Orbitally ordered state in Y$_{1-x}$Ca$_x$TiO$_3$ studied by resonant X-ray scattering

Hironori NAKAO$^{1,*}$, Masami TSUBOTA$^2$, Soukichi KODAMA$^1$, Fumitoshi IGA$^2$, Kazuyuki UCHIHIRA$^2$, Toshihiro NAKANO$^2$, Toshiro TAKABATAKE$^2$, Yoiuchi MURAKAMI$^{1,3}$, Kenichi KATO$^4$

$^1$Department of Physics, Tohoku University, Sendai 980-8578, Japan
$^2$Department of Quantum Matter, ADSM, Hiroshima University, Higashihiroshima, 739-8526, Japan
$^3$Synchrotron Radiation Research Center, JAERI, Sayo, 679-5148, Japan
$^4$Japan Synchrotron Radiation Research Institute, Sayo, 679-5198, Japan

Introduction
A perovskite-type transition metal oxide, Y$_{1-x}$Ca$_x$TiO$_3$, shows drastic Mott metal-insulator transition (MIT) induced by the substitution of Ca for Y [1]. This parent material YTiO$_3$ is a Mott-insulator and shows a ferromagnetic (FM)-insulator phase below $T_c \approx 30$ K. The FM interaction is theoretically considered to be caused by the orbital ordering of Ti$^{3+} t_{2g}$-electron [2]. The theoretical predictions are consistent with the experimentally obtained orbital ordering [3]. By the substitution, the number of 3$d$-electron on Ti ion can be controlled form 1 to 0. The FM ordering disappears at $x_{FM} \approx 0.15$, while the insulating state is preserved up to $x_{MI} \approx 0.4$. At the $x_{MI}$ the drastic MIT occurs and the paramagnetic-metal phase is stabilized above $x_{MI}$. However, the origin of the respective phase transition is still unclear. The orbital degree of freedom in the transitions may play an important role. To make clear the orbital state in the respective phases, we have systematically investigated the orbitally ordered state in Y$_{1-x}$Ca$_x$TiO$_3$ using the resonant X-ray scattering (RXS) technique.

Experiment
The high quality single crystals of Y$_{1-x}$Ca$_x$TiO$_3$ were grown by a floating-zone technique. The powder x-ray diffraction at room temperature was performed to check the sample quality and the crystal structure at beam line(BL) 1B at Photon Factory. The RXS experiments were carried out by a four-circle diffractometer at BL-16A2. Polarizer with a PG(004) analyzer crystal was used in some experiments. The incident x-ray energy is about 4.97 keV of Ti K-edge and the energy resolution is about 1 eV.

Results
For the investigation of the orbitally ordered state of Ti 3$d$-electron in Y$_{1-x}$Ca$_x$TiO$_3$, we have searched the RXS at the forbidden reflections, (001), (011) and (100), near Ti K-edge. The energy dependences of RXS intensity at (001) are shown in the figure as a function of Ca concentration. The RXS intensity is only a $\sigma$- $\pi$ component. The energy spectra have two large peaks at $E \approx 4.980$ (main-edge) and 4.994 keV. A small resonant peak is also observed at $E \approx 4.972$ keV (pre-edge). The RXS intensities decrease monotonically and the energy spectra indicate no drastic change with increasing Ca concentration, x. The RXS at pre-edge (1s$\rightarrow$3d transition energy) is caused by the hybridization between the Ti 4$p$ and the neighboring orbitally ordered Ti 3$d$-s. Therefore, the RXS intensity at the pre-edge is proper for the measurement of the order parameter of ordered 3$d$-orbital. The RXS intensities at pre-edge rapidly decrease in $0 < x < 0.15$ and barely survives at $x \approx 0.30$ in the insulator phase before $x_{MI}$. In the metal phase, the intensity almost disappears. Namely, the orbital ordering is strongly suppressed toward $x_{MI}$ and almost vanishes near $x_{MI}$. The hole concentration dependence of Jahn-Teller distortion determined by the x-ray structural analysis is also consistent with that of the orbitally ordered state.

On the other hand, the RXS at main-edge in metal phase may arise from the tilts of the neighboring TiO$_6$ octahedra as theoretically suggested [4].

References
* nakao@iuyo.phys.tohoku.ac.jp