2016
doi:10.1017/S143192761901081X

Microsc. Microanal. 25 (Suppl 2), 2019

Domain Structures and Pr_{Co} Antisite Point Defects in Double-perovskite $PrBaCo_2O_{5+\delta}$

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Double-perovskite materials, such as $PrBaCo_2O_{5+\delta}$, show better cathode performance for solid oxide fuel cells (SOFCs) operating at an intermediate temperature (IT) ranges of 500-800 °C. Using traditional diffraction contrast and 4D scanning transmission electron microscopy (STEM) virtual aperture technique [1], we revealed high-density antiphase domain boundaries (APBs) and 90° domain walls in $PrBaCo_2O_{5+\delta}$ grains [2]. Electron energy-loss spectroscopy (EELS) reveals the composition variation across some of the 90° domain walls. There are fewer Co and more Ba ions approaching the 90° domain walls, while the changes in Pr and O ions are not detectable. We assume that the extra Ba^{2+} cations replace the Pr^{3+} cations, while the Pr^{3+} cations go to the Co site to form Pr_{Co} antisite point defects and become Pr^{4+}. In this case, the Pr^{4+} cations will help to balance the local charges and have compatible ionic radius with that of Co^{3+}. The local strain field around the 90° domain walls play a crucial role in the stabilization of such Pr_{Co} antisite point defects. The antisite point defects have been observed in our high-resolution TEM (HRTEM) images and aberration-corrected high-angle annular dark-field (HAADF) STEM images. After Ca^{2+} doped into $PrBaCo_2O_{5+\delta}$ to improve the structure stability, we observed tweed structures in the $PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$ grain. The tweed structure is composed of high-density intersected needle-shaped 90° domain walls, which is linked to a strong local strain field and composition variation. Even when the temperature is increased to 750 °C, the domain structures are still stable as revealed by our *in situ* TEM investigation. Therefore, the influence of the domain structures and the Pr_{Co} antisite defects on the ionic and electric conductivities must be considered.

Figure 1(a) is a 4D STEM image from a $PrBaCo_2O_{5+\delta}$ grain. The 2D diffraction patterns from the two pixels B and C in (a) are displayed in Fig. 1(b) and (c), respectively. It is clear that there is a 90° rotation relationship between Fig. 1(b) and (c). Two virtual apertures are applied to 010 and 010' diffraction spots to separate the 90° domains, which are colored in red and green in the composite images in Fig. 1(d). Figure 1(e) and 1(f) are the composite images from the two rectangle areas in (a) with higher spatial resolution. The dark curves in the single-color area are the APBs.

Figure 2(a) and (b) are two HRTEM images recorded from a $PrBaCo_2O_{5+\delta}$ grain with different projected thickness, and the incident electron-beam is along the [100] axis. The simulated results from the antisite point defects as 50% Co^{3+} replaced by Pr^{4+} are displayed in Figs. 2(c) and 2(d), corresponding to the sample thickness of 2.33 nm and 5.44 nm. The reduced contrast of the bright dots is well reproduced in both simulated images. Figure 2(e) is a HAADF images from our $PrBaCo_2O_{5+\delta}$ grain. At the dashed yellow ring circled area, there is a bright dot much stronger than the nearby Co column. The stronger dot at the B site in Fig. 2(e) can serve as direct evidence of the existence of the Pr_{Co} antisite defect in the $PrBaCo_2O_{5+\delta}$ grain. [3]

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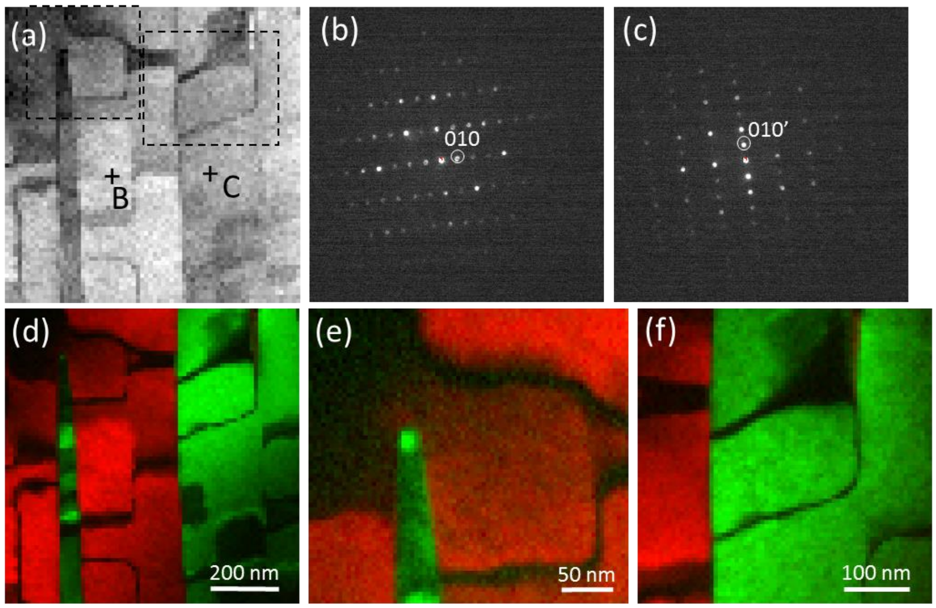

Figure 1. (a) 4D STEM image from a $PrBaCo_2O_{5+\delta}$ grain, two diffraction patterns from pixels B and C are in (b) and (c). The composite images in (d)-(f) show the 90° domains in red and green colors respectively. The curved boundaries are APBs.

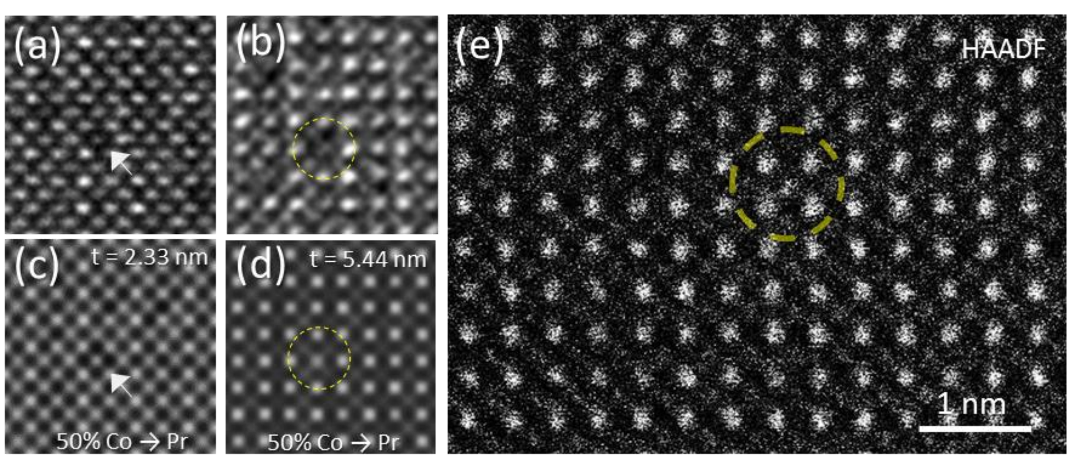

Figure 2. (a) - (d) HRTEM images and simulated ones of Pr_{Co} antisite defects. (e) HAADF STEM image to show the antisite defect.

https://doi.org/10.1017/S143192761901081X Published online by Cambridge University Press