

Roles of Oxygen Vacancy in Improper Ferroelectrics

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Multiferroics have attracted much attention due to the strong coupling between ferroelectricity and ferromagnetism, which can lead promising applications in multifunctional devices [1]. Accompanied with robust ferroelectricity ($T_C \sim 900\text{K}$) and low-temperature antiferromagnetism ($T_N \sim 70\text{K}$) [2], hexagonal RMnO_3 (R=rare-earth elements) shows its potential as a single-phase multiferroic material. Such a system is known for the novel improper ferroelectric mechanism that generates superior characteristics, including insensitivity to depolarization field [3]. This improper ferroelectricity comes from opposing dipoles caused by opposite displacement of yttrium ions at two symmetry inequivalent sites and is associated with tilting and distortion of MnO_5 bipyramids [3,4]. Therein, specific oxygen atoms play a vital role in the interaction between the nontrivial trimerization of MnO_5 bipyramids and the displacement of yttrium [4,5], which determines the nature of improper ferroelectricity and the topologically protected domain structure [6]. Questions then arise as to how improper ferroelectricity would be altered by the existence of oxygen vacancies and what the effects are for oxygen vacancies at different symmetry sites. Answers to these questions can be helpful for understanding the underlying atomic mechanism of improper ferroelectricity and allowing tuning coupling effects between ferroic orders.

Here, we report the critical roles of oxygen vacancies at different symmetry sites in modulating improper ferroelectricity in hexagonal YMnO_3 . Combining atomic resolved high-angle annular dark field scanning transmission microscope (HAADF-STEM) images and electron energy loss spectra (EELS), magnitudes of ferroelectric polarization in both stoichiometric and oxygen-deficient areas are extracted based on precisely measured yttrium positions. The latter shows remarkable polarization deterioration, which depends on the concentration of oxygen vacancies. Using *ab initio* density functional theories (DFT) calculations, we find that such phenomena originate from the significantly decreased strength of hybridizations between O-2*p* and Y-4*d_{z²}* orbitals when oxygen vacancies, especially in-plane oxygen vacancies, are created. Furthermore, eight possible vacancy configurations are constructed and calculated to obtain variations of polarization magnitudes with various oxygen vacancy concentrations. The ferroelectric polarization shows a monotonous decrease with the increase of oxygen vacancy concentration. Our results verify the importance of O-2*p* and Y-4*d_{z²}* hybridizations in driving improper ferroelectricity in hexagonal manganites and provide a possible tuning strategy. The insights from this work that the oxygen vacancy can be considered as an atomic multiferroic tuning element suggest the new thinking of material design and implementation [7].

References:

- [1] S. Dong *et al*, *Adv. Phys.* **64** (2015), p. 519.
 [2] S. B. Cheng *et al*, *Adv. Funct. Mater.* **26** (2016), p. 3589.
 [3] N. Sai *et al*, *Phys. Rev. Lett.* **102** (2009), p. 107601.
 [4] S. Q. Deng *et al*, *ACS Appl. Mater. Interfaces* **9** (2017), p. 27322.
 [5] S. B. Cheng *et al*, *Appl. Phys. Lett.* **106** (2015), p. 062905.
 [6] S. Q. Deng *et al*, *J. Am. Ceram. Soc.* **100** (2017), p. 2373.
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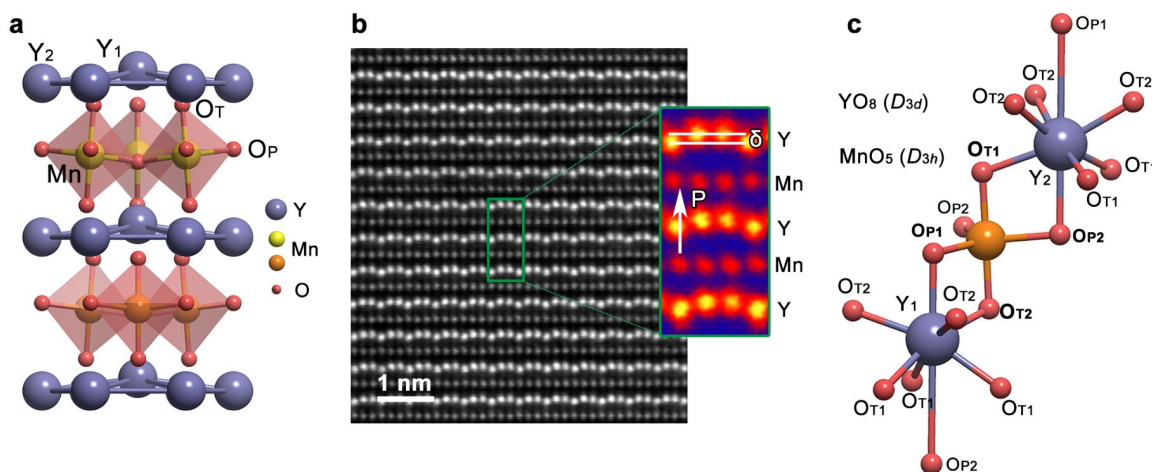


Figure 1. Atomic structure of hexagonal YMnO₃. **(a)** Crystal model. **(b)** A typical HAADF-STEM image, showing up-up-down lattice periodicity of Y, which indicates upward ferroelectric polarization. Y displacement is marked by δ in the inset. **(c)** YO₈ and MnO₅ cages including oxygen atoms at different symmetry sites.

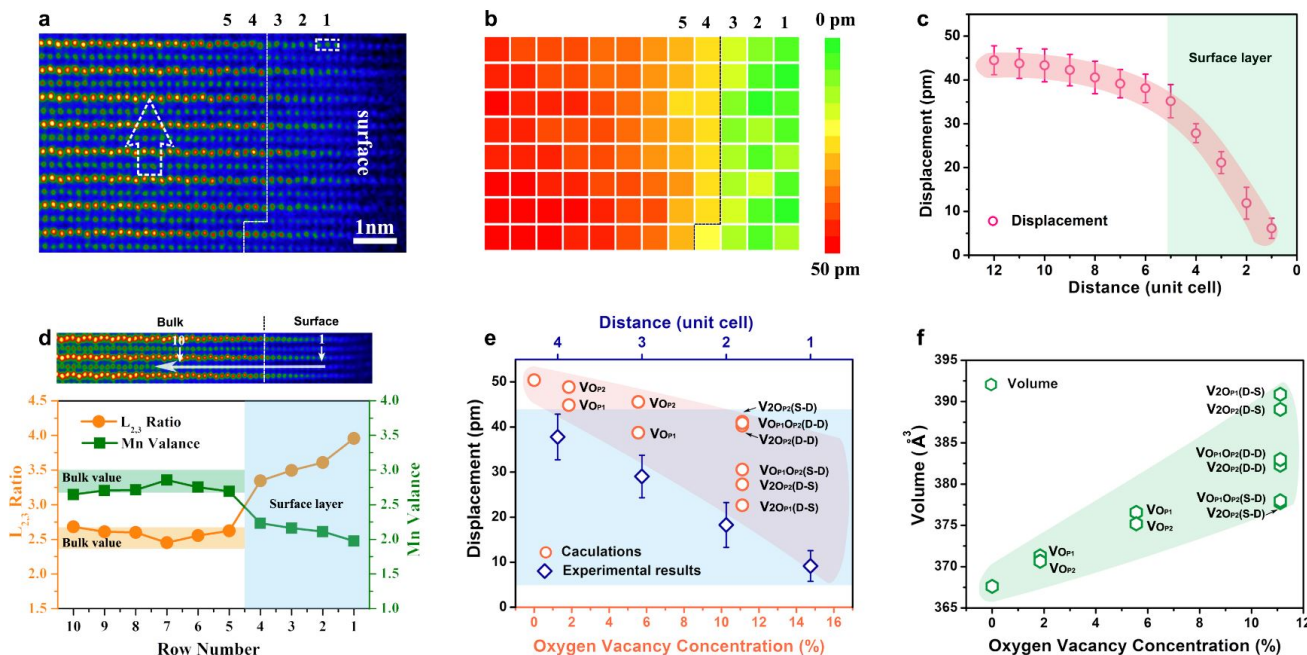


Figure 2. Dependence of ferroelectric polarizations on oxygen vacancies. **(a)** A HAADF-STEM image, showing upward polarization at bulk region (left part) and decreased Y displacement at surface (right part). **(b)** Magnitude map of Y displacement. **(c)** Average displacements as a function of distance from surface. **(d)** $L_{2,3}$ ratios and Mn valence states as a function of distance marked by number, which are measured by EELS. Oxygen-deficient areas correspond to the polarization decrease areas. **(e-f)** Variations of polarizations **(e)** and unit cell volumes **(f)** with oxygen vacancy concentration.