Colossal Magnetoresistance and Improper Ferroelectric Polarization Explicated in Quadruple Perovskites

From various designed high-pressure synthesized AMn_7O_{12} series, the specific electron stripes arrangement provides mechanistic understanding of how magnetoresistance might be enhanced, and how the novel charge ordered state reveals novel coupling of electronic and ferroelectric order parameters.

Magnetoresistance (MR) is such a technologically important phenomenon that the resistivity of a material changes with an applied magnetic field. Such a property can be observed in many conducting materials, but the changes of resistance are typically about a few percent and with rather limited sensitivity. Nowadays MR materials are widely used in our daily life, as reader heads of hard drives in computer or consumer electronics. More functional materials have been further explored for potential technological application; for instance, in 1990s the colossal magnetoresistance (CMR) was demonstrated in the manganite perovskites. The archetypal $LaMnO_3$ based system was intensively investigated, in which a colossal change in resistance against magnetic field can be realized on tuning the electronic configuration of the system. An optimal MR response was soon established with a specific doped region, but the phase diagrams such as $La_{1-x}Ca_xMnO_3$ (LCMO) remain controversial. The CMR was believed to result from electronic phase segregation between ferromagnetic metallic and antiferromagnetic insulating states.[1] It is, however, a long-standing conundrum that such a precise doping value leads to a maximized MR effect; the phase segregation has prevented an atomistic-level understanding of the orbital ordered state at this doping level.

Wei-Tin Chen (National Taiwan University), Mark Senn (University of Warwick, UK), Yu-Chun Chuang and Chin-Wei Wang (NSRRC) recently demonstrated a successful collaboration to provide structural insight for a mechanistic understanding of such intriguing physical phenomena. These properties are exhibited in strongly correlated electron systems that tend to have dense and strongly bound structures. The application of high-pressure high-temperature (HPHT) synthesis techniques is therefore particularly useful to explore novel functional materials as unstable structural distortions and metastable magneto-electric phases might be stabilized under extreme conditions. Chen's research group is dedicated in HPHT techniques and utilizes $AA'_3B_4O_{12}$ quadruple perovskites as a model framework to investigate target functional properties, such as CMR and multiferroicity (MF) (**Fig. 1**). Detailed crystallographic information was extracted from high-resolution synchrotron X-ray powder diffraction (SXRD) data collected from the **TPS 19A** beamline at the NSRRC, and high-resolution neutron powder diffraction (NPD) data collected from beamline **ECHIDNA** at Australian Nuclear Science and Technology Organisation (ANSTO); furthermore, it is particularly beneficial to investigate a tiny sample obtained from a HPHT synthesis with high-intensity neutron powder diffraction instrument **WOMBAT**, at ANSTO. With assistance of thorough systematic symmetry element examination, Chen and Senn provided crucial structural evidence to understand the intrinsic properties.

The archetypal CMR systems are the doped manganite

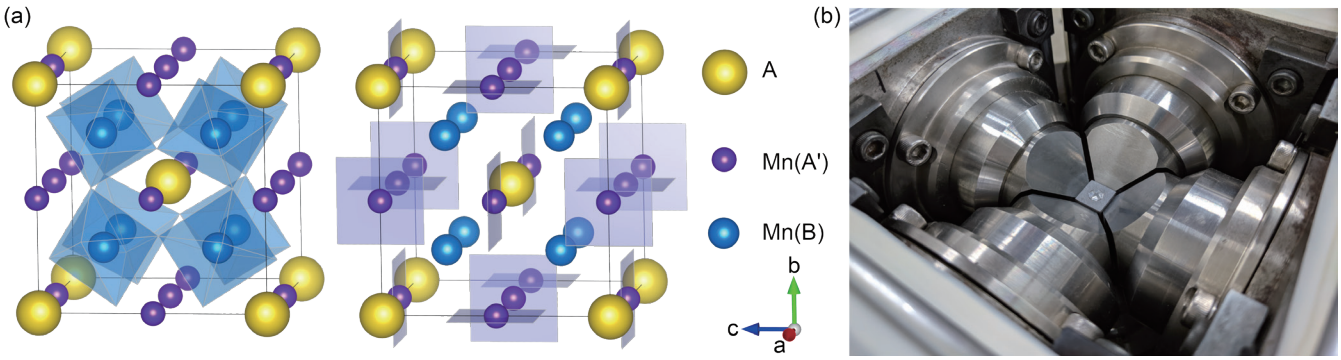

Fig. 1: (a) Schematic crystal structure of AMn_7O_{12} quadruple perovskites, showing B-site octahedra Mn (left) and A'-site square-planar Mn (right). (b) DIA-type cubic anvil high-pressure apparatus employed in the related studies. The pressure cell is placed at the center of six tungsten carbide anvils for HPHT synthesis. [Image courtesy of Wei-Tin Chen]

perovskites; the key regime has been established that $x = 3/8$ in narrow-bandwidth $Pr_{1-x}Ca_xMnO_3$ and $La_{1-x}Ca_xMnO_3$ systems corresponds to a maximum MR effect. With HPHT-synthesized 134 quadruple perovskites $AMn_3Mn_4O_{12}$ (or AMn_7O_{12}) solid solution, in which $A = La_{1-x}Ca_x$ and $Na_{1-x}Ca_x$ at intervals $\Delta x = 0.1$, the system can serve as a prototype to revisit the $x = 0$–$1/2$ doped regime of the LCMO manganites in detail.[2] There are several advantages that make the current 134 system a sufficient model for the present study. The small variations in cell volume (< 2%) and octahedral tilt angles (138.7° ± 1.2°) of the entire solid solution prevent the band-narrowing physics to the electronic doping accordingly. The octahedral tilt pattern of the series is locked as $a^+a^+a^+$ in Glazer's notation with phase transitions so that further lattice distortion becomes indicative of long-range orbital ordering. The degree of crystallinity of these HPHT synthesized samples is much greater than simple perovskites of similar composition; the microstrain remains exceptionally low across phase transitions ($e_0 \leq 0.015\%$), evident of the absence of significant intrinsic phase segregation. From detailed variable-temperature SXRD and NPD experiments, four distinct crystallographic phases and a comprehensive

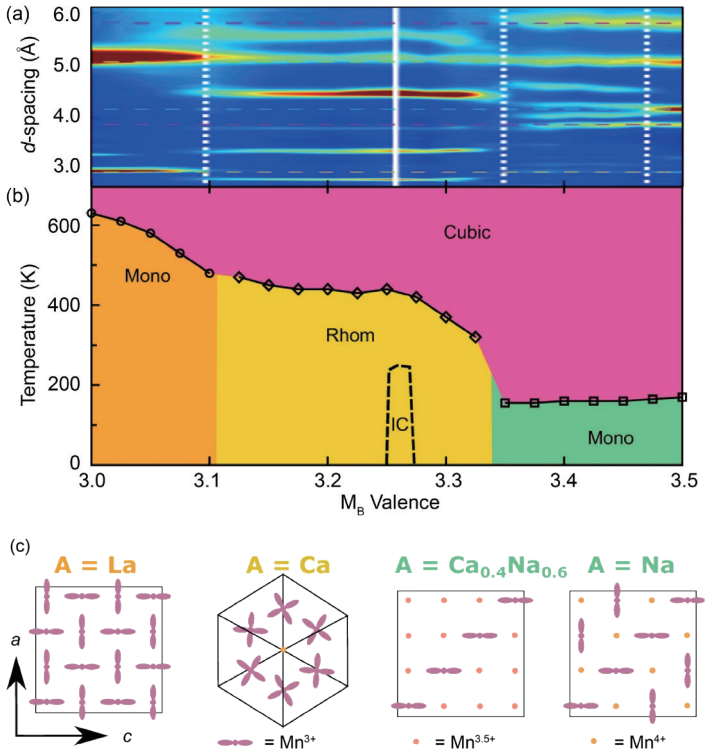

Fig. 2: (a) Magnetic phases observed from heat map of NPD patterns at base temperature. (b) Detailed temperature and compositional phase diagram of $AMn_3Mn_4O_{12}$ solid solution. (c) Four distinct structural phases with various orbital ordering at representative A-site compositions. [Reproduced from Ref. 2]

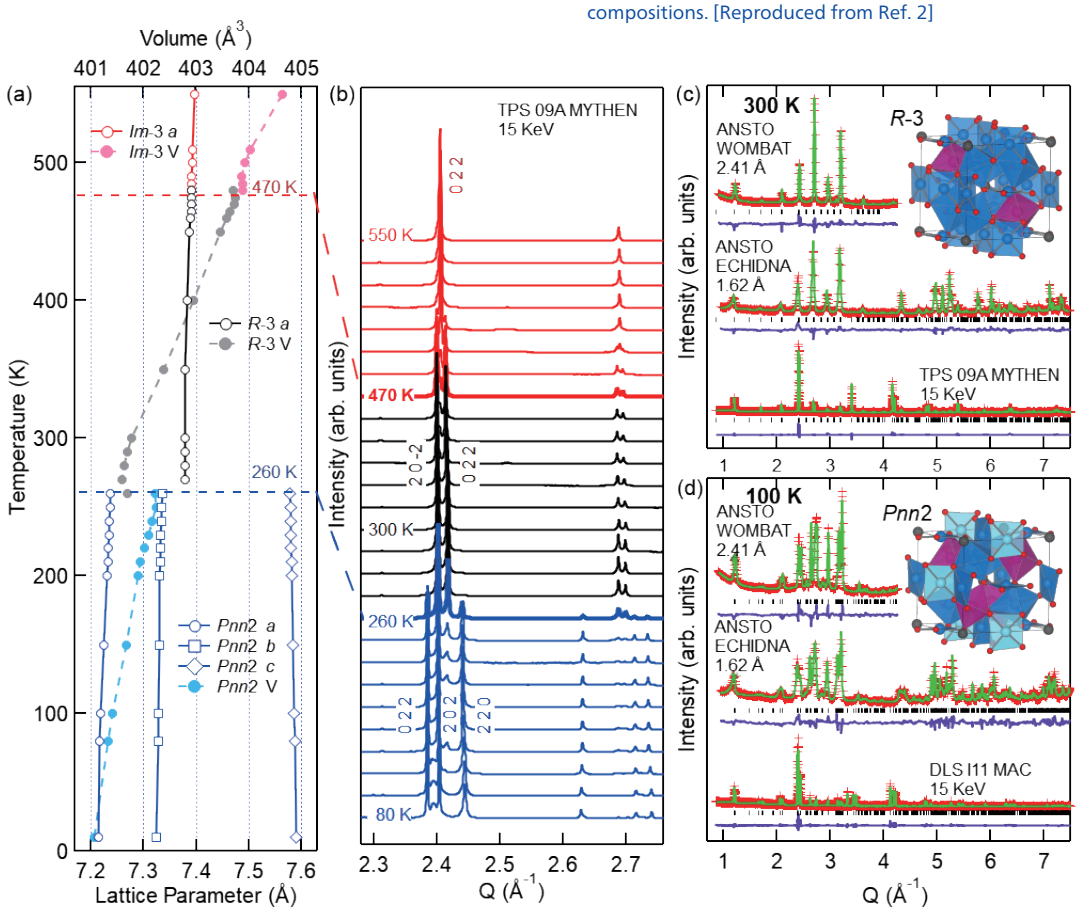

Fig. 3: Structural phase transitions of HMO from high-temperature cubic to intermediate-temperature rhombohedral and to low-temperature orthorhombic phases. (a,b) Evolution of lattice parameters, volume and selected SXRD pattern across the phase transitions. (c,d) Detailed structure and symmetry-element analysis from SXRD and NPD joint Rietveld refinements of data at 300 and 100 K. [Reproduced from Ref. 4]

temperature and compositional phase diagram were obtained; a new magnetic ordered phase was observed (**Fig. 2**). the Utilizing web-based symmetry analysis tool, *ISODISTORT*,[3] the evolution of tetragonality and the transformation of orbital-ordering distortion modes were revealed. At a particular doping region, an arrangement of alternating ordered-insulating and disordered-conducting electron stripes forms a new state of matter. Such structural insight provides evidence showing how an external magnetic field induces the collapse of an insulating state, and how the MR effect might be enhanced in operational temperatures and sensitivities.

The collaborative team by using symmetry-analysis approach also demonstrated a new paradigm of improper ferroelectric polarization. In type-II MF mechanism, the polarization is a secondary order parameter of the primary magnetic ordering. Novel $HgMn_7O_{12}$ (HMO) quadruple perovskite was prepared with HPHT techniques, exhibiting a MF property at low temperarture.[4] Compared to its analogue $CaMn_7O_{12}$, in addition to the charge-ordering phase transition from cubic to rhombohedral phases at high temperature, HMO experienced a further symmetry-lowering transition on cooling at ~260 K to orthorhombic phase *Pnn*2 according to SXRD and NPD joint Rietveld refinement (**Fig. 3**). It was revealed from symmetry element analysis that the improper ferroelectric polarization in HMO originated from the lattice instabilities directly linked to charge and orbital degrees of freedom.

In summary, the recent work of Chen and his collaborators demonstrated that the detailed crystallographic information was basic but essential to explain the physical properties intrinsically. The systematic examination of symmetry elements has provided crucial structural insight and mechanistic understanding of intriguing physical phenomena that are not only fascinating in fundamental research but also important in technological application. Collaborative projects adopting symmetry-analysis approach continue to further examine the magnetic structures and commensurate-incommensurate magnetic-phase transitions of the related functional materials. (Reported by Wei-Tin Chen, National Taiwan University)

This report features the quadruple perovskite-related work of Wei-Tin Chen and his collaborators published in Nat. Commun. ***12****, 6319 (2021) and Phys. Rev. B* ***97****, 144102 (2018).*

ANSTO WOMBAT – High-intensity Powder Diffractometer
ANSTO ECHIDNA – High-resolution Powder Diffractometer
TPS 19A High-resolution Powder X-ray Diffraction

- NPD, PXRD
- Materials Science, Condensed-matter Physics, Chemistry

References

1. M. Uehara, S. Mori, C. H. Chen, S. W. Cheong, Nature **399**, 560 (1999).
2. W.-T. Chen, C.-W. Wang, C.-C. Cheng, Y.-C. Chuang, A. Simonov, N. C. Bristowe, M. S. Senn, Nat. Commun. **12**, 6319 (2021).
3. B. J. Campbell, H. T. Stokes, D. E. Tanner, D. M. Hatch, J. Appl. Crystallogr. **39**, 607 (2006).
4. W.-T. Chen, C.-W. Wang, H.-C. Wu, F.-C. Chou, H.-D. Yang, A. Simonov, M. S. Senn, Phys. Rev. B **97**, 144102 (2018).