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Local Structure Study of $CaMnO_3$ by means of X-ray Fluorescence Holography

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$CaMnO_3$ exhibits a giant dielectric constant (10^4–10^6) with a broad temperature-dependent maximum around 120 K [1]. It crystallizes in an orthorhombic perovskite structure with lattice constants; a=5.40 Å, b=7.57 Å, and c=5.33 Å, in which the MnO_6 octahedra are tilted by approximately 25~26° with respect to the crystallograhic axis.

Although the origin of the dielectric anomaly has attracted considerable attention; however, no structural changes associated with temperature variation have been detected by conventional x-ray diffraction (XRD) measurements. In the present study, the temperature dependence of the local structure was investigated using x-ray fluorescence holography (XFH).

The XFH measurements were carried out at BL-6C of the Photon Factory. A single crystal of $CaMnO_3$ was used for the XFH measurements, which were performed in the inverse mode [2]. Holograms were recorded at seven incident x-ray energies ranging from 7.0 to 10.5 keV in 0.5 keV steps. Each hologram was measured for approximately 3 hours. Mn $K\alpha$ fluorescence was detected, allowing reconstruction of the local atomic arrangement around Mn atoms. Measurements were carried out at room temperature (RT) and 120 K. The sample was cooled using liquid nitrogen.

Figure 1 shows the reconstructed atomic images around the central Mn atoms at RT, sliced at z = 2.67, and 5.33 Å, corresponding to 1/2 and 1 times the lattice parameter c, respectively. The reconstructed atomic images are shown by black features, while the crystallographic atomic positions determined from XRD are indicated by colored circles. The reconstructed Mn images appear slightly shifted toward the center relative to the ideal crystallographic positions, whereas the Ca images are located close to the expected positions.

Figure 2 shows the reconstructed atomic image obtained at 120 K. The Ca atomic images remain close to the ideal crystallographic positions, whereas the Mn atomic images exhibit noticeable deviations. In addition, eight image spots are observed around the center in z = 2.67 Å. Similar features have previously been reported for the giant dielectric material $CaCu_3Ti_4O_{12}$ [3]. These observations may suggest enhances positional fluctuation of Mn atoms.

The present XFH study revealed a clear temperature dependence of the local structure in $CaMnO_3$ between RT and 120 K. While the Ca atomic positions remain

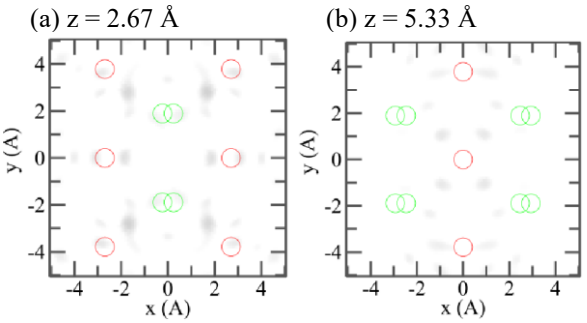

Fig. 1: Reconstructed atomic images around the central Mn atom at room temperature (RT). The images represent cross-sections at (a) z = 1/2 and (b) z = 1 in units of the lattice constant c. The circles indicate atomic positions determined from XRD data (Mn: ○, Ca: ○).

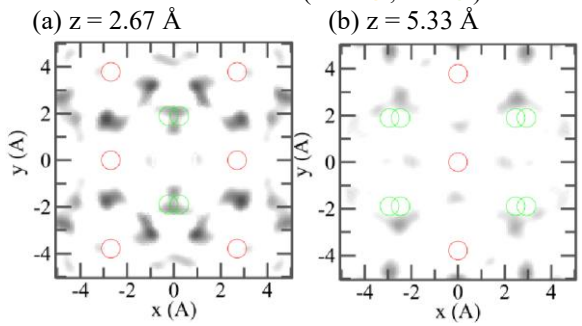

Fig. 2: Reconstructed atomic images around the central Mn atom at 120 K. The images represent cross-sections at (a) z = 1/2 and (b) z = 1 in units of the lattice constant c. The circles indicate atomic positions determined from XRD data (Mn: ○, Ca: ○).

essentially unchanged, the Mn-related atomic images show pronounced temperature-dependent behavior. These results suggest that the dielectric properties may be closely related to the local structural variations around Mn atoms. Further XFH measurements using Ca $K\alpha$ fluorescence, together with detailed hologram simulations, are expected to provide additional structural information. Moreover, x-ray emission spectroscopy measurements may offer complementary insight into the electronic structure. Such studies will contribute to a deeper understanding of the origin of the dielectric anomaly in $CaMnO_3$.

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