

Direct Observation of Atomic Ordering in PrBaCo₂O_{5+δ} Layered Perovskite Oxide

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Perovskite oxides (ABO₃) have extensively been studied because of their structural flexibility and excellent catalytic properties for the solid oxide fuel cells (SOFCs), metal air batteries, solar cells, and other applications. Generally, the catalytic properties of the perovskite oxides are determined by the dynamics and concentration of oxygen vacancies. In terms of the oxygen kinetics, a layered perovskite oxide has attracted much attention due to its specific structural characteristic. The layered perovskite has a constitutional formula of AA'B₂O_{5+δ} with a stacking sequence of [A'O_δ]-[BO₂]-[AO_δ]-[BO₂] such as LnBaCo₂O_{5+δ} (Ln = Pr, Nd, Sm, and Gd). It is well known that most oxygen vacancies are located on the LnO layer, enhancing the mobility of oxygen ion. However, the location of the oxygen vacancies in the layered perovskite is still not clearly demonstrated. Here, we directly visualize the A-site cation ordering and the location of the oxygen vacancies in the complex oxide compound PrBaCo₂O_{5+δ} (PBCO) layered perovskite using scanning transmission electron microscope (STEM) technique.

The PBCO powder samples were prepared by the Pechini method, and sintered at 1200 °C for 12 h in air. The cross-sectional TEM samples of the PBCO pellet were fabricated by a focused ion beam (FIB) technique and an additional Ar nanomilling system. The conventional electron diffraction (ED) pattern and a high-resolution TEM (HRTEM) image from a large single grain showed the ordered perovskite phase with weak additional spots between main rectangular spots. In order to confirm the exact atomic positions, we performed a high-angle annular dark-field (HAADF) STEM imaging using an FEI Titan³ G2 60-300 with a double Cs corrector at an acceleration voltage of 200 kV. The atomic-scale HAADF STEM image viewed in a [100] direction showed a regular contrast change of BaO and PrO layers along the c axis due to the different atomic numbers between Ba and Pr, confirming the A-site cation ordering. To more clearly investigate the A-site cation ordering in the PBCO, chemically elaborate analysis was performed by atomic-scale energy dispersive spectroscopy (EDS) elemental mapping using FEI's Super-X EDS detection system. It is noted that the atomic positions of Pr and Ba are alternately located in each layer, and Co is located between A-site layers. In order to visualize the oxygen atomic columns, we utilized the annular bright field (ABF) STEM images by a JEOL JEM-ARM 200F microscope. We demonstrate remarkably that oxygen vacancies are mainly located in PrO layer, making an alternate CoO₆ octahedra and CoO₅ pyramids.

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