Unusual inhomogeneous microstructures in charge glass state of PbCrO$_3$

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We investigated the microstructures and local structures of perovskite PbCrO$_3$, which shows a metal-to-insulator transition and a 9.8% volume collapse, by electron diffraction, high-resolution transmission electron microscopy (TEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). It is revealed that the charge glass state is characterized by the unique coexistence of the crystalline state with a cubic symmetry on average and the noncrystalline state. HAADF-STEM observation at atomic resolution revealed that Pb ions were displaced from the ideal A site position of the cubic perovskite structure, which gives rise to characteristic diffuse scatterings around the fundamental Bragg reflections. These structural inhomogeneities are crucial to the understanding of the unique physical properties in the charge glass state of PbCrO$_3$. © 2018 The Japan Society of Applied Physics

Transition metal oxides show various remarkable properties such as superconductivity, metal–insulator transitions, functional catalysts, and coupled charge, orbital, and spin orderings.$^{1-4}$ The charge ordering or the charge disproportionation in systems with integer or half integer charge number per atom often gives rise to the insulator–metal transition by varying temperature and compositions. PbCrO$_3$ has a cubic perovskite structure (space group; $Pm\overline{3}m$) with a lattice constant of approximately $a_0=0.40$ nm, and it shows a large pressure-induced volume collapse of 9.8% accompanied by an insulator–metal transition.$^{5}$ The oxidation state of PbCrO$_3$ under ambient condition has long been considered to be Pb$^{2+}$Cr$^{4+}$O$_3$ similarly to CaCrO$_3$ and SrCrO$_3$.$^{6}$ However, the origin of its insulating nature and having a lattice parameter larger than that of SrCrO$_3$, has been unclear when the Cr$^{4+}$ oxidation state is assumed. A tetragonal-to-cubic structural transition was proposed as the origin of volume collapse from first-principles calculations,$^7$ but such a tetragonal distortion has never been observed experimentally so far. On the other hand, a Pb–Cr antisite disorder was proposed as the origin of the insulating nature,$^8$ but such an antisite disorder was not detectable by neutron diffraction.$^9$ In addition, the charge disproportion of Cr ions was argued as another assumption of the Cr oxidation state.$^{10}$ Recently, hard X-ray photoelectron spectroscopy (HAXPES) has revealed the presence of Pb$^{2+}$/Pb$^{4+}$ charge disproportion,$^{11}$ and the charge distribution of Pb$_{0.5}^{3+}$Pb$_{0.5}^{4+}$Cr$^{3+}$O$_3$ was proposed. This oxidation state consistently explains the insulating nature and a large lattice parameter, and a large pressure-induced volume collapse accompanied by an insulator–metal transition can be explained by the intermetallic charge transfer from Pb$_{0.5}^{3+}$Pb$_{0.5}^{4+}$Cr$^{3+}$O$_3$ to Pb$^{2+}$Cr$^{4+}$O$_3$. Besides, the local structure in PbCrO$_3$ was examined by electron diffraction (ED) analysis, high-resolution transmission electron microscopy (TEM),$^{11,12}$ and pair distribution function (PDF) analysis of synchrotron X-ray total scattering.$^{11}$ The modulated structure with a length of $a_0 \times 3a_0 \times (14\sim18)a_0$ was attributed to the periodical distribution of Pb deficiency.$^{12}$ On the other hand, the short-range ordering of Pb$^{2+}$ and Pb$^{4+}$ with $3a_0 \times 3a_0 \times 3a_0$, which can be termed as the charge glass, was found by recent PDF analysis.$^{11}$ However, the long-period superstructure with $3a_0 \times 3a_0 \times 3a_0$ has not been solved yet and remains controversial.

Here, we report unique microstructures characterized by the coexistence of crystalline and noncrystalline structures in PbCrO$_3$, which were revealed by atomic resolved high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). In the crystalline region characterized as charge glass, Pb$^{2+}$ ions with a 6$s^2$ lone pair are distributed over a multisplitted A-site position in the perovskite structure, which gives rise to ring-shaped diffuse scattering around fundamental Bragg reflections. Atomic-resolved HAADF-STEM images directly demonstrated the spatial distribution of displacements of Pb$^{2+}$ around the A-site position.

Polycrystalline samples were prepared from a mixture of PbO and CrO$_3$ at a ratio of 1.1:1. These mixtures were sealed into gold capsules with a diameter of 3.6 mm and a height of 5 mm and were treated at 8 GPa and 1073 K for 30 min in a cubic-anvil-type high-pressure apparatus. The obtained PbCrO$_3$ sample was crushed into powder and washed with dilute HCL and to remove the remaining PbO and other impurities.

Thin samples for TEM were prepared by Ar-ion milling. Aberration-corrected HAADF-STEM was used, because atomic column displacements are directly imaged.$^{13-15}$ Thus, the new-generation high-resolution STEM system, equipped with a spherical aberration corrector is advantageous for the characterization of microstructures and local structures in the charge glass state of PbCrO$_3$. In this work, HAADF-STEM images were acquired using a JEOL ARM 200F (S)TEM system operated at 200 keV and with acceptance angles of 70–280 mrad.

Firstly, we examined the spatial distribution of diffuse scatterings in the reciprocal space by obtaining a large number of ED patterns with various electron beam incident directions, which was found in the charge glass state of PbCrO$_3$ at room temperature. As has been reported previously,$^{11,12}$ the characteristic ring-shaped diffuse scatterings
around fundamental Bragg reflections exist in the charge glass state of PbCrO₃. Figures 1(a)–1(c) show [001]-, [110]-, and [112]-zone axis selected-area electron diffraction (ED) patterns, respectively, in which the Bragg reflections have been indexed according to the ideal cubic perovskite unit cell. All the ED patterns, including the three ED patterns shown in Figs. 1(a)–1(c), exhibit the characteristic ring-shaped diffuse scatterings around the fundamental Bragg reflections. In the insets of Figs. 1(a)–1(c), ring-shaped diffuse scatterings are emphasized and these results are completely consistent with those of previous works.¹¹,¹² One of the significant features in the diffuse scatterings is that there exists the intensity distribution in the ring-shaped diffuse scatterings. On the basis of all the ED patterns obtained in this work, we constructed the intensity distribution in the ring-shaped diffuse scatterings in the reciprocal space, as shown in Fig. 1(d). In addition to the ring-shaped diffuse scatterings, halo-ring diffuse scatterings, as indicated by arrowheads in Figs. 1(a) and 1(b), can be observed in all the ED patterns obtained in this work. We also noticed that there exists halo-ring diffuse scatterings in the ED patterns of Fig. 4 in Ref. 5. Halo-ring diffuse scatterings often appear in noncrystalline (amorphous) compounds such as amorphous metallic materials and glassy materials.¹⁸–²¹

In a previous study, structural analysis was performed by the PDF analysis of the synchrotron X-ray total scatterings, assuming a long-period structure of ₃ₐ₀ × ₃ₐ₀ × ₃ₐ₀.¹¹ In this work, ED patterns were acquired from various regions, and the positions of the maximum intensity in the reciprocal space were carefully examined. Figures 2(a)–2(c) show three typical ED patterns along the ⟨100⟩ direction, showing the diffuse scatterings around the fundamental Bragg reflections. We measured the positions of the maximum intensity in the reciprocal space by obtaining line profiles along the ⟨100⟩ direction from the 2/300 to 200 reciprocal positions. Figures 2(d)–2(f) show the line profiles along the ⟨100⟩ directions, which were obtained from the ED patterns shown in Figs. 2(a)–2(c), respectively. As can be seen from the line profiles in Fig. 2(d), it was found that the maximum intensity positions exist at incommensurate positions that deviated from the 1/₃, 0, 0 reciprocal position. A detailed structural analysis considering the incommensurate long-period superstructure has not been carried out yet. Here, we focus on microstructures that give rise to two distinct types of diffuse scatterings, namely, the characteristic ring-shaped diffuse scatterings around the fundamental Bragg reflections and the halo-ring scatterings around the 000 position.

To elucidate the microstructures in the charge glass state of PbCrO₃, HAADF-STEM was carried out. As evident from the HAADF-STEM images shown in Fig. 3(a), complicated microstructures consisting of the crystalline state and the noncrystalline (amorphous-like) state are formed. The region with dark contrast corresponds to the noncrystalline state and the region with bright contrast corresponds to the crystalline state with the cubic perovskite structure. Bright dots corresponding to the Pb and Cr ions in the region with bright contrast can be clearly observed in the magnified image of Fig. 3(b). These supported the notion that the bright regions can be identified as the crystalline state with the cubic

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**Fig. 1.** (Color online) Selected-area ED patterns obtained from the charge glass state of PbCrO₃ along the (a) [001]-, (b) [110]-, and (c) [112]-zone axes. In (a)–(c), the yellow arrows indicate ring-shaped diffuse scatterings around Bragg reflections and the red arrows indicate the presence of the halo pattern. In the insets of (a)–(c), ring-shaped diffuse scatterings around Bragg reflections are magnified. (d) Schematic description of the reciprocal lattice for PbCrO₃, showing the presence of ring-shaped diffuse scatterings around the Bragg reflections. Note that the indexes of the ED patterns are based on the cubic perovskite structure.

**Fig. 2.** (Color online) (a)–(c) Parts of electron diffraction patterns along the ⟨100⟩ direction showing the ring-shaped diffuse scatterings. These electron diffraction patterns are obtained from three different regions in the sample. (d) Line profiles in (d)–(f) along the ⟨100⟩ directions are obtained from the ED patterns in (a)–(c), respectively. The blue, red, and green arrows indicate the positions with the maximum intensity.
perovskite structure and the dark region can be identified as the noncrystalline state. Note that no characteristic contrast due to the presence of Pb and Cr atomic columns can be seen in the noncrystalline region. Unexpectedly, PbCrO$_3$ under ambient condition shows the coexistence of the crystalline and noncrystalline states. Namely, the noncrystalline regions give rise to the halo-ring patterns around the 000 position, and the crystalline regions give rise to the ring-shaped diffuse scatterings. These results are consistent with the ED patterns shown in the inset of Fig. 3(a). The coexistence of the crystalline and noncrystalline states in other oxides such as SiO$_2$ stishovite prepared at high pressures has been reported recently.$^{18}$

To clarify what gives rise to the ring-shaped diffuse scatterings in PbCrO$_3$, we investigate the atomic displacements of Pb ions by obtaining HAADF-STEM images at atomic resolution. Figure 4(a) shows a typical HAADF-STEM image in the (001) plane of the crystalline structure. In the HAADF-STEM image, Pb and Cr atomic columns are visualized as bright dots. Figure 4(b) shows the atomic-resolved HAADF-STEM image magnified from the red rectangular region of Fig. 4(a), in which Pb and Cr atoms are shown as blue and yellow dots, respectively. In the ideal cubic perovskite structure, Cr ions should form a square lattice with a lattice constant of 0.4 nm in the (001) plane. Thus, we investigated the positions of Pb and Cr columns by obtaining intensity profiles along the red (Pb) and green (Cr) lines in Fig. 4(b). The spacing between two adjacent Cr columns can be estimated to be approximately 0.4 nm, and the Cr ions located on the square lattice have a lattice constant of 0.4 nm. On the other hand, the magnitudes of deviations of Pb from the ideal A-site position range from 0 to 36 pm. These imply that a portion of the Pb ions are displaced from the ideal A-site positions in the cubic perovskite structure and the remaining Pb ions are located at the center of the square lattice formed by Cr ions. Two distinct valence states of Pb$^{2+}$ and Pb$^{4+}$ are mixed in the charge glass state of PbCrO$_3$, as suggested by the results of recent synchrotron X-ray diffraction, HAXPES, and PDF analyses.$^{11}$ Pb$^{2+}$ ions with a lone-pair electronic configuration$^{22-27}$ of [Xe] (6s$^2$) should be displaced from the ideal A-site position in the cubic perovskite structure. From the HAADF-STEM images, it is revealed that a portion of Pb ions are located at the center of the Cr square lattices, and a portion of the Pb ions are displaced from the center.
The present experimental results suggest that the displacements of Pb ions from the ideal A-site positions give rise to the characteristic ring-shaped diffuse scatterings around fundamental Bragg reflections. Fast-Fourier transformation (FFT) patterns are obtained from the three different regions, in order to confirm the origin of ring-shaped diffuse scatterings observed in Fig. 1. FFT patterns obtained from the square regions with (a) blue, (b) green, and (c) yellow colors in the HAADF-STEM image of Fig. 4(a) are shown in Figs. 5(a)–5(c), respectively, and diffuse scattering spots around Bragg reflections are reproduced. Furthermore, Fig. 5(d) shows the FFT pattern obtained from the whole regions of the HAADF-STEM image shown in Fig. 4(a) and reproduced the ring-shaped diffuse scatterings. These results imply that the short-range correlation of the displacements of Pb ions gives rise to the ring-shaped diffuse scatterings in the reciprocal space.

In conclusion, the microstructures and local structures at the atomic level were investigated using a newly synthesized phase-pure samples. HAADF-STEM clearly demonstrated the unique phase coexistence of the nanodomains with a short-range modulated structure, which gives rise to the characteristic ring-shaped diffuse scatterings around the fundamental Bragg reflections. In order to understand the unique physical properties of PbCrO₃, the structural inhomogeneities including the short-range correlations of the displacements of Pb²⁺ ions from the ideal cubic perovskite structure found in this work should be clarified in future works.

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1) M. A. Peña and J. L. G. Fierro, Chem. Rev. 101, 1981 (2001).
2) J. Kirschbaum, Phys. Rev. B 12, 3690 (1975).
3) Y. Zhou and S. Ramanathan, Jpn. J. Appl. Phys. 57, 053001 (2018).

Fig. 5. (Color online) (a)–(c) FFT patterns obtained from the square regions in (a) blue, (b) green, and (c) yellow in the HAADF-STEM image in Fig. 4(a). (d) FFT pattern obtained from the whole region in the HAADF-STEM image in Fig. 4(a).