Imaging the Phase Evolution Processes in Brownmillerite-Structured Strontium Ferrite Thin Films

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The creation, clustering, and ordering of oxygen vacancies (V_{OS}) in perovskite-structured oxides (ABO₃, B being a transition metal) give rise to a special class of materials, such as Brownmillerite (BM) structured SrFeO₂.₅ (BM-SFO), SrCoO₂.₅, and rhombohedral structured SrCrO₂.₈. The BM-SFO structure emerges from SrFeO₃ with one-sixth of the oxygen atoms removed. These oxygen vacancy channels (OVCs) form along the [010] crystallographic direction, resulting in alternating oxygen deficient BO₄ tetrahedral and fully oxygenated BO₆ octahedral layers. In between these two phases, there are other intermediate states (SrFeO₂.₅⁺δ 0<δ<0.5) as the oxygen stoichiometry can change gradually. The OVCs allow the facile oxygen-ion transport, which has been exploited in oxygen membranes and electrolytes in solid-oxide fuel cells. Moreover, reversible topotactic phase transition between BM- and P-phases have been shown to induce resistive switching phenomena, in many cases involving a metal-to-insulator transition (MIT), which could be used in memristor devices.

In this work, epitaxial thin films of SrFeO₃.δ were grown on various lattice matched substrates by pulsed laser deposition to examine the effect of growth and processing conditions on their structural and physical properties. We show that by varying synthesis and processing conditions, the orientation of OVCs can be selectively controlled. Optical ellipsometry, in-plane transport, °¹ isotope exchange, and scanning transmission electron microscopy studies reveal that these configurations offer distinct different physical and oxygen transport properties. The topotactic phase transition from BM-SFO to perovskite SrFeO₃ can be promoted, delayed, or prohibited based on the interfacial strain conditions, highlighting the importance of interface engineering in designing robust and efficient ion conducting materials. In addition, using in situ TEM, we reveal that electron beam in STEM mode can provide a reducing environment, and facilitate the sample reduction from perovskite SrFeO₃ to BM-SFO as shown in Fig. 1. On the other hand, in TEM mode, the internal electrical field induced by local charging promote the oxygen out-diffusion from the substrate, which leads to the oxidation of the BM-SFO to P-SrFeO₃. A deeper understanding of the BM phase formation and evolution processes provides further insight into the oxygen-diffusion mechanism and anisotropic ionic conduction behavior, which can lead to the predictive synthesis of materials and design of novel functionality.
Figure 1. In situ STEM images illustrating the evolution of Brownmillerite phases with imaging time ranging from 0 s (a), 18 s (b), 36 s (c), 54 s (d) to 72 s (e). The corresponding mappings of the in-plane (IP) and out-of-plane (OOP) lattice spacing between Sr sites of the yellow rectangle box areas are shown below the HAADF images, respectively. Note that the acquisition time of each HAADF-STEM image is ~18 s and there is no additional electron beam irradiation between capturing the successive HAADF-STEM images.