HAADF-STEM Study on Unusual Inhomogeneous Microstructures in Charge-Glass State of $PbCrO_3$

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Transition metal oxides show various remarkable properties such as superconductivity, metal-insulator transitions, functional catalysts, and coupled charge, orbital and spin orderings. The charge ordering or the charge disproportionation in systems with integer or half integer charge number per atom often give rise to the insulator-metal transition by varying temperature and compositions. $PbCrO_3$ has a cubic perovskite structure (space group; *P*m-3m) with lattice constant of approximately a_0 = 0.40 nm, and shows a large pressure-induced volume collapse of 9.8% accompanied by an insulator-metal transition. Here we report unique microstructures characterized by the coexistence of crystalline and non-crystalline structures in $PbCrO_3$, which were revealed by atomic resolved high-angle annular dark-field scanning transmission electron microscopic (HAADF-STEM) observation. In the crystalline region characterized as the charge glass, Pb^{2+} ion with $6s^2$ lone pair is distributed over a multi-splitted *A*-site position in the perovskite structure and give rise to ring-shaped diffuse scattering around fundamental Bragg reflections. Atomic-resolved HAADF-STEM images directly demonstrated spatial distribution of displacements of Pb^{2+} around the *A*-site position.

Figure 1 shows a typical HAADF-STEM image obtained from the charge-glass state of $PbCrO_3$ at RT. The HAADF-STEM image revealed the complicated coexisting state consisting of the crystalline and non-crystalline regions elongating along the <100> direction. In the electron diffraction pattern showing the inset of Figure 1, halo-pattern showing the presence of the non-crystalline regions can be seen, in addition to the ring-shaped diffuse scatterings around the fundamental Bragg reflections. These results imply that the charge-glass state is characterized as the nanoscale coexisting state of the crystalline regions with the cubic structure and the non-crystalline regions. Furthermore, to clarify what gives rise to the ring-shaped diffuse scatterings around the fundamental Bragg reflections, we investigated the atomic-resolved HAADF-STEM image and EDX mappings of $PbCrO_3$. The HAADF-STEM experiments at the atomic resolution in Figure 2 revealed that Pb ions were displaced from the ideal A site position of the cubic perovstkite structure, which gives rise to characteristic diffuse scatterings around the fundamental Bragg reflections. These structural inhomogeneities should be crucial to understand the unconventional physical properties in the charge glass state of $PbCrO_3$ [3].

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2. A. M. Arévalo-Lòpez and M. A. Alario-Franco, *J. Solid State Chem*. **180**, 3271 (2007).
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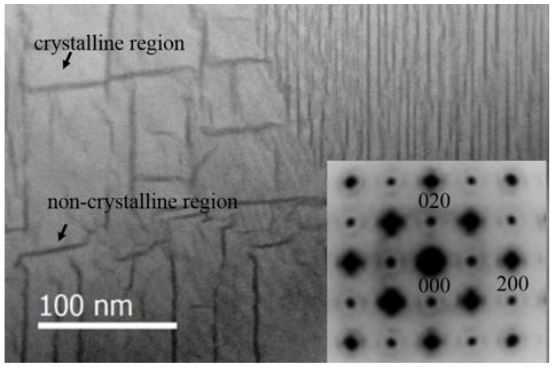

Fig. 1. (a) Atomic–resolved HAADF-STEM image showing the coexistence of the crystalline and non-crystalline phases. (inset) Electron diffraction pattern obtained from the coexisting region. Halo-pattern and diffuse scatterings can be clearly seen.

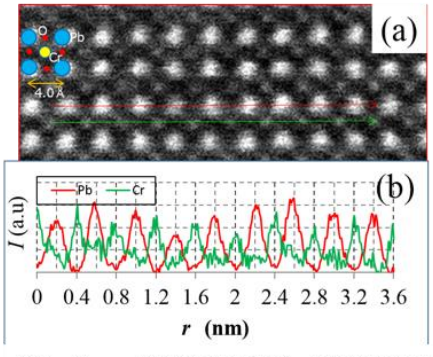

Fig. 2. Atomic-resolved HAADF-STEM image obtained from the crystalline region. Pb and Cr columns can be clearly seen as bright dots. (b) Intensity profile obtained by scanning along the <100> direction. Red and green lines show the intensity profiles of the bright dots due to the Pb and Cr columns, respectively.