2358
doi:10.1017/S1431927622009059

Microsc. Microanal. 28 (Suppl 1), 2022

Melting of Polar Vortex Arrays in an Oxide Superlattice Probed by *In Situ* STEM EELS

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Oxide superlattices provide a platform for leveraging charge, orbital, and lattice degrees of freedom to manipulate order parameters and access exotic phases and phenomena. A prominent example is the family of $SrTiO_3$/$PbTiO_3$ superlattices, which exhibits a variety of topological phases tuned by the periodicity of the paraelectric and ferroelectric layers. In short-period structures interfacial coupling of rotational distortions gives rise to improper ferroelectricity [1], while in long-period structures flux-closure domains emerge [2], and in the intermediate range (tens of unit cells) exotic topologies such as waves, vortices, and skyrmions can be observed [3]. In this intermediate range $(SrTiO_3)_{16}(PbTiO_3)_{16}$ has been shown to host ferroelectric polarization vortex arrays which exhibit long-range order at room temperature [4]. Spatially resolved electron energy loss spectroscopy (EELS) measurements on this system have shown that the material's electronic structure is modulated within the polar vortex structures that emerge in the ferroelectric $PbTiO_3$ layers. Changes to the local crystal field are reflected in the Ti-$L_{2,3}$ edge, where vortex cores and edges are differentiated by the symmetry of the e_g peaks [5]. Here, we characterize $(SrTiO_3)_{16}(PbTiO_3)_{16}$ with EELS as it undergoes an order-disorder transition driven by heating the material.

A cross-sectional lamella of the $(SrTiO_3)_{16}(PbTiO_3)_{16}$ superlattice was prepared by focused ion beam lift-out, mounted onto a MEMS chip, and heated *in situ* with a DENSsolutions Wildfire heating holder in a scanning transmission electron microscope (STEM). The sample was imaged on the $[010]_{pc}$ zone axis (Fig. 1a), exposing vortex cores as depicted schematically in Fig. 1e for the ordered room temperature structure. EEL spectra of the Ti-$L_{2,3}$ and O-K edges were continuously acquired with a Continuum IS and automatically tagged with the live sample temperature through several heating and cooling cycles from 26 to 400 °C with Gatan DigitalMicrograph. To separate their contributions, $SrTiO_3$ and $PbTiO_3$ layers were measured separately over identical temperature cycles. While both layers retained strong Ti^{4+} character through the cycling, modulations in the fine structure of the Ti-$L_{2,3}$ edge in the $PbTiO_3$ layers were detected. As shown in Fig. 1b, during a gradual 300 second cooling ramp the titanium L_2 and L_3 e_g peaks were suppressed while the t_{2g} peaks remained relatively unchanged. On the other hand, in the $SrTiO_3$ layer no significant changes were observed the Ti-$L_{2.3}$ edge through the temperature ramp (Fig. 1f). Similarly, the O-K edge showed small modulations in the $PbTiO_3$ layer as the sample was cooled (Fig. 1c), while in the $SrTiO_3$ layer the edge was virtually unchanged (Fig. 1g).

Characterizing both structural and electronic responses to external stimuli is crucial to probe the origins of phases arising in strongly correlated electronic systems and to design materials which leverage these degrees of freedom. This work demonstrates the capability of *in situ* EELS to characterize these responses with correlated, atomically resolved structural and electronic measurements, and potential to inform the development of novel quantum materials [6].

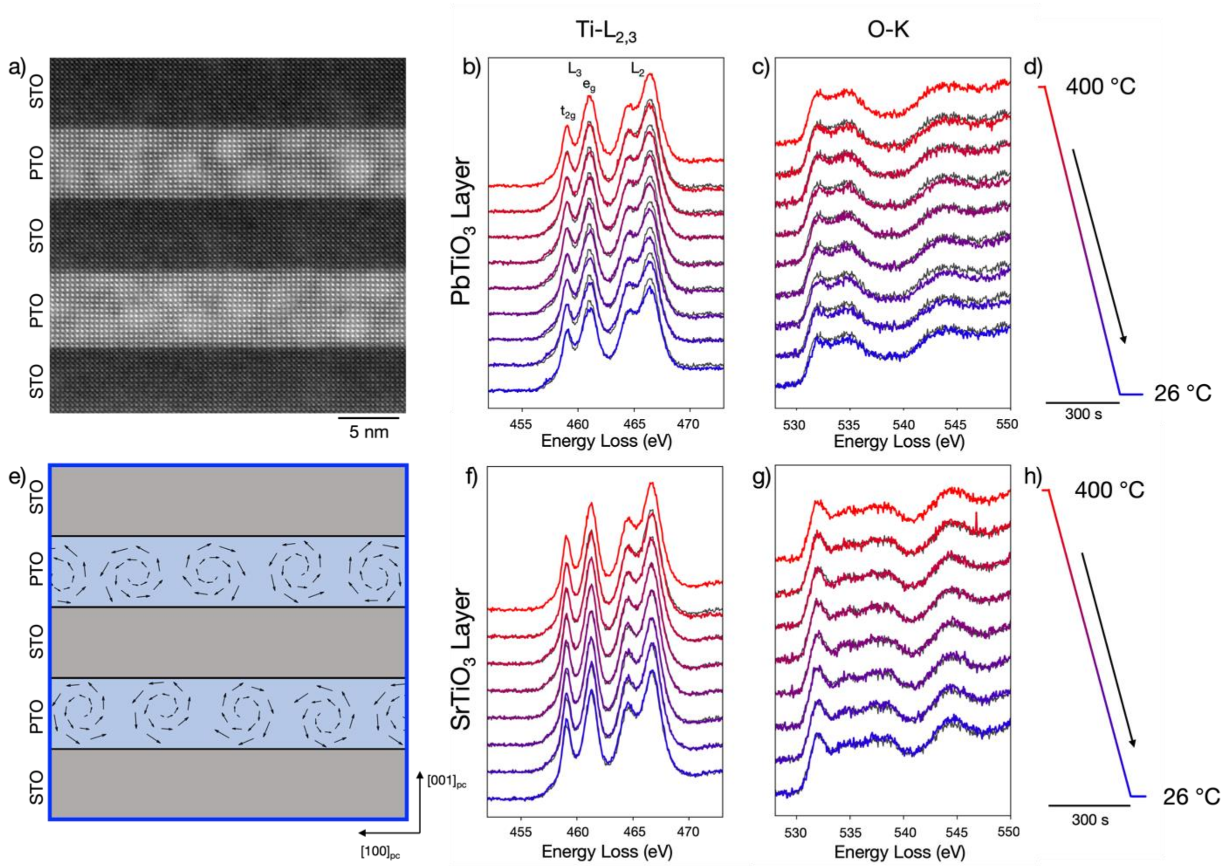

Figure 1. (a) Overview high-angle annular dark-field STEM image of the $[010]_{pc}$ $(SrTiO_3)_{16}(PbTiO_3)_{16}$ structure. **(b,f)** Ti-$L_{2,3}$ EEL spectra acquired in a $PbTiO_3$ layer (b) and $SrTiO_3$ layer (f) during cooling ramps from 400 °C (top,red) to 26 °C (bottom, blue). High-temperature spectra are underlaid in gray for each successive spectrum to highlight changes. **(c,g)** O-K EEL spectra acquired in a $PbTiO_3$ layer (c) and $SrTiO_3$ layer (g) during the same cooling ramps. **(d,h)** Plots of the temperature through the cooling ramps for the $PbTiO_3$ (d) and $SrTiO_3$ (h), color is mapped to temperature and corresponds to spectra colors. **(e)** Schematic of the room temperature polar vortex phase in the $[010]_{pc}$ zone axis.

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[6] This work was supported by the National Science Foundation (Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM)) under Cooperative Agreement No. DMR-2039380 and Graduate Research Fellowship (DGE-2139899). This work made use of the Cornell Center for Materials Research Shared Facilities which are supported through the NSF MRSEC program (DMR-1719875).

https://doi.org/10.1017/S1431927622009059 Published online by Cambridge University Press