

## Crystal structure evolution in mercury containing quadruple perovskites

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$AMn_7O_{12}$  manganite belongs  $AA'_3B_4O_{12}$  quadruple perovskite family, where  $Mn^{A'}$   $Mn^B$  cations occupy square-planar and heavily tilted octahedral sites, respectively. Novel quadruple perovskite  $AMn_7O_{12}$  ( $A = Hg, HMO$ ) was prepared by high pressure high temperature (HPHT) synthesis techniques and exhibit multiferroic property at low temperature. [1] In addition to the charge ordering phase transition from cubic to rhombohedral phases observed at its analogue cousin  $CaMn_7O_{12}$ , HMO experiences a further symmetry-lowering phase transition to  $Pnn2$  orthorhombic phase close to room temperature  $\sim 260$  K. It was revealed from symmetry element analysis that the improper ferroelectric polarization in HMO originates from the lattice instabilities directly linked to charge and orbital degrees of freedom. On the other hand,  $AMn_7O_{12}$  solid solution ( $A = La_{1-x}Ca_x$  and  $Na_{1-x}Ca_x$ ) series were also realized by HPHT techniques. [2] Detailed crystallographic study revealed the evolution of tetragonality and the transformation of orbital ordering distortion modes in the solid solution. An alternating ordered-insulating and disordered-conducting electron stripes arrangement was observed at particular doping region, showing a new state of matter. From these studies, it was demonstrated that while the  $A'$ -site is rather robust, the charge and orbital ordering and their intrinsic coupling are very sensitive to the  $A$  cation oxidation state and consequently  $B$  cation valence. In this report, the rhombohedral to orthorhombic phase transition observed in HMO is further investigated with chemical pressure, electron- and hole-doping, and the crystal structure evolution of HMO pristine material are discussed.

[1] Chen, W.-T., Wang, C.-W., Wu, H.-C., Chou, F.-C., Yang, H.-D., Simonov, A. & Senn, M. S. (2018). *Phys. Rev. B*, **97**, 144102.

[2] Chen, W.-T., Wang, C.-W., Cheng, C.-C., Chuang, Y.-C., Simonov, A., Bristowe, N. C. & Senn, M. S. (2021). *Nat. Commun.*, **12**, 6319

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