears that in thinner films, which are more strained, the charge ordering is weaker, or less stable, and therefore more susceptible to the argon laser light illumination, than that for thicker, more relaxed films, which exhibit very small photoinduced resistivity changes. The influence of strain on the CO of thin films was reported previously.^{14,15,17-19} It was noted that the CO in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ thin films grown on STO and LAO was destroyed by the application of a much weaker magnetic field than that required for a bulk material of the same composition.^{15,17} However, thinner films of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ were less susceptible to the influence of magnetic field than thicker films,¹⁵ while our results show that the CO in thinner films of $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ can be more easily destabilized by light than that in thicker films. CO transition in bulk $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ is accompanied by a structural transition, which leads to a sharp increase of lattice parameters a and c ($a=c$) and a sharp decrease of lattice parameter b .¹² Such changes provide lattice distortion necessary for existence of the CO phase. They are typical for all the CO materials.^{1,2} Compressive strain should reduce in-plane lattice parameters (a and c) in films grown on LAO resulting in smaller lattice distortion, which could make the CO weaker in these samples. On the other hand, tensile strain provided by STO substrate should increase in-plane lattice parameters, result-

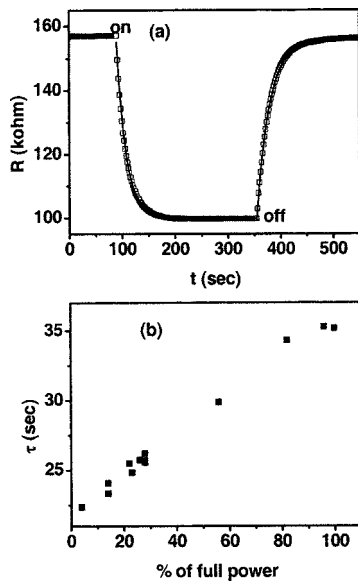


FIG. 3. (a) Time dependence of resistance of a 40 nm $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ film on LAO at $T=100$ K with 29% of full laser power switched on and off. Solid lines are fits to the exponential time dependence $\Delta R \propto \exp(-t/\tau)$. (b) Dependence of the time constant τ on intensity expressed as a percent of full laser power for the relaxation process after light was switched off at $T=100$ K.

ing in larger distortion, which does not contradict the distortion typical to the CO. However, a detailed x-ray study on these films is needed in order to confirm this hypothesis. Such studies are currently being conducted.¹³

Usually, it is difficult to separate heat-induced effects from light-induced effects in such studies, since the laser beam has significant power. However, in our case, we can give an upper limit for the estimated light-induced heating in our experimental setup. Since experimental conditions were identical for all studied films, we presume that the heating effects are identical also. Therefore, the maximal heat-induced effect can be estimated from Fig. 2(c), if we assume that the light-induced resistivity change in this case is caused by heating only. This upper limit estimate gives a change in temperature of about 1–1.5 K. The large photoinduced resistivity changes shown in Figs. 2(a) and 2(b) cannot be explained by such minute heating.

Another interesting feature of the observed photoinduced resistivity changes in the 40 nm $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ thin film on LAO is the relatively long lifetime of the photoinduced low-resistance state. Figure 3(a) shows the relaxation behavior of the resistance at 100 K after illumination was switched on or off. These time dependencies can be fitted to the exponential law: $\Delta R \propto \exp(-t/\tau)$. The relaxation time was measured in temperature interval from 100 to 210 K. The relaxation time decreases when temperature increases. Such behavior is natural, since thermal fluctuations (which grow with temperature) should be responsible for the relaxation into the charge-ordered ground state. Relaxation times τ are of the order of half a minute. This effect is drastically different from photoinduced resistivity changes reported for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ single crystals^{5,20} and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ thin films,⁶ where time scales were of the order of tens of microseconds. The lifetime of the photoinduced low-resistance state increases with the increase in intensity of the light [Fig. 3(b)], which is promising for photonic device applications.

This increase in the relaxation time with intensity is in agreement with our previous results,¹⁰ where for much higher power density (approximately 5×10^6 W/cm²), permanent (more than 1 h) photoinduced optical reflectivity changes were observed.

In conclusion, we have developed charge-ordered $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ thin films with CO temperature near room temperature. We have observed large photoinduced resistivity changes in these films associated with melting of the CO by visible light with wavelength around 500 nm. The substrate-induced strain makes the CO less stable and more susceptible to breakdown by illumination with visible light. Thus, thinner films grown on different substrates exhibit a larger drop in resistivity under illumination than do thicker films. The largest photoinduced resistivity changes were observed for thin, 40 nm, films grown under small compressive strain (on LAO). The lifetime of the photoinduced low-resistance state is of the order of half a minute and increases with intensity. Reported photoinduced resistivity changes in thin films of $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ make this material very promising for photonic device application.

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