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## Room temperature optical anisotropy of a LaMnO<sub>3</sub> thin-film induced by ultra-short pulse laser

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We observed ultra-short laser pulse-induced transient optical anisotropy in a LaMnO<sub>3</sub> thin film. The anisotropy was induced by laser pulse irradiation with a fluence of less than 0.1 mJ/cm<sup>2</sup> at room temperature. The transmittance and reflectance showed strong dependence on the polarization states of the pulses. For parallel and perpendicular polarization states, there exists a difference of approximately 0.2% for transmittance and 0.05% for reflectance at 0.3 ps after the irradiation with a pump pulse, respectively. The theoretical values for optical transmittance and reflectance with an assumption of an orbital ordering of 3d *e<sub>g</sub>* electrons in Mn<sup>3+</sup> ions showed good agreement with the experimental results, demonstrating that the transient optical anisotropy in LaMnO<sub>3</sub> thin film is due to the photo-induced symmetry-breaking of orbital ordering in excited states. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4914094>]

Optically anisotropic materials exhibit different optical reflectance and transmittance depending on the polarization state of incident light. The anisotropy arises from the non-transient and inherent broken symmetry of the lattice. However, if the anisotropy is transient and can be induced by ultra-short laser pulses within a picosecond time scale, it has great potential to be used as detectors, switches, and recording devices that operate at extremely high speeds.

Photo-induced changes in the reflectance or transmittance of complex transition metal oxides have been previously observed.<sup>1–3</sup> In particular, optical birefringence was found in a charge-orbital ordered manganese oxide, La<sub>0.5</sub>Sr<sub>1.5</sub>MnO<sub>4</sub>.<sup>4</sup> The birefringence was attributed to the melting of the charge-orbital ordered state as a result of strong perturbation by an external light field. Such an intriguing phenomenon may allow for potential applications for the material. However, since the phenomenon was observed at a very low temperature (20 K) and under relatively strong light fluence ( $\geq 2$  mJ/cm<sup>2</sup>), device application of this material is impractical.

In this letter, we report that the ultra-short laser pulse induces anisotropic polarization dependence of the transmittance and reflectance of a LaMnO<sub>3</sub> thin film grown on a SrTiO<sub>3</sub> substrate. The experiment was carried out at room temperature, and the laser pulse fluence required for the photo-induced anisotropy was less than 0.1 mJ/cm<sup>2</sup>. A numerical simulation based on a simple Hubbard model suggests that the laser pulse causes the anisotropy through symmetry change in the Mn *e<sub>g</sub>* electron orbital state.

We also present the polarization-dependent transmittance and reflectance of a Nd<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> thin film grown on a SrTiO<sub>3</sub> substrate for comparison. A Nd<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> thin film has the chemical composition and lattice structure similar to those of LaMnO<sub>3</sub> thin film. In Nd<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub>, Mn *e<sub>g</sub>* orbitals are optically active and known to form a charge-orbital ordering at a low temperature (<150 K).<sup>5</sup> However, the orbitals of Nd<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> become disordered at room temperature, while the orbitals of LaMnO<sub>3</sub> remain ordered. The comparison between LaMnO<sub>3</sub> thin film and Nd<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> thin film was performed to clarify the role of orbital ordering in the laser pulse-induced anisotropy of LaMnO<sub>3</sub> thin film.

The LaMnO<sub>3</sub> thin film was grown epitaxially by pulsed-laser deposition on a double-side polished single-crystal SrTiO<sub>3</sub> (001) substrate. The thickness of the thin film was about 100 nm,<sup>6</sup> and the structural properties and linear optical conductivity were reported in previous studies.<sup>7–9</sup> The Nd<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> thin film was also grown epitaxially using the same technique on a double-sided polished single-crystal SrTiO<sub>3</sub> (001) substrate. The growth conditions and physical properties of Nd<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> thin film were determined in a previous study.<sup>10</sup> For the pump-probe measurement, laser pulses were generated from a custom-built mode-locked Ti:sapphire oscillator, and the center wavelength of the pulse was 800 nm (1.5 eV) with a pulse duration of 10 fs. The pulse energy was about 1.5 nJ at a repetition rate of 140 MHz. The bandwidth of the laser pulse is shown in Fig. 1. The details of the laser pulse used in this study can be found in a previous report.<sup>11</sup>

The laser beam was split into a pump beam (~80% of the total pulse energy), a probe beam (~10%), and a

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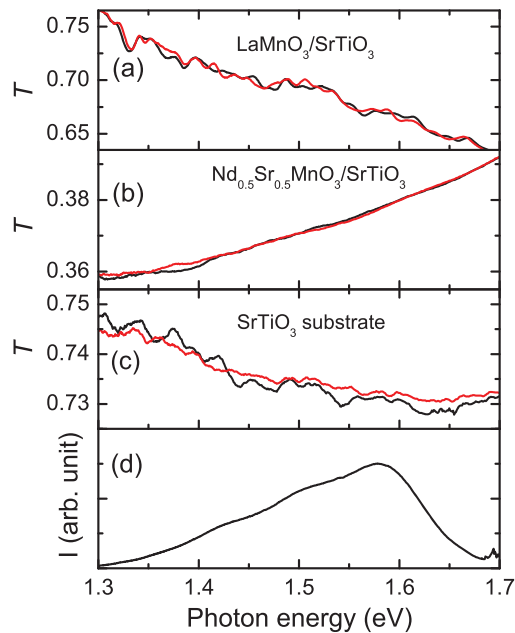


FIG. 1. Transmittance ( $T$ ) of (a) a  $\text{LaMnO}_3$  thin film grown on a  $\text{SrTiO}_3$  substrate, (b) a  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  thin film grown on  $\text{SrTiO}_3$ , and (c) a  $\text{SrTiO}_3$  (001) substrate at different electric field polarizations. Black (red) lines represent the data for light polarization parallel (perpendicular) to the  $\text{SrTiO}_3$  substrate [100] direction. (d) The intensity profile of the laser pulse used in the pump-probe experiment.

reference beam ( $\sim 10\%$ ). The pump and probe beams were focused on the surface of the sample with a diameter of about  $100\ \mu\text{m}$ . The pump beam was normally incident to the sample surface, and the angle between the probe beam and the surface normal was approximately  $8^\circ$ . The transmitted or reflected probe beam was detected with a photodiode, and the temporal coincidence between the probe and pump pulses was determined using the sum frequency signal. The zero-time-delay was defined at the time delay point where the sum frequency signal was the strongest. The transmittance and reflectance were measured by comparing the probe beam with the reference beam. When the pump pulse was blocked, the reference beam intensity was tuned to be the same as that of the probe beam. The reference beam intensity was fixed during the measurement. The intensity change of the transmitted or reflected probe beam due to the pump beam irradiation was obtained as transmittance change ( $\Delta T$ ) or reflectance change ( $\Delta R$ ), respectively. All experiments were conducted at room temperature.

Figure 1(a) shows the polarization-dependent transmittance ( $T$ ) of a  $\text{LaMnO}_3$  thin film measured using a conventional optical spectrometer. The  $T$  of the electric field polarization ( $E$ ) parallel ( $\parallel$ ) to the [100] direction of the  $\text{LaMnO}_3$  film is identical to that of  $E \parallel$  [010], within experimental error, indicating that  $T$  was isotropic. The  $T$  of a  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  thin film grown on a  $\text{SrTiO}_3$  (001) substrate (Fig. 1(b)) and of a  $\text{SrTiO}_3$  (001) substrate (Fig. 1(c)) are shown for comparison and are also isotropic.

Figure 2 shows the change in transmittance,  $\Delta T$ , induced by the pump pulse as a function of time delay ( $\tau$ ) between the pump pulse and the probe pulse. The sharp features around the zero-time-delay ( $\tau = 0$ ) are due to artifact,<sup>12</sup> and

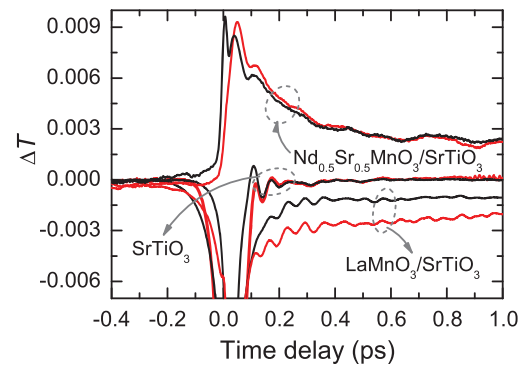


FIG. 2. Pump-probe transmittance changes ( $\Delta T$ ) in thin films and  $\text{SrTiO}_3$  substrate. Black and red lines correspond to the probe polarization ( $E$ ) parallel ( $\parallel$ ) and perpendicular ( $\perp$ ) to the pump polarization, respectively.

the exponential decrease (or increase) at a finite  $\tau$  is due to charge excitation and relaxation processes.

Laser pulse-induced transmittance change in  $\text{LaMnO}_3$  film is not isotropic, exhibiting transient anisotropy. The probe pulse polarization is modulated in order to investigate the polarization dependence of the finite  $\tau$  response. The pump pulse polarization is maintained along the [100] direction of the  $\text{SrTiO}_3$  substrate, and the probe pulse polarization is varied parallel and perpendicular to the pump pulse polarization. The  $\Delta T$  of the two probe pulse polarizations is the same before the pump pulse irradiation ( $\tau < -0.2$ ) but becomes different after the pump pulse irradiation ( $\tau > -0.2$ ). The difference is about 0.2% at 0.3 ps after pump pulse irradiation. The  $\Delta T$  of a  $\text{SrTiO}_3$  (001) substrate and a  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  thin film grown on a  $\text{SrTiO}_3$  (001) substrate are shown for comparison and do not show any significant differences.

Figure 3 shows the pump-probe reflectance changes ( $\Delta R$ ) of the  $\text{LaMnO}_3$  thin film. The  $\Delta R$  for the two polarizations is the same before pump pulse irradiation. After the pump pulse irradiation,  $\Delta R$  showed an abrupt increase, anisotropic response, and an exponential relaxation at later time delay. The difference between the two polarizations is about 0.05% at 0.3 ps after pump pulse irradiation.

It should be noted that the pump pulse-induced transient anisotropy is negligible for the  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  thin film and

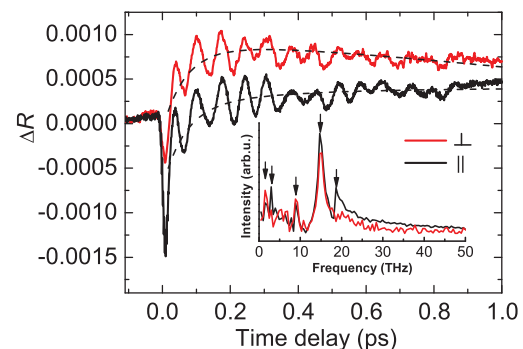


FIG. 3. Pump-probe reflectance changes ( $\Delta R$ ) in the  $\text{LaMnO}_3$  thin film. The black and red lines correspond to the probe polarization ( $E$ ) parallel ( $\parallel$ ) and perpendicular ( $\perp$ ) to the pump polarization, respectively. Dashed lines represent fitting lines for the exponential change in the background. Inset: Fourier transform of the data after subtracting the electronic background. Arrows mark the coherent phonon modes.

SrTiO<sub>3</sub> substrate. This suggests that the anisotropy is not due to the interface or the substrate but is an intrinsic property of the LaMnO<sub>3</sub> film. LaMnO<sub>3</sub> has a famous chessboard type orbital-ordered state, even at room temperature.<sup>13</sup> The orbital ordering temperature for a single crystal is about 800 K, and the temperature is about 600 K for the thin film grown on SrTiO<sub>3</sub> substrate.<sup>14</sup> Orbital ordering is stable at room temperature, and the observed anisotropy originates from a similar mechanism to that suggested for La<sub>0.5</sub>Sr<sub>1.5</sub>MnO<sub>4</sub> below the charge/orbital ordering temperature.<sup>4</sup>

In addition to the anisotropy, an oscillating signal is observed as a result of coherent phonon oscillation.<sup>15,16</sup> The inset of Fig. 3 shows the Fourier transformations of the data after subtracting the exponentially changing background. Five modes are observed at 1.05, 2.74, 8.65, 14.47, and 18.11 THz. The frequencies and amplitudes of these modes are consistent with those in prior literature,<sup>15</sup> suggesting that the optical properties of the thin film sample are close to those of a single crystal. The modes at 1.05 and 2.74 THz are not observed in data of the single crystal. The origin of the 1.05 THz mode is not clear, while the 2.74 THz mode could be related to the La-ion oscillation observed in the resonant Raman scattering experiment.<sup>17</sup>

The relaxation behavior is slightly different from that observed in bulk LaMnO<sub>3</sub> single crystal.<sup>15</sup> Two exponential curves were sufficient for single crystal data fitting.<sup>15</sup> However, for the thin film, three exponential curves ( $\sum_{i=1}^3 C_i e^{-t/\tau_i}$ ) yielded a better fit. The relaxation time constants obtained from the fitting are  $\tau_1 \sim 60$  fs,  $\tau_2 \sim 0.3$  ps, and  $\tau_3 \sim 10$  ps.  $\tau_1$  can be attributed to electron-electron thermalization time and  $\tau_2$  to electron-phonon or orbital-phonon thermalization.  $\tau_3$  was not observed in bulk LaMnO<sub>3</sub>. This may be due to the thermal diffusion time from the sample to the substrate,<sup>18,19</sup> which slows the relaxation process in the thin film sample.

A microscopic model was established in order to understand the origin of the anisotropy in  $\Delta T$  and  $\Delta R$ . A quasi-two-dimensional two-orbital Hubbard Hamiltonian was numerically solved to obtain the time-dependent optical conductivity, and  $\Delta T$  and  $\Delta R$  were obtained from optical conductivity change. Details of the model and calculation can be found in a previous study.<sup>16</sup> Effects of multiple reflections at the interfaces are ignored to simplify the calculations. The energy relaxation from system to environment is not considered in the model; therefore the exponential decay can not be found in the simulated data.

Figures 4(a) and 4(b) show the calculated  $\Delta T$  and  $\Delta R$  from the model, respectively. The simulated data demonstrate clear anisotropy, qualitatively consistent with the experimental data. It is noteworthy that the anisotropy can be obtained only when the Mn-ion  $e_g$  orbital ordering ground state is assumed in our simulation, which suggests that the anisotropy is related to the spatial symmetry of the orbitals in the photo-excited states. The spatial symmetry of the ideal orbital ordered state prevents optical anisotropy. However, when the pump pulse excites the Mn-ion  $e_g$  electrons and generates holes and double-occupied sites with different orbital configurations, the symmetry can be broken, resulting in an anisotropic optical response for the probe pulse. A case

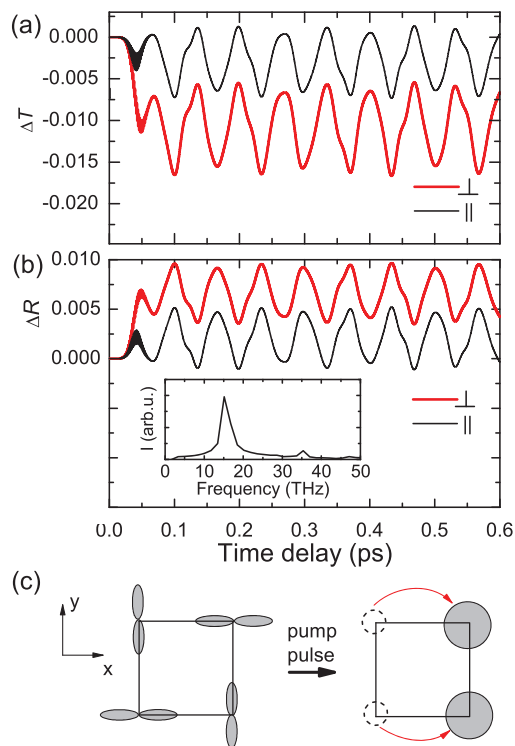


FIG. 4. (a) and (b) The thick red and thin black lines represent the theoretical optical transmittance change ( $\Delta T$ ) and reflectance change ( $\Delta R$ ) for the probe polarization ( $E$ ) parallel ( $\parallel$ ) and perpendicular ( $\perp$ ) to the pump polarization, respectively, as a function of the time delay between the pump and probe pulses. Inset of (b): Fourier transform of the  $\Delta R$  as a function of photon frequency. (c) An example of photo-excitation generated by a pump laser light. Left: ideal orbital ordered ground state of Mn  $e_g$  electron orbitals. One electron occupies one Mn-ion site. Spatial symmetry is conserved. Optical responses along the  $x$ - and  $y$ -axes are the same. Right: photo-excited state. Two holes and two double-occupied sites are generated by pump pulse. Spatial symmetry is broken. Optical responses along the  $x$ - and  $y$ -axes are different.

of the symmetry-broken pump pulse-induced photo-excited state is illustrated in Fig. 4(c).

The data also show oscillations caused by interference between the quantum states.<sup>16</sup> The inset of Fig. 4(b) shows the Fourier transform result. The strong peak around 15 THz was due to the Jahn-Teller  $Q_2$  phonon mode, and the weak peak around 35 THz was due to the phonon-orbital coupled excitation.<sup>16</sup> Other phonon modes observed in the experimental data are not considered in the calculation.

The simulation overestimates the anisotropy of transmittance and reflectance by factors of about 4 and 12, respectively. We can consider two possible origins of the overestimation. First is the small size (four-atom-cluster) of the model system. In the model, all electrons of four Mn atom sites should be excited by the laser field. This corresponds to a situation involving the much higher pump laser pulse fluence in the real experiment, which is different from our experimental condition. The second possibility is the discrepancy in the orbital ordering configuration between the model and real material. We assumed perfect spatial ordering of ideal  $3x^2 - r^2$  and  $3y^2 - r^2$  orbitals at 0 K. However, in real material, the orbital ordering may be different from the ideal case because of imperfections, high temperature, and substrate strain.



In conclusion, ultra-short laser pulse-induced optical anisotropy was observed in a LaMnO<sub>3</sub> thin film, and the anisotropy could be induced using a small laser pulse fluence (<0.1 mJ/cm<sup>2</sup>) at room temperature. This material can be potentially used for ultrafast optical switching devices. The theoretical model suggests that the anisotropy is related to the orbital ordering. Therefore, careful engineering involving the control of the substrate-induced strain or varying the chemical pressure can result in increased anisotropy. Also, further study is required to detect anisotropy at lower laser pulse fluencies.

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<sup>1</sup>K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, *Phys. Rev. Lett.* **78**, 4257 (1997).

<sup>2</sup>T. Ogasawara, T. Kimura, T. Ishikawa, M. Kuwata-Gonokami, and Y. Tokura, *Phys. Rev. B* **63**, 113105 (2001).

<sup>3</sup>R. I. Tobey, R. Prabhakaran, A. T. J. Boothroyd, and A. Cavalleri, *Phys. Rev. Lett.* **101**, 197404 (2008).

<sup>4</sup>R. Singla, A. Simoncig, M. Först, D. Prabhakaran, A. L. Cavalieri, and A. Cavalleri, *Phys. Rev. B* **88**, 075107 (2013).

<sup>5</sup>J. Herrero-Martín, J. García, G. Subías, J. Blasco, and M. C. Sánchez, *Phys. Rev. B* **70**, 024408 (2004).

<sup>6</sup>Z. Marton, S. S. A. Seo, T. Egami, and H. N. Lee, *J. Cryst. Growth* **312**, 2923 (2010).

<sup>7</sup>W. S. Choi, Z. Marton, S. Y. Jang, S. J. Moon, B. C. Jeon, J. H. Shin, S. S. A. Seo, T. W. Noh, K. Myung-Whun, H. N. Lee, and Y. S. Lee, *J. Phys. D: Appl. Phys.* **42**, 165401 (2009).

<sup>8</sup>W. S. Choi, D. W. Jeong, S. S. A. Seo, Y. S. Lee, T. H. Kim, S. Y. Jang, H. N. Lee, and K. Myung-Whun, *Phys. Rev. B* **83**, 195113 (2011).

<sup>9</sup>W. S. Choi, D. W. Jeong, S. Y. Jang, Z. Marton, S. S. A. Seo, H. N. Lee, and Y. S. Lee, *J. Korean Phys. Soc.* **58**, 569 (2011).

<sup>10</sup>S. Y. Jang, N. Nakagawa, S. J. Moon, T. Susaki, K. W. Kim, Y. S. Lee, H. Y. Hwang, and K. Myung-Whun, *Solid State Commun.* **149**, 1760 (2009).

<sup>11</sup>B. Tsermaa, B. K. Yang, J. S. Kim, and K. Myung-Whun, *Opt. Commun.* **284**, 1955 (2011).

<sup>12</sup>P. Munkhbaatar, N. Nakagawa, H. Y. Hwang, J. S. Kim, and K. Myung-Whun, *Solid State Commun.* **152**, 1541 (2012).

<sup>13</sup>Y. Murakami, J. P. Hill, D. Gibbs, M. Blume, I. Koyama, M. Tanaka, H. Kawata, T. Arima, Y. Tokura, K. Hirota, and Y. Endoh, *Phys. Rev. Lett.* **81**, 582 (1998).

<sup>14</sup>J. H. Song, J. H. Park, K.-B. Lee, J. M. Lee, and Y. H. Jeong, *Phys. Rev. B* **66**, R020407 (2002).

<sup>15</sup>S. Wall, D. Prabhakaran, A. T. Boothroyd, and A. Cavalleri, *Phys. Rev. Lett.* **103**, 097402 (2009).

<sup>16</sup>P. Munkhbaatar and K. Myung-Whun, *J. Mod. Opt.* **61**, 197 (2014).

<sup>17</sup>M. N. Iliev, M. V. Abrashev, H. G. Lee, V. N. Popov, Y. Y. Sun, C. Thomsen, R. L. Meng, and C. W. Chu, *Phys. Rev. B* **57**, 2872 (1998).

<sup>18</sup>E. Beaurepaire, J. C. Merle, A. Daunois, and J. Y. Bigot, *Phys. Rev. Lett.* **76**, 4250 (1996).

<sup>19</sup>H. Tamaru, K. Ishida, N. Ogawa, Y. Kubo, and K. Miyano, *Phys. Rev. B* **78**, 075119 (2008).