Structural origin of 'hidden state' in manganite thin film revealed by picosecond time-resolved X-ray diffraction

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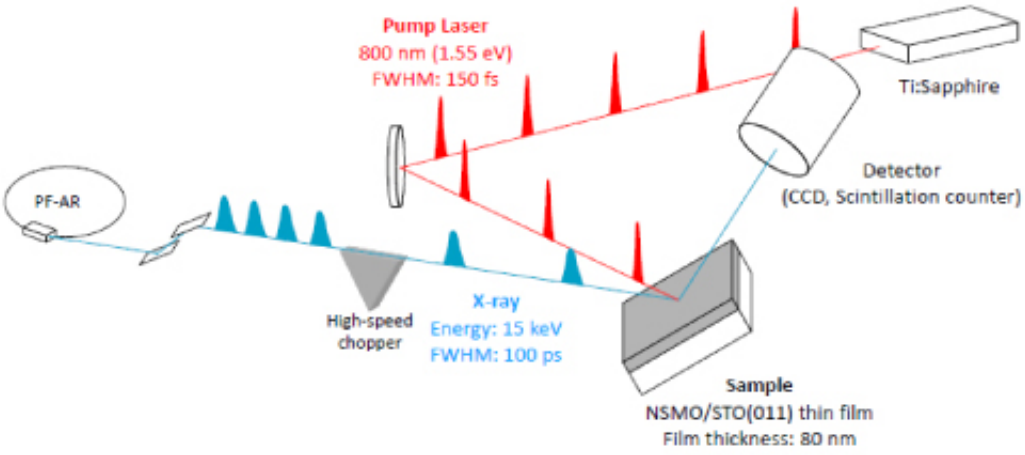

Fig. 1: Experimental setup of 100-ps TR-XRD.

Photo-induced phase transition (PIPT) has caused great excitement in materials science because ultra-fast alteration of the magnetic, dielectric, structural and optical properties of materials can be brought about with very weak photonic excitation as a result of cooperative interactions. An essential question that arises is how we can identify a novel phase of solid that is uniquely generated under photo-excited conditions. Such a novel phase is often referred to as a 'hidden state'. Despite intensive efforts to identify the structures of hidden states in various systems, few

cases have been explored so far because of the technical difficulty of studying the transient lattice structure of solids.

For example, perovskite manganese oxides such as Pr0.5Ca0.5MnO3 (PCMO) and Nd0.5Sr0.5MnO3 (NSMO) show thermally induced structural phase transitions coupled with an insulator-to-metal (IM) transition and changes in magnetic properties reflecting the ordering of d-orbitals and the charge of Mn ions because the shape of the eg orbitals alters the in-plane and out-of-plane structural distortions of MnO6 octahedra. Whether this system involves a photo-induced hidden phase under ultrafast laser excitation conditions is of great interest.

Researchers of the ERATO Koshihara Non-equilibrium Dynamics Project (JST) and IMSS have demonstrated by picosecond time-resolved X-ray diffraction (TR-XRD) that a charge and orbitally ordered (COO) hidden state of manganite thin film can only be generated by photo-excitation, and is not reachable under thermal equilibrium conditions. An 80 nm epitaxial thin film of perovskite manganite NSMO on the (011) surface of a perovskite SrTiO3 (STO) (NSMO/STO(011)) was used for the TR-XRD studies. Figure 1 shows the experimental setup, which used beamline NW14A of the Photon Factory Advanced Ring (PF-AR) at KEK. The sample was cooled down to 100 K, and the fs Ti:sapphire laser was use to excite the sample. 100-ps X-ray pulses at 946 Hz, synchronized with the pump laser, were selected from pulse trains at 794 kHz from the PF-AR by a high-speed chopper, and further used for the X-ray diffraction experiment.

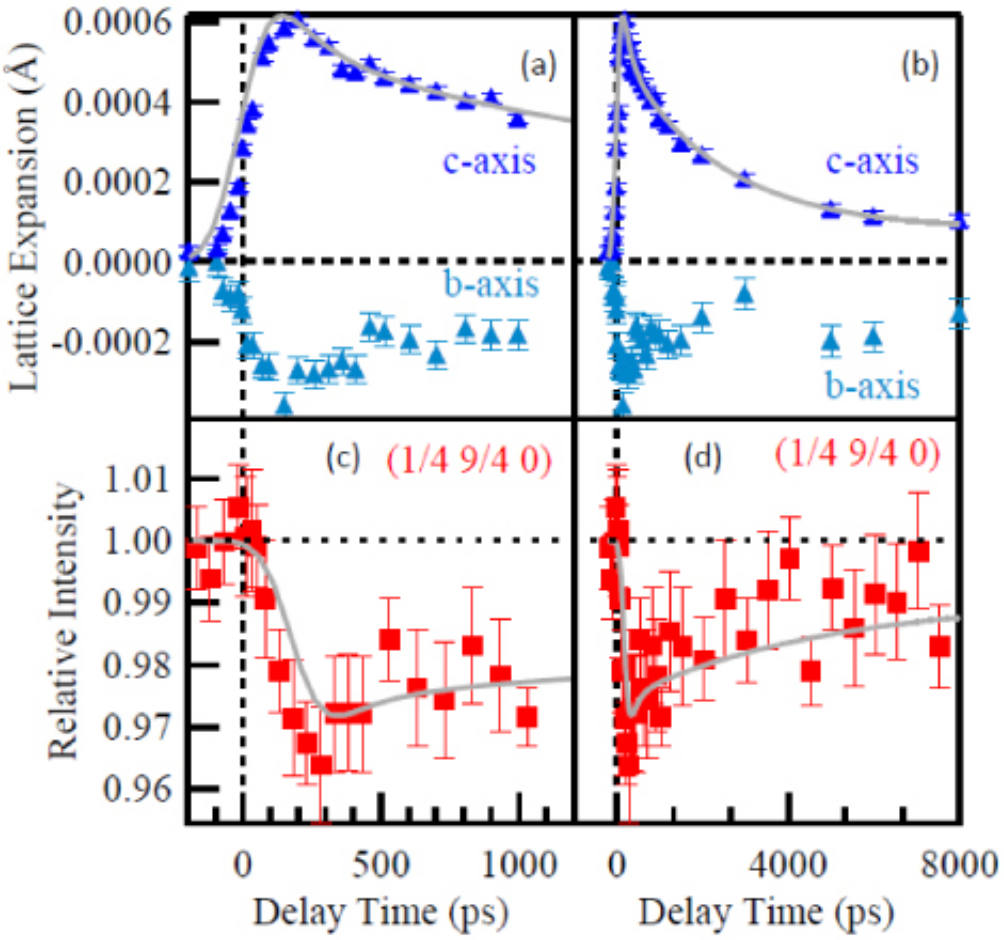

Fig. 2: (a),(b), Time course of photo-induced changes in the lattice constants on b and c axes. (c),(d), Relative intensity changes of the (1/4 9/4 0) superlattice.

Figures 2(a) and (b) show time profiles of the photo-induced change of lattice constants on the b and c axes observed at 100 K by TR-XRD. Photo-induced expansion on the c axis and shrinkage on the b axis have been clearly observed. The changes in lattice parameters occur just after photo-excitation, reach their maximum value at about 200 ps and finally return to their original values after 3 ns. In addition, a photo-induced decrease of about 5% in the intensity of super-lattice reflection due to an orbital-ordered phase has been observed (Figs.2(c) and (d)).

In the case of thermal phase transition, an increase in diffusive scattering intensity around the reciprocal space of Q = 6.58 Å-1 has been observed. However, photo-excitation induces only a shift of the Bragg peak and does not produce any subsequent increase in diffusive scattering intensity. Thus, the heating effect of the laser irradiation is estimated as less than 10 K. In contrast to any thermal effect, time-resolved diffraction data is consistently explained by the formation of a 'hidden state' with COO, which occurs in the relaxation process from the high carrier density state ("M phase") generated just after (within 100 fs) photo-excitation.

Photo-excitation of NSMO/STO(011) generates an insulator phase, which is a new COO state. This state cannot be realized under thermal equilibrium conditions, leading to its classification as a hidden state. The estimated excitation photon density in the present study corresponds to one excitation photon for every 100 Mn ions even in the case of the most intense excitation (0.8 mJ/cm2). The highly sensitive photo-response and minimal heating (less than 10 K) in the ps region clearly shows that photo-induced structural effects in NSMO/STO(011) are driven via cooperative interactions in a spin-orbital-charge coupled system. In the near future, a femtosecond X-ray light source will enable us to explore other types of COO and/or spin-charge-orbital coupled hidden states induced by photo-excitation.

More information: Photoinduced Phase Transitions, edited by K. Nasu (*World Scientific*, New Jersey, 2004)
H. Ichikawa et al., *Nature Materials*, 10, 101 (2011)

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