Picosecond Time-Resolved X-Ray Structural Study of "Hidden State" in a Manganite Thin Film

An epitaxial thin film of perovskite manganite $Nd_{0.5}Sr_{0.5}MnO_3$ (NSMO) is excited by an ultrashort optical laser pulse (150 fs duration, 1.55 eV) and the short-lived intermediate phase is captured by picosecond time-resolved X-ray diffraction (TR-XRD) measurement. We have successfully demonstrated for the first time that a "charge and orbitally ordered (COO) hidden state" of the manganite thin film is solely generated by the photo-excitation.

Photo-induced phase transition has attracted attention in materials science because the ultra-fast conversion of magnetic, dielectric, structural, and optical properties of materials is achievable by very weak light excitations as a result of cooperative interactions [1]. These features are expected to be of great use in the development of ultrafast magnetic storage and photo-switching devices. An essential question that arises in this field is how we can identify a novel phase of a solid that is uniquely generated under photo-excited conditions. Such a novel phase is often referred to as a "hidden state". In spite of intensive studies to identify the hidden state structurally in various systems, very few cases have been explored so far, due to the technical difficulties involved in studying the transient lattice structure of solids.

For example, perovskite manganese oxides such as $Pr_{0.5}Ca_{0.5}MnO_3$ (PCMO) and $Nd_{0.5}Sr_{0.5}MnO_3$ (NSMO) show thermally induced structural phase transitions coupled with insulator-to-metal transition. This also changes the magnetic property that reflects the ordering of d-orbitals and the charge of Mn ions, because the shape of the e_g orbital switches the in-plane and out-of-plane structural distortions of MnO_6 octahedra. Whether this system involves a photo-induced hidden state under ultrafast laser excitation conditions is of great interest.

We have successfully demonstrated for the first time, using picosecond time-resolved X-ray diffraction (TR-XRD), that a "charge and orbitally ordered (COO) hidden state" of the manganite thin film is solely generated by photo-excitation at 1.55 eV; this COO hidden state is not attainable under thermal equilibrium conditions [2]. An epitaxial thin film of perovskite manganite NSMO on the (011) surface of perovskite $SrTiO_3$ (STO) with a thickness of 80 nm was used for these TR-XRD studies. This thickness enables the penetration depth of X-rays and visible pulses to be matched to the sample. Figure 1 shows a schematic of the experimental setup of the TR-XRD experiment performed at AR-NW14A. The sample was cooled to 100 K, and a Ti:sapphire laser (150 fs duration, 1.55 eV) was used to excite the sample. X-ray pulses (100 ps duration, 15 keV) that were synchronized with the pump laser were selected from pulse trains at 794 kHz from PF-AR using a high-speed chopper, and were further used for the X-ray diffraction experiment.

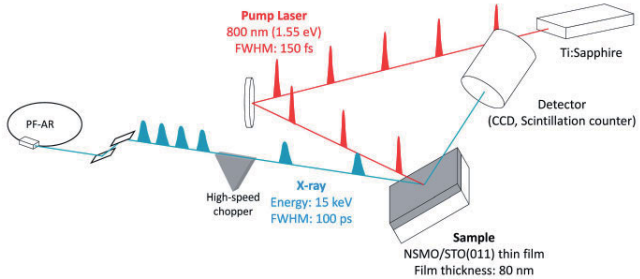

Figure 1
Schematic of experimental setup of 100-ps TR-XRD [2].

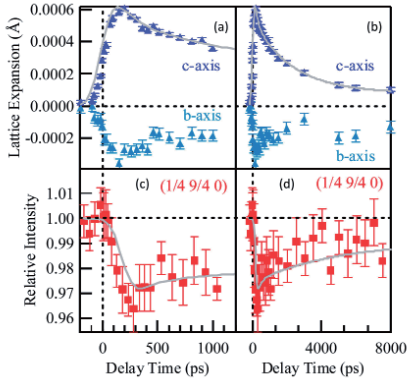

Figure 2
(a), (b) Time course of photo-induced changes in the lattice constants of *b* and *c* axes. (c), (d) Relative intensity changes in the (1/4 9/4 0) superlattice [2].

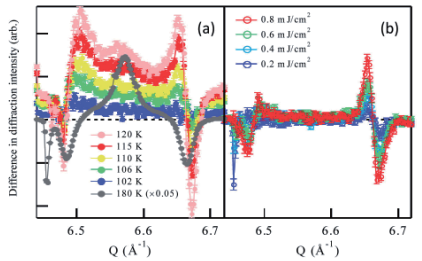

Figure 3
(a) Temperature effects on the differences in diffraction intensity due to the thermal phase transition. The diffraction pattern at 100 K is subtracted from those obtained at various temperatures in the heating run without laser excitation. (b) Photo-induced effects on the difference in diffraction intensity. The diffraction pattern at 100 K observed immediately prior to the laser pulse ($\Delta t = -5$ ps) is subtracted from those at $\Delta t = 150$ ps following laser irradiation at various fluencies. [2].

Figures 2(a) and (b) show time profiles of the photo-induced changes in the lattice constants of the *b* and *c* axes observed at 100 K by TR-XRD. As can be seen in the figures, photo-induced expansion of the *c* axis and shrinkage of the *b* axis are clearly observed. The changes in the lattice parameter occur immediately following photo-excitation, reach an optimum at a delay time of about 200 ps, and finally return to the original lattice parameters with a lifetime of 3 ns. In addition, a photo-induced decrease in the intensity of the reflection due to an expanded unit cell (superlattice) associated with the orbital ordered phase can be observed (Figs. 2(c) and (d)).

In the case of a thermal phase transition, an increase in the diffusive scattering intensity around the reciprocal space of $Q = 6.58$ Å^{-1} has been observed (Fig. 3(a)). However, photo-excitation only induces a shift in the Bragg peak, and does not show an increase in the diffusive scattering intensity following photo-excitation (Fig. 3(b)). Thus, the heat-up effect due to laser irradiation is estimated as being less than 10 K. In contrast to thermal effects, the time-resolved diffraction data is consistently explained by the formation of a "hidden state" with COO, which occurs in the process of relaxation from the high carrier density state (the so-called M phase) generated immediately following (within 100 fs) photo-excitation [2].

The photo-excitation of NSMO/STO(011) generates an insulator phase, which is characterized as a new COO state and is thus classified as a "hidden state". The estimated excitation photon density in the present study corresponds to one excitation photon for every 60 Mn ions, even in the case of the most intense excitation (0.8 mJ/cm^2). The highly sensitive photo-response and low heat-up effect (less than 10 K) in the ps region clearly show that the photo-induced structural effects in NSMO/STO(011) are driven by cooperative interaction in the spin-orbital-charge coupled system. Future femtosecond X-ray light sources will enable us to explore various types of COO and/or spin-charge-orbital coupled 'hidden states' induced by photo-excitation.

REFERENCES

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S. Koshihara[1,3], H. Ichikawa[1], S. Nozawa[1,2], T. Sato[1,2,3], A. Tomita[1,3], K. Ichiyanagi[1], M. Chollet[3], L. Guerin[1], N. Dean[4], A. Cavalleri[4,5], S. Adachi[1,2], T. Arima[6], H. Sawa[2], Y. Ogimoto[7], M. Nakamura[7], R. Tamaki[7], K. Miyano[7], ([1]KEK-PF(ERATO), [2]KEK-PF, [3]Tokyo Inst. of Tech. (CREST), [4]Univ. of Oxford, [5]Max Planck, [6]Tohoku Univ., [7]The Univ. of Tokyo(CREST))