

Critical Role of Atomic-scale Defects in Modulating Multiferroicity in Rare-earth Ferrite Multiferroics

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By subtly mediating local crystal and electronic structures, the atomic-scale defects, including vacancy, dislocation, and substitution atom, have been well recognized and proven to be the inherent origin of or the key control parameter for emergent phenomena or novel functionalities in closely correlated materials [1,2]. Especially in multiferroics, like representative rare-earth ferrites ($REFeO_3$ ($RE =$ rare-earth)) [3,4], since different degrees of freedom are closely correlated therein, atomic-scale defects will strongly interact with host lattice and thus introduce emergent properties. Hence delving into the underlying interactions and atomic-scale local structures to fully understand the critical roles of different types of atomic-scale defects can enable the community to give full play to their potential to further improve the multiferroicity. Herein, we present the study of critical roles of two kinds of typical atomic-scale defects, i.e., substitution atom and oxygen vacancy, in modulating multiferroicity in rare-earth ferrites, including the Type-I multiferroics h - $Lu_{1-x}Sc_xFeO_3$ and Type-II multiferroics o - $SmFeO_{3-\delta}$ film.

In h - $Lu_{1-x}Sc_xFeO_3$, we unravel how the individual Sc substitution atom can modulate both local electronic states and atomic lattices to influence the local improper ferroelectricity [1]. With the help of C_s -corrected STEM, the intriguing topologically-protected vortex ferroelectric domain stabilized by Sc substitution is demonstrated for the first time at the atomic resolution. Atomic-scale quantitative analysis of local chemistry and ferroelectricity directly correlates local variations in polar-displacement of the vortex ferroelectric domain to the concentration fluctuation of the Sc atoms (Fig.1(c-e)). Combining atomic-scale spectroscopy study (Fig.1(f)) with theoretical calculation (Fig.1(g)), we reveal the atomic origin of this close correlation in which Sc atoms significantly modify the local electronic structure and ferroelectric order by changing the magnitude of FeO_5 trimer distortion and the strength of Lu/Sc-O hybridization. Accordingly, the strong dependence of the improper ferroelectricity on Sc substitution atoms is clarified regarding both their atomic-scale distribution and concentration. By establishing the fundamental role of individual substitution atoms on the delicate energetic balance in multiferroics, this study also sheds light on the still debated mechanism underlying improper ferroelectricity in general.

In o - $SmFeO_{3-\delta}$ thin films, the critical role of purposely introduced oxygen vacancies has been clarified in inducing room temperature colossal polarization of $4.14 \mu C/cm^2$ that is two orders of magnitude larger than its bulk (Fig.2(a,b)) [2]. By quantitatively analyzing the atomic-scale lattice using C_s -corrected STEM, we show that oxygen vacancies in Fe-O layers can strongly distort the FeO_6 octahedral cage and drive the Fe ion away from its high-symmetry position (Fig.2(e,f)). This, therefore, contributes to the local symmetry breaking and electric dipoles. Combining thorough experimental investigations of thin films with variable oxygen contents with in-depth theoretical studies, we unambiguously reveal the

underlying mechanism for ferroelectric enhancement by well correlating positions and concentrations of oxygen vacancy with the enhanced polarization. It advances our understanding of the nature of ferroelectricity and internal close correlations among different degrees of freedom in Type-II multiferroic rare-earth ferrites and will shed light on the controversy of previous studies [4-6].

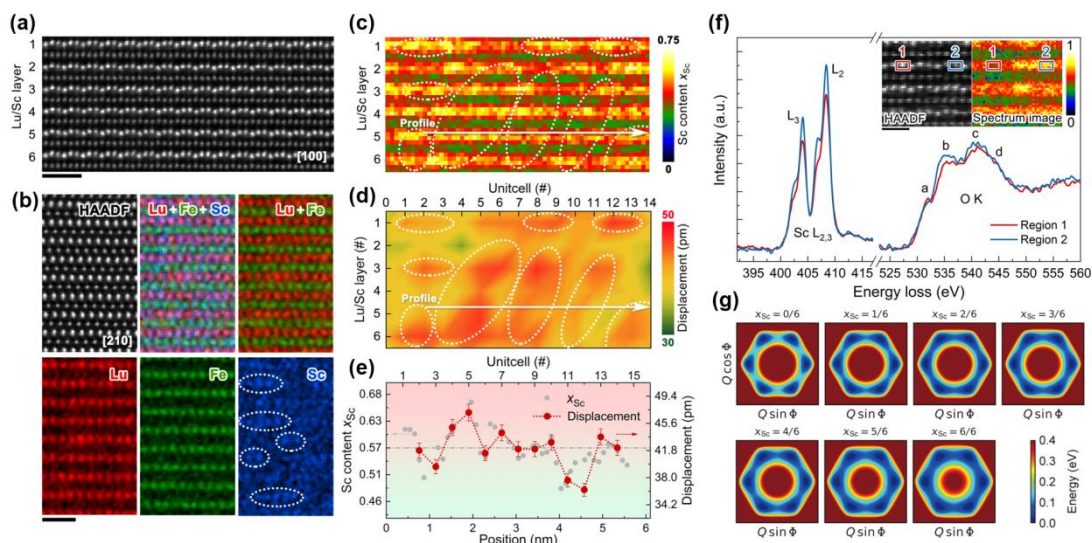


Figure 1. (a) [100] zone axis HAADF image where the EELS spectrum image is taken. (b) Atomically resolved EDXS maps. Scale bars are 1 nm. (c) x_{Sc} map of (a). (d) Polarization displacement map of (a). (e) Profiles along white arrows in (c) and (d). (f) EELS spectra showing Sc-L_{2,3} and O-K edges from Region 1 and 2. Scale bar is 5 Å. (g) Free-energy landscapes for different x_{Sc} (fixed lattice parameters).

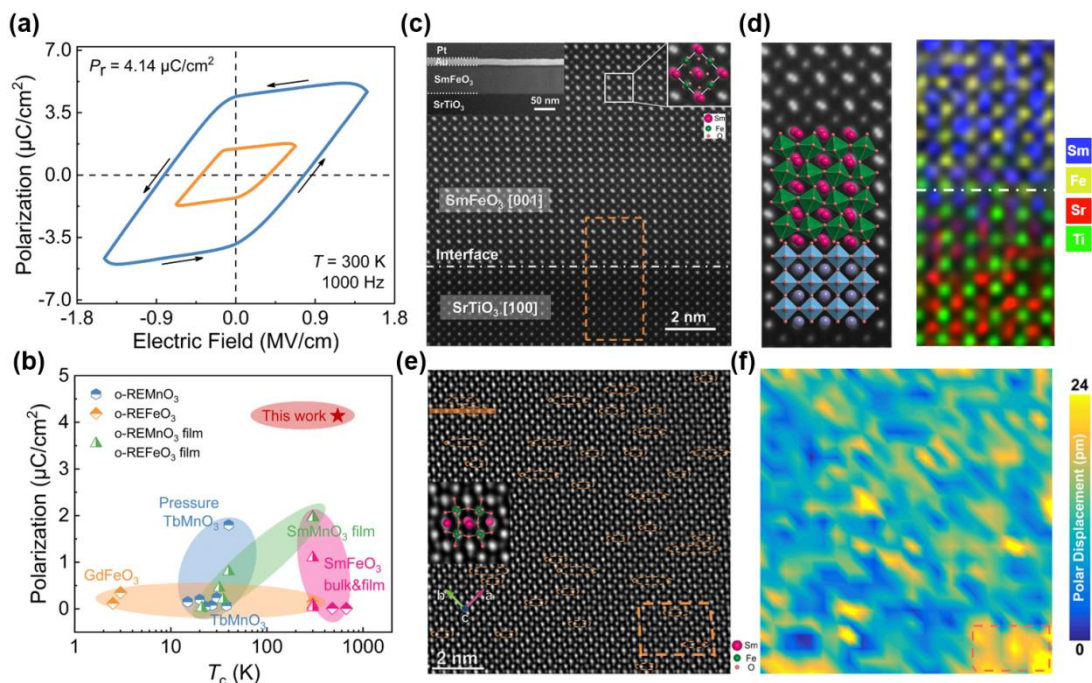


Figure 2. (a) P - E loops. (b) Comparison of polarization values versus T_c of rare-earth ferrites and manganites. (c) HAADF image of the SFO-STO interface. (d) Enlarged interface and its corresponding EDXS map. (e) Atomically resolved iDPC image. (f) Polar displacement map of the region in (e).

References:

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