X-Ray Photo-Induced Phase Transition Enabled by Impurity Doping in Layered Manganite

In the charge-orbital order (COO) phase of perovskite manganite $Pr_{0.7}Ca_{0.3}MnO_3$, photo-conversion phenomena have been observed, such as a melting of the COO phase by X-ray irradiation, which corresponds to the transition from the COO phase to a charge-orbital disordered phase. In contrast, the X-ray photo-induced effect has not been observed in impurity undoped layered perovskite manganite $La_{0.5}Sr_{1.5}MnO_4$. In this study, we investigated the effect of impurity doping on the X-ray photo-induced phenomena in Fe-doped layered perovskite manganite $La_{0.5}Sr_{1.5}Mn_{0.97}Fe_{0.03}O_4$.

Phase transition triggered by light irradiation, or so-called photo-induced phase transition (PIPT), has attracted much research for photonic and materials science. Many PIPT materials have been found to exhibit novel transient phases not observed in thermal equilibrium. In general, the photo-induced phases are rather unstable and their lifetimes are very short, typically being between picoseconds and microseconds. To achieve a persistent photo-induced phase conversion, the initial and final states should be separated by a high potential barrier. If the free energy allows bistability between the initial and final phases, photo-excitation may induce phase conversion beyond the potential barrier between the two phases by the assistance of cooperative interactions in photo-excited states.

Impurity undoped $La_{0.5}Sr_{1.5}MnO_4$ is a typical crystal showing the charge-orbital order (COO) and CE-type antiferromagnetic (AFM) phase with inherent phase competition with the ferromagnetic (FM) phase (Fig. 1). In the AFM/COO phase, photo-conversion phenomena have been observed, such as a partial melting of the COO phase by X-ray irradiation, which corresponds to the transition from the COO phase to a charge-orbital disordered (DO) phase. In this study, we investigated X-ray PIPT phenomena in Fe-doped layered perovskite manganite $La_{0.5}Sr_{1.5}Mn_{0.97}Fe_{0.03}O_4$. The substitution of Mn ions with Fe ions would destroy the CE-type AFM order locally and form a small FM cluster, and finally the phase-separated state between the AFM/COO and FM/DO phases would be realized. The doping impurity, as a quenched disorder, may have the effect of enhancing the photo-conversion effect and lowering the threshold for the emergence of PIPT.

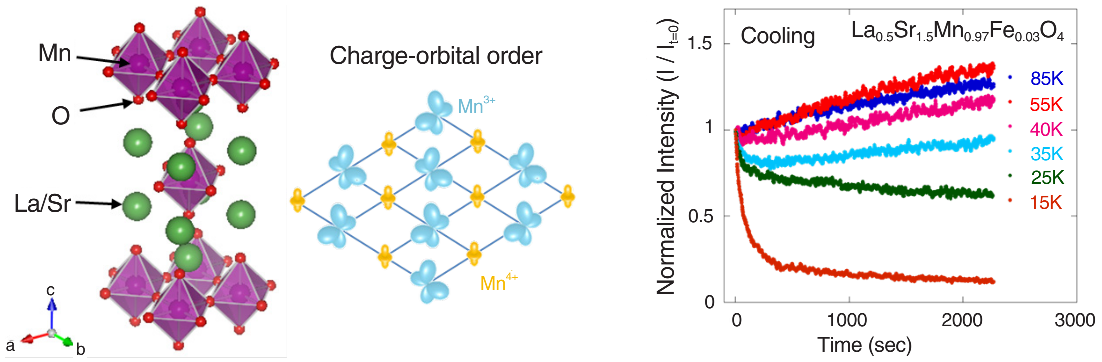

Figure 1: (left panel) Schematic of crystal structure and charge-orbital order in $La_{0.5}Sr_{1.5}MnO_4$. (right panel) The X-ray exposure time dependence of OO intensities for (1/4 7/4 0) in $La_{0.5}Sr_{1.5}Mn_{0.97}Fe_{0.03}O_4$. The incident X-ray energy was tuned to 6.5 keV and the X-ray photon flux was 2.5×10^{16} photons/m^{2}s.

It was revealed that 3% doping of Fe for Mn reduces the orbital order (OO) intensity by ~1/30, indicating that only a few percent of the Fe ions, functioning as quenched disorders, effectively suppress the long-range OO phase. Accordingly, this doping induces a weak ferromagnetism (FM) below 40 K. The produced ferromagnetism is subject to the magnetic field annealing effect, where the value of the saturation moment smoothly increases with an increase in the annealing magnetic field, which is generic of phase-separated states.

We found that impurity doping leads to dramatic enhancement of the X-ray induced effect. As shown in Fig. 1, the OO intensity for (1/4 7/4 0) reflection decreases during X-ray exposure with negligible incubation time below 35 K. The ac susceptibility is enhanced during X-ray exposure at 15 K, indicating that X-ray PIPT corresponds to phase conversion from the OO phase to the FM phase. In contrast, a reverse phase conversion from the FM phase to the OO phase was observed above 40 K (Fig. 1). As a consequence, this material exhibits persistent and bidirectional X-ray induced phase transition, whose direction is switched with varying temperature.

The initial state can be considered to be a metastable state protected by a potential barrier from which the incident X-ray can induce transition to the thermodynamically stable state. Switching of the direction of X-ray PIPT can be elucidated by postulating an alteration of the most stable state with varying temperature. In the present case, impurity doping plays a crucial role in forming the phase separated state and also in determining the rate of X-ray PIPT. Tuning of the impurity concentration and selection of the dopant element may provide fertile ground for clarifying X-ray PIPT phenomena and discovering new PIPT materials.

REFERENCE

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BEAMLINES

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