doi:10.1017/S1431927618010061
Microsc. Microanal. 24 (Suppl 1), 2018

High Resolution S/TEM Imaging of High Density Domain Stacking and Coexisting Polar-nonpolar Phases in Layered Perovskite $Ca_3Mn_2O_7$

Leixin Miao[1], Debangshu Mukherjee[1], Rongwei Hu[2], Sang-Wook Cheong[2], Nasim Alem[1]

[1.] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, USA.
[2.] Rutgers Center for Emergent Materials and Department of Physics and Astronomy, Rutgers University, Piscataway, USA.

The “hybrid improper ferroelectricity” in $Ca_3Mn_2O_7$ was first proposed by Nicole A. Benedek and Craig J. Fennie in 2011. Their simulation suggested that by combining two non-polar modes with different symmetry, the rotation of the octahedrons can induce the ferroelectricity, magnetoelectric and weak ferromagnetism in this layered perovskite oxide [1]. These properties, especially the potential strong magnetoelectric coupling, can lead to the development of the next generation memory devices [2].

$Ca_3Mn_2O_7$ is considered to have a Ruddlesden-Popper phase layered perovskite structure similar to the ferroelectric $Ca_3Ti_2O_7$, which possesses the hybrid improper ferroelectricity [3]. Despite their analogous structures, ferroelectricity has not been measured in $Ca_3Mn_2O_7$, although the polar domain structures in this phase have been reported [4]. Recently, the origin of non-switchable polarization has been investigated by DF-TEM, suggesting there is stacking of alternating domains with the polarization directions rotated by 90 degrees along the [001] axis in the crystal. Such alternating domain ordering indicates an unusual domain wall structure in $Ca_3Mn_2O_7$ [5].

Recent studies indicate that there is a polar-nonpolar phase coexistence in an unusually large temperature range in $Ca_3Mn_2O_7$ during the first order phase transition [6]. While the polar phase of the material at the low temperature range is reported to have octahedron tilting of $a^-a^-c^+$ with the $A2_1am$ space group, the competing non-polar phase at higher temperature has the octahedron tilting of $a^0a^0c^-$ with the space group of Acaa and a Tc to be approximately at room temperature [5] [6]. Since the space group $A2_1am$ does not form the subgroup of Acaa, and the lowest symmetry subgroup of both, Fmmm, possesses an additional lattice strain mode than the highest symmetry phase I4/mmm, there is no direct path for this phase transition to happen [6]. This complexity of structural transition and coexistence of multiple phases can make the structure of $Ca_3Mn_2O_7$ intriguing at room temperature since there are stacking of 90-degree rotated domains as well as potentially an observable phase trapping mechanism. In addition the domain walls and the phase boundaries can possess unusual atomic ordering and polarization giving rise to dissimilar properties compared with the bulk. In this investigation we use aberration-corrected high resolution scanning/transmission electron microscopy (S/TEM) imaging to uncover the atomic structure, coexistence of polar and non-polar structures and polarization in $Ca_3Mn_2O_7$.

Figure 1 demonstrates a TEM image in the crystal structure of $Ca_3Mn_2O_7$ and the presence of domain walls as well as the stacking fault in bulk $Ca_3Mn_2O_7$ layered perovskite. The lower resolution image of the edge-on domain wall going through the layered structure is shown in Figure 1a. S/TEM imaging of this crystal is performed at 200 kV accelerating voltage from $(011)_{pc}$ zone to have the domain walls parallel to the zone axis. From this orientation, the in-plane components of the polarization along crystallographic [100] and [010] directions can be successfully imaged and quantified. The high resolution electron microscopy image Figure (1c) and the streaking in the diffraction pattern (Figure 1b) from this crystal confirm the presence of stacking faults in the perovskite layer separated by the CaO rocksalt layers. This work will further present the structure of the domain walls and their local symmetry and structural distortions [7].

References:

[1] N. A. Benedek and C. J. Fennie, Physical Review Letter **106** (2016): 107204.
[2] T. Birol et al, Current Opinion in Solid State & Materials Science **227** (2012), p. 227.
[3] Y. Oh et al, Nature Materials **14** (2015), p. 407.
[4] F.-T. Huang et al, Nature Communications **7** (2015): 11602.
[5] B. Gao et al, Applied Physics Letters **110** (2017): 222906.
[6] M. S. Senn et al, Physical Review Letters **114** (2015): 035701.
[7] L.M., D.M., and N.A. were funded by the Penn State Center for Nanoscale Science, an NSF MRSEC under the grant number DMR-1420620.

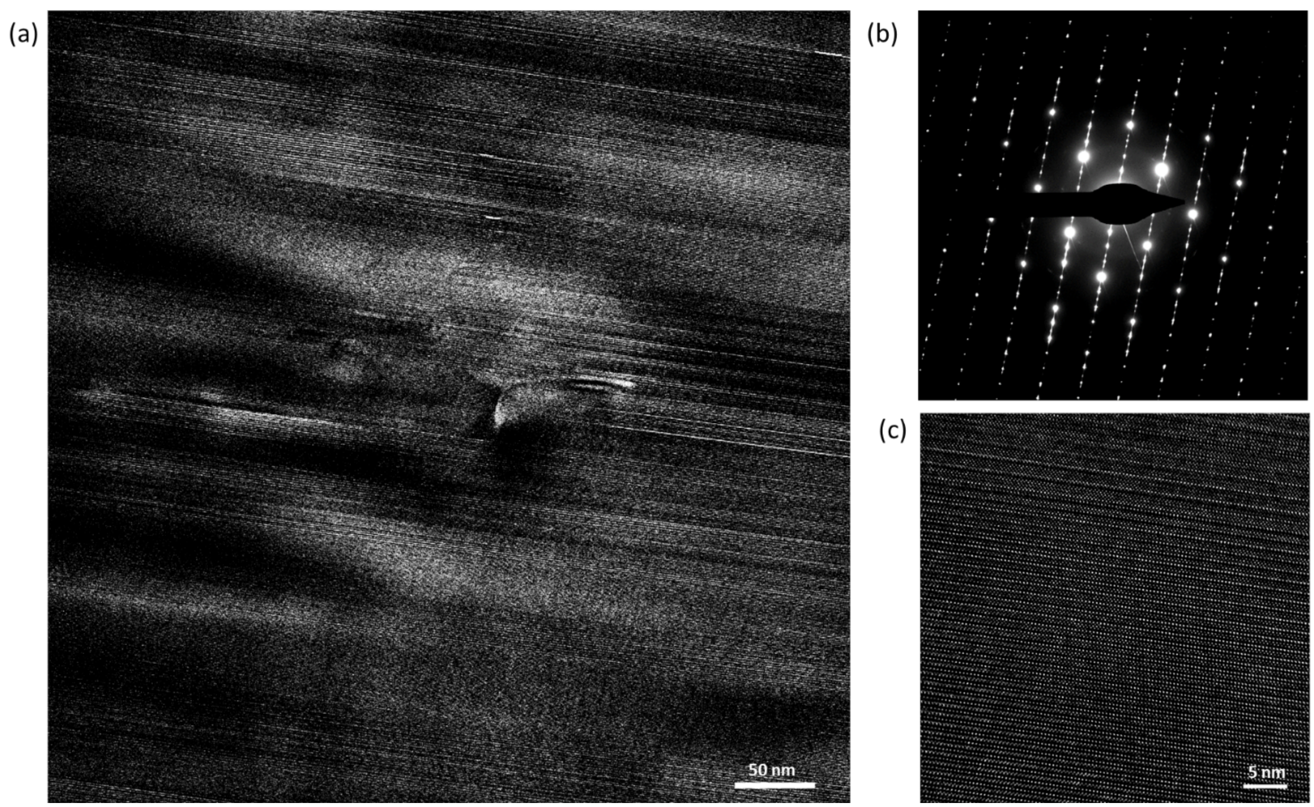

Figure 1. (a) The domain wall penetrating through layers imaged by the diffraction contrast from local symmetry distortions at the wall, viewing from the [110] zone axis. (b) The diffraction pattern along the [110] direction showing stacking faults. (c) HRTEM image of the $Ca_3Mn_2O_7$ along [110] zone axis showing the RP perovskite crystal structure as well as the stacking faults.

https://doi.org/10.1017/S1431927618010061 Published online by Cambridge University Press