

## ***In situ* Negative Cs HRTEM Imaging of Topotactic Phase Transformation from Perovskite SrFeO<sub>3</sub> to Brownmillerite SrFeO<sub>2.5</sub>**

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SrFeO<sub>3</sub>, a candidate electrode material for solid oxide fuel cell, undergoes topotactic phase transition reversibly to SrFeO<sub>2.5</sub> brownmillerite at relatively low temperatures. It has been known that during the topotactic phase transition the cation sub-lattice remains almost unchanged while oxygen ions (or vacancies) diffuses through the lattice along the specific crystallographic channels to modify the local coordination and valence states of cations. Previous x-ray diffraction [1] and sequential STEM HAADF imaging have been used to characterize the phase transition of this type of materials. However, neither of these methods can directly observe the channeling of oxygen vacancies, which is challenging due to the low scattering power of oxygen ions.

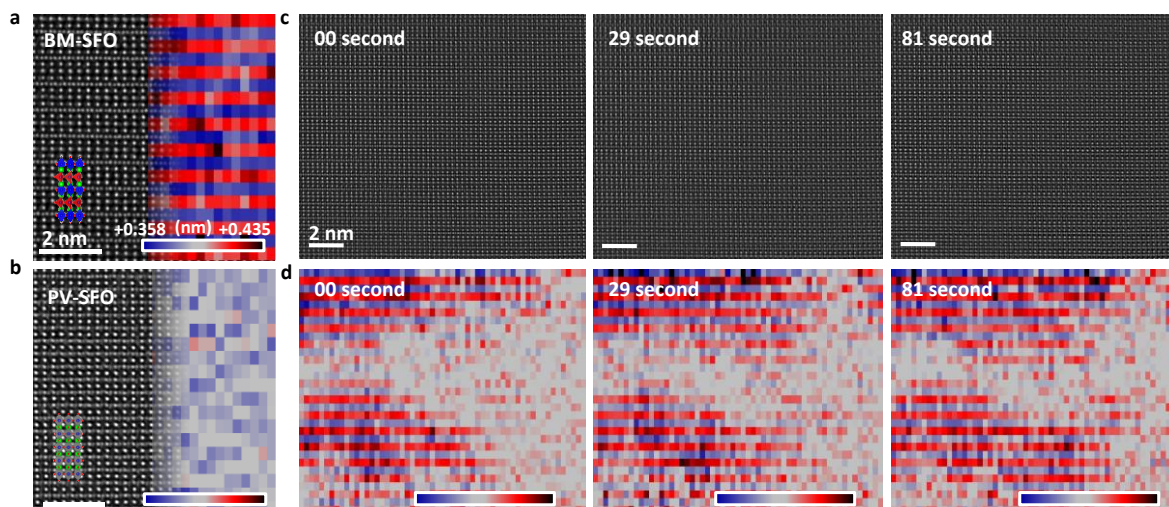
Here we report *in situ* HRTEM observation of the phase transition of a SrFeO<sub>3</sub> epitaxial thin film to SrFeO<sub>2.5</sub> brownmillerite phase in a Cs-corrected TEM (Grand ARM300F) operated at 300 kV. The TEM samples were prepared by focused ion beam milling and attached on a Si MEMS chip for heating using a TEM holder (DENSsolutions Wildfire). By using negative spherical aberration imaging (NCSI) technique, we successfully imaged all types of atomic columns in SrFeO<sub>3</sub> over large field of view, which enables direct observation of oxygen vacancy channeling, formation and growth of SrFeO<sub>2.5</sub> brownmillerite phase. The obtained real-time HRTEM movies were further processed to enhance the precision of the position and intensity measurement of atomic columns.

The cation (Sr) sub-lattice parameter map was used to differentiate SrFeO<sub>2.5</sub> phase from SrFeO<sub>3</sub> matrix as SrFeO<sub>2.5</sub> is comprised of alternating stack of contracted and expanded layers compared with that of SrFeO<sub>3</sub> (Fig. 1). In addition, the intensity of oxygen columns was quantified to access the local occupancy and therefore the formation of oxygen vacancy (data not shown). The Sr sub-lattice parameter and the oxygen intensity maps showed that the topotactic phase transition first occurs by forming brownmillerite lattice framework and then gradual increase of oxygen vacancies without formation of intermediate phases [2]. The results also showed that the formation of FeO<sub>4</sub> tetrahedron from FeO<sub>6</sub> octahedron by oxygen vacancy formation occurs directionally along easy oxygen vacancy channeling path in a zigzag pattern, probably to minimize the associated strain energy. In addition, the change of local coordination of Fe associated with the formation and ordering of oxygen vacancy accompanies the change of valence state from Fe<sup>+4</sup> in FeO<sub>6</sub> octahedron to Fe<sup>+2</sup> in FeO<sub>4</sub> tetrahedron. The STEM EELS O K-edge and Fe L<sub>2,3</sub>-edge of SrFeO<sub>2.5</sub> show that the electron energy-loss near edge structures (ELNES) of both FeO<sub>6</sub> and FeO<sub>4</sub> in SrFeO<sub>2.5</sub> are different from those of FeO<sub>6</sub> in SrFeO<sub>3</sub> and thus used to determine the local valence state of Fe. We have carried out in-situ STEM EELS during the phase transformation to monitor the local

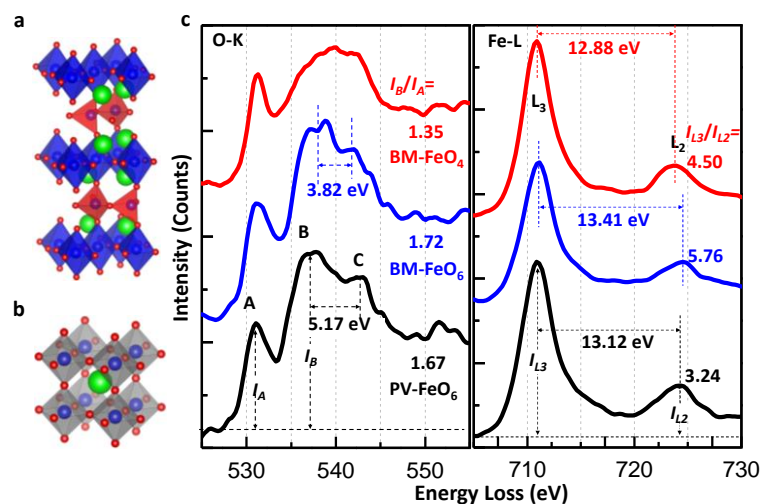
valence change of Fe ions associated with oxygen vacancy ordering and compared with the structural change assessed by in-situ HRTEM results.

#### References:

- [1] A. Khare, et al., *Advanced Materials* **29** (2017), p. 1606566.  
 [2] J. P. Hodges, et al., *Journal of Solid State Chemistry* **151** (2000), p. 190.  
 [3] This work was supported by Samsung Research Funding & Incubation Center of Samsung Electronics under Project Number SRFC-MA1702-01.



**Figure 1.** In-situ HRTEM images taken at a NCSI condition of (a)  $\text{SrFeO}_{2.5}$  (b)  $\text{SrFeO}_3$ . The Sr sub-lattice parameter map is overlaid. (c) Selected images from a real-time HRTEM movie recorded at 300 °C for 81 s. (d) Sr sub-lattice parameter maps obtained after image processing of the HRTEM images shown in (c), which distinguish  $\text{SrFeO}_3$  (gray colored pixels) from  $\text{SrFeO}_{2.5}$  (red/blue colored pixels).



**Figure 2.** Atomic model of (a)  $\text{SrFeO}_{2.5}$  and (b)  $\text{SrFeO}_3$ . (c) STEM EELS O K-edge and Fe L<sub>2,3</sub>-edge obtained from FeO<sub>6</sub> (black) in  $\text{SrFeO}_3$  and FeO<sub>6</sub> (blue) and FeO<sub>4</sub> (red) in  $\text{SrFeO}_{2.5}$ . The energy difference between peaks and their intensity ratio are noted.