4th International Conference Photoinduced Phase Transitions and Cooperative Phenomena, Wrocław 2011

Femtosecond Reflection Spectroscopy in $La_{1.5}Sr_{0.5}CoO_4$

T. Egawa[a], Y. Okimoto[a,*], R. Fukaya[a,b], K. Onda[c], T. Ishikawa[a], S.-Y. Koshihara[a,b], A. Isayama[d] and T. Sasagawa[d]

[a]Department of Materials Science, Tokyo Institute of Technology, Megro-ku, Tokyo 152-8551, Japan

[b]CREST, JST, Meguro-ku, Tokyo 152-8551, Japan

[c]Department of Environ. Chem. and Engineering, Tokyo Institute of Technology
4259 Nagatsuta, Yokohama, 226-8503 Japan

[d]Materials and Structures Laboratory, Tokyo Institute of Technology
4259 Nagatsuta, Yokohama, 226-8503 Japan

Ultrafast optical response has been investigated using fs laser system on a perovskite-type cobalt oxide, $La_{1.5}Sr_{0.5}CoO_4$. After the photoirradiation at room temperature, the time profile of relative change of reflectance ($\Delta R/R$) shows a sudden change within the pulse duration (≈ 150 fs) and decays with a lifetime of ≈ 330 fs. The sign of $\Delta R/R$ after the photoexcitation is positive in the mid-infrared region (at 0.50 eV) while negative in the visible energy region (at 2.0 eV), implying photoinduced change of the electronic structure after the photoexcitation.

PACS: 78.47.J−, 78.47.jg

1. Introduction

The phase transition caused by light illumination is called photoinduced phase transition (PIPT) and has been of current interest during the past decades [1]. In the course of the many exploring researches, many interesting examples of PIPT have been reported especially in so-called strongly correlated materials. Among such PIPT materials, a perovskite-type oxide system is one of the typical examples. A perovskite-type manganite, e.g., is known to show the PIPT between the charge ordered insulating state and the ferromagnetic metallic state [2], and some intriguing demonstrations using recent femtosecond techniques have been reported [3].

Another example is a perovskite-type cobalt oxide. Very lately, we reported PIPT and the resultant ultrasonic propagation of the photoinduced metallic region in $Pr_{0.5}Ca_{0.5}CoO_3$ [4, 5]. In this paper, we chose a layered perovskite-type cobalt oxide, $La_{1.5}Sr_{0.5}CoO_4$ as a research target and explored a novel PIPT phenomenon in terms of a time resolved femtosecond reflection spectroscopy.

The crystal structure of $La_{1.5}Sr_{0.5}CoO_4$ is K_2NiF_4--type structure. The nominal valence of the cobalt ion is $Co^{2.5+}$, in which Co^{2+}:Co^{3+} = 1:1. According to the X-ray diffraction measurement [6], those Co^{2+} and Co^{3+} show checker board-type ordering in the *ab* plane at about $T_{CO} \approx 800$ K as shown in the inset to Fig. 1. In addition, the recent X-ray absorption spectroscopy [7], neutron diffraction [8], and band calculation [9] revealed that the electronic states of Co^{2+} and Co^{3+} are high-spin (HS, $e_g^1 t_{2g}^5$) and low spin (LS, t_{2g}^6). Upon T_{CO}, it is reasonable to consider some spin state transition in Co^{3+} may occur but it has not been clarified. Hereafter, we report on the results of the ultrafast pump–probe measurement in $La_{1.5}Sr_{0.5}CoO_4$ and demonstrate the ultrafast PIPT from the insulating state at room temperature.

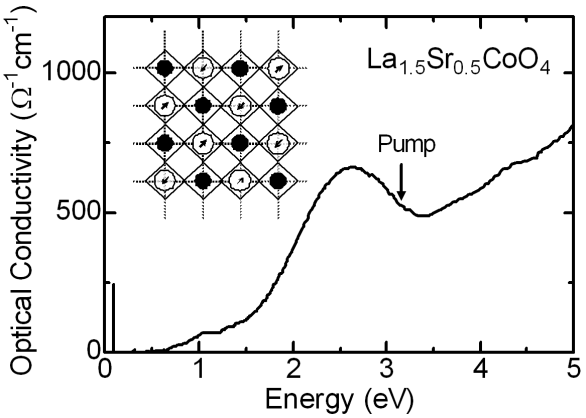

Fig. 1. Optical conductivity spectrum in the polarization of the *ab*-plane. The inset shows a schematic of the charge ordering of Co^{2+} (open circles) and Co^{3+} (closed circles) reproduced from Refs. [7] and [8].

* corresponding author; e-mail: yokimoto@cms.titech.ac.jp

2. Experiment

A single crystal sample of $La_{1.5}Sr_{0.5}CoO_4$ was grown by the floating zone method. Relative change of reflectivity ($\Delta R/R$) after irradiating femtosecond laser pulses was obtained by the conventional pump–probe technique using a Ti:sapphire regenerative amplifier system (the photon energy is 1.6 eV, pulse width $\approx$ 120 fs, and repetition rate 1 kHz) as a light source. The amplified light was divided into two beams; one was used as a pump light after the frequency was doubled (3.2 eV). The fluence of the pump light on the sample was ≈ 1.8 mJ/cm^2. The other is used as a probe pulse, which is converted by an optical parametric amplifier (0.50 eV and 2.0 eV). In Fig. 1, we show the in-plane optical conductivity ($\sigma(\omega)$) spectrum for $La_{1.5}Sr_{0.5}CoO_4$ crystal. (A spiky structure around 0.1 eV is due to the optical phonon mode.) $\sigma(\omega)$ shows a peak at around 2.6 eV. The peak energy corresponds to the charge transfer (CT) energy from O $2p$ band to the empty Co $3d$ band. The arrow denotes the photon energy of the pump light which causes such a CT transition.

3. Results and discussion

Figure 2 shows the time profiles of $\Delta R/R$ at 0.50 eV and 2.0 eV (open circles) in the $La_{1.5}Sr_{0.5}CoO_4$ crystal. After the photoexcitation, both the time dependences in $\Delta R/R$ show a sudden change. The value of $\Delta R/R$ largely increases at 0.50 eV while decreases at 2.0 eV compared with before the excitation. (The linear reflectance values are $\approx$ 13.2% at 0.50 eV and $\approx$ 15.1% at 2.0 eV.) Photoinduced $\Delta R/R$ decays within $\approx$ 1 ps. To estimate the time scale of the fast decaying, we fitted the $\Delta R/R$ profile by the following function:

$$f(t) = I_1 \exp(t/\tau_1) + I_2. \quad (1)$$

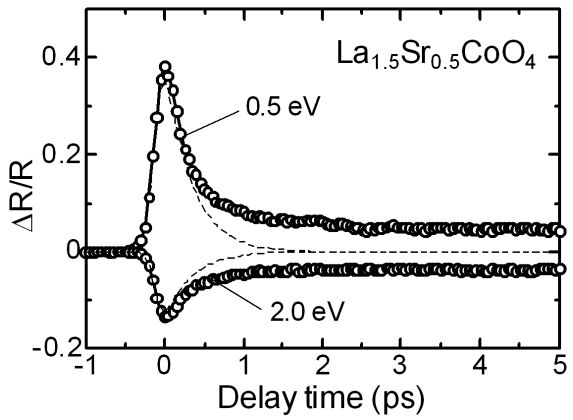

Fig. 2. Time profile of the reflectance change ($\Delta R/R$) at 2 eV and 0.50 eV (open circles). The dashed lines denote the fast component extracted by the fitting procedure in terms of Eq. (1) (see text).

The first term denotes an exponential decay of the photoexcited state, and I_1 and τ_1 denote the amplitude of the reflectivity change and the lifetime. The second term is a constant component after the fast decay. Taking the effect of the finite pulse duration on the profile of $\Delta R/R$ into account, we performed the fitting analysis considering the convolution between $f(t)$ and the response function of the present fs laser system. We also plotted the first term in Eq. (1) by dashed lines in each profiles of $\Delta R/R$, which was extracted by the fitting procedure. The evaluated decay time is about $\approx$ 330 fs in both the probe energies, indicating ultrafast photoresponse in $La_{1.5}Sr_{0.5}CoO_4$. Importantly, the sign of $\Delta R/R$ after the photoexcitation is positive in the mid-infrared region, while negative in the visible energy region. One scenario is the appearance of Drude-like transient spectrum by the photoexcitation.

Another plausible one is photoinduced polaronic state as observed in the cuprate [10] and cobaltite [11] especially in the mid-infrared region. Very recently, Kanamori et al. [12] have calculated the photoexcited state using a two-band Hubbard model and revealed the formation of a high spin polaron bound state by the photoirradiation. Such a bound state brings about the mid-infrared absorption, which might explain the observed enhancement of reflectivity at 0.50 eV. The ultrafast spectroscopy between the two energies would deserve further study to clarify the photoexcited state in $La_{1.5}Sr_{0.5}CoO_4$.

4. Summary

In summary, we performed time resolved reflection spectroscopy on the cobalt perovskite, $La_{1.5}Sr_{0.5}CoO_4$ using fs laser pulses, and observed the ultrafast change of the reflectivity. The fitting analysis of the time profiles indicates ultrafast lifetime of the photoexcited state ($\approx$ 330 fs). The transient reflectivity increases in the mid-infrared energy (0.50 eV) and decreases in the visible region (2.0 eV), which signals PIPT in $La_{1.5}Sr_{0.5}CoO_4$ crystal.

Acknowledgments

The authors thank M. Kurashima for technical assistance. This work was supported by Grant-in-Aid for Scientific Research on Innovative Areas (grants No. 21104514) and G-COE in Tokyo Institute of Technology.

References

[1] For a review, *Photoinduced Phase Transitions*, Ed. K. Nasu, World Sci., Singapore 2004.

[2] K. Miyano, T. Tanaka, Y. Tomioka, Y. Tokura, *Phys. Rev. Lett.* **78**, 4257 (1997).

[3] M. Rini, R. Tobey, N. Dean, J. Itatani, Y. Tomioka, Y. Tokura, R.W. Shoenlein, A. Cavalleri, *Nature* **449**, 72 (2007); D. Polli, M. Rini, S. Wall, R.W. Shoenlein, Y. Tomioka, Y. Tokura, G. Cerullo, A. Cavalleri, *Nature Mater.* **6**, 643 (2007).

[4] Y. Okimoto, X. Peng, M. Tamura, T. Morita, K. Onda, T. Ishikawa, S. Koshihara, N. Todoroki, T. Kyomen, M. Ito, *Phys. Rev. Lett.* **103**, 027402 (2009).

[5] Y. Okimoto, M. Kurashima, K. Seko, T. Ishikawa, K. Onda, T. Ishikawa, S. Koshihara, T. Kyomen, M. Ito, *Phys. Rev. B* **83**, 161101 (2011).

[6] I.A. Zaliznyak, J.P. Hill, J.M. Tranquada, R. Erwin, Y. Moritomo, *Phys. Rev. Lett.* **85**, 4353 (2000).

[7] C.F. Chang, Z. Hu, Hua Wu, T. Burnus, N. Hollmann, M. Benomar, T. Lorenz, A. Tanaka, H.-J. Lin, H.H. Hsieh, C.T. Chen, L.H. Tjeng, *Phys. Rev. Lett.* **102**, 116401 (2009).

[8] L.M. Helme, A.T. Boothroyd, R. Coldea, D. Prabhakaran, C.D. Frost, D.A. Keen, L.P. Regnault, P.G. Freeman, M. Enderle, J. Kuld, *Phys. Rev. B* **80**, 134414 (2009).

[9] H. Wu, T. Burnus, *Phys. Rev. B* **80**, 081105(R) (2009).

[10] H. Okamoto, T. Miyagoe, K. Kobayashi, H. Uemura, H. Nishioka, H. Matsuzaki, A. Sawa, Y. Tokura, *Phys. Rev. B* **83**, 125102 (2011).

[11] Y. Okimoto, T. Miyata, M.S. Endo, M. Kurashima, K. Onda, T. Ishikawa, S. Koshihara, M. Lorenc, E. Collet, H. Cailleau, T. Arima, *Phys. Rev. B* **84**, 121102(R) (2011).

[12] Y. Kanamori, H. Matsueda, S. Ishihara, *Phys. Rev. Lett.* **107**, 167403 (2011).