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High Resolution S/Transmission Electron Microscopy Investigation of $Ca_3Mn_2O_7$ Phase Transformation under In-situ Heating Condition

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The $Ca_3Mn_2O_7$ was proposed to be a prototypical material for achieving the strong magnetoelectric coupling at room temperature. The magnetoelectric coupling in this system can be obtained via the mechanism called "hybrid improper ferroelectricity". This mechanism includes combining two non-polar mode, i.e. the X_3 tilting mode and the X_2 rotation mode [1]. The combination of the two modes induces ferroelectricity in the material and can potentially couple the ferroelectricity and the ferromagnetism with the same set of modes [2]. The magnetoelectric coupling induced by the hybrid improper ferroelectrics has drawn a lot of interests due to its potential application in the next generation memory devices [3].

The switching via the hybrid improper ferroelectricity mechanism has been demonstrated in several other crystals systems [4], [5]. However, $Ca_3Mn_2O_7$ has shown difficulties with the polarization switching, due to complex domain morphology in the crystal and the polar-nonpolar phase coexistence at room temperature [2]. The high-temperature phase of the $Ca_3Mn_2O_7$ belongs to the I4/mmm space group, and transforms into the low-temperature polar phase of space group $A2_1am$ via an intermediate non-polar phase of the space group Acaa [6]. The phase transition introduces the oxygen octahedra rotation/tilt degeneracy [7]. The previous DF-TEM study indicates that such degeneracy caused the ferroelectric domains with polarization towards [100] or [010] directions of the crystal to be stacked along the c-axis. Additionally, the Acaa/$A2_1am$ phases coexist in a broad temperature range [6]. Since the phase transformation in the $Ca_3Mn_2O_7$ directly impacts the domain morphology, understanding the phase coexistence and its effect on polarization switching is crucial to achieve the future magnetoelectric applications.

In this study, we will utilize high resolution STEM to probe the domain morphology and phase coexistence in the $Ca_3Mn_2O_7$ crystal. Since slight Sr A-site doping increases the transition temperature without changing the structure in the $Ca_3Mn_2O_7$, the $A2_1am$/Acaa phase coexistence will be more prominent in the crystal at room temperature. This investigation shows the direct imaging of polar/nonpolar phase coexistence, by utilizing the aberration-corrected STEM on a Sr-doped $Ca_{2.9}Sr_{0.1}Mn_2O_7$. Furthermore, this study uncovers the local structural phase transition from the polar to nonpolar mode under in-situ heating.

Figures 1(a-b) show the atomic structure of the crystal from [010] axis at room temperature and after being heated to 650 °C, respectively. The linear features perpendicular to the [001] axis in the images are the polar phases trapped in the crystal. Upon heating, the density of the linear features representing the trapped polar phase started to decrease and eventually almost disappeared in the crystal, which demonstrated the

dramatic change in the crystal at elevated temperature during the in-situ heating TEM experiment. Figure 1c shows an atomic resolution annular bright field (ABF) STEM image taken at the trapped polar $A2_1am$ phase region with O, Ca, and Mn, indicating the oxygen octahedra tilt are significantly strengthened locally comparing to the Acaa non-polar phase matrix [8].

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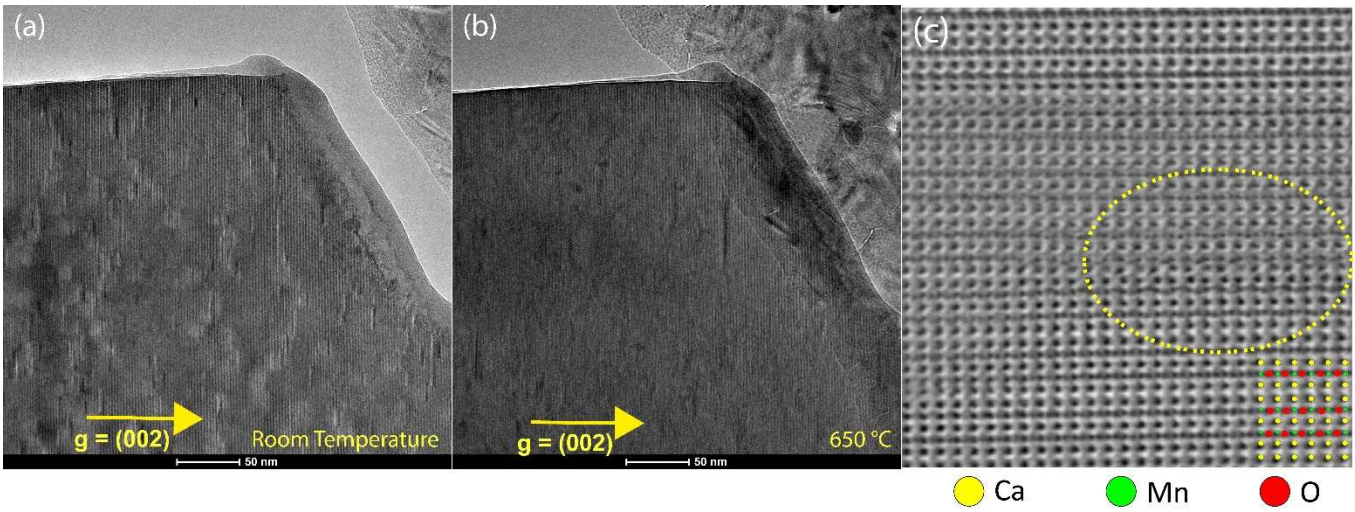

Figure 1. The TEM images taken during the in-situ heating experiment at (a) Room temperature and (b) 650 °C respectively. The linear feature perpendicular to the [001] axis are the trapped polar phase in the $Ca_{2.9}Sr_{0.1}Mn_2O_7$ crystal. As temperature is raised, the density of the trapped polar phase decreases dramatically. (c) ABF-STEM image taken at the phase trapping site, showing enhanced oxygen octahedra tilting locally at the polar phase.

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