Poster

Hybrid improper ferroelectricity in columnar $(NaY)MnMnTi_4O_{12}$

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Perovskite-type oxides (ABO_3) are largely engineered for the realisation of multiferroic materials as they can host proper ferroelectric instabilities. The perovskite framework can also support the more exotic, yet easier to engineer, mechanism of electric polarisation known as hybrid proper improper ferroelectricity. However, this mechanism has been limited to layered structures [1,2]. Here, we report two new quadruple perovskite structures of $(NaY)MnMnTi_4O_{12}$ with the same nominal composition. These samples were analysed using neutron diffraction, synchrotron X-ray diffraction, second harmonic generation measurements and piezoresponse force microscopy. We show that cation ordering on A site columns, oppositely displaced via coupling to B site octahedral tilts, results in a polar phase of the columnar perovskite $(NaY)MnMnTi_4O_{12}$, see Figure 1. This scheme is similar to hybrid improper ferroelectricity found in layered perovskites, and can be considered a realisation of hybrid improper ferroelectricity in columnar perovskites. The cation ordering is controlled by annealing temperature and when present it also polarises the local dipoles associated with the proper instability of the pseudo-Jahn–Teller active Mn^{2+} ions to establish an additional ferroelectric order. Below $T_N \approx 12$ K, Mn^{2+} spins order, making the columnar perovskites rare systems in which ordered electric and magnetic dipoles may reside on the same transition metal sublattice. The columnar perovskite framework provides great chemical flexibility, and one might anticipate a number of materials similar to $(NaY)MnMnTi_4O_{12}$ that can realise hybrid improper ferroelectricity with cross-coupled polar instabilities intimately related to magnetism.

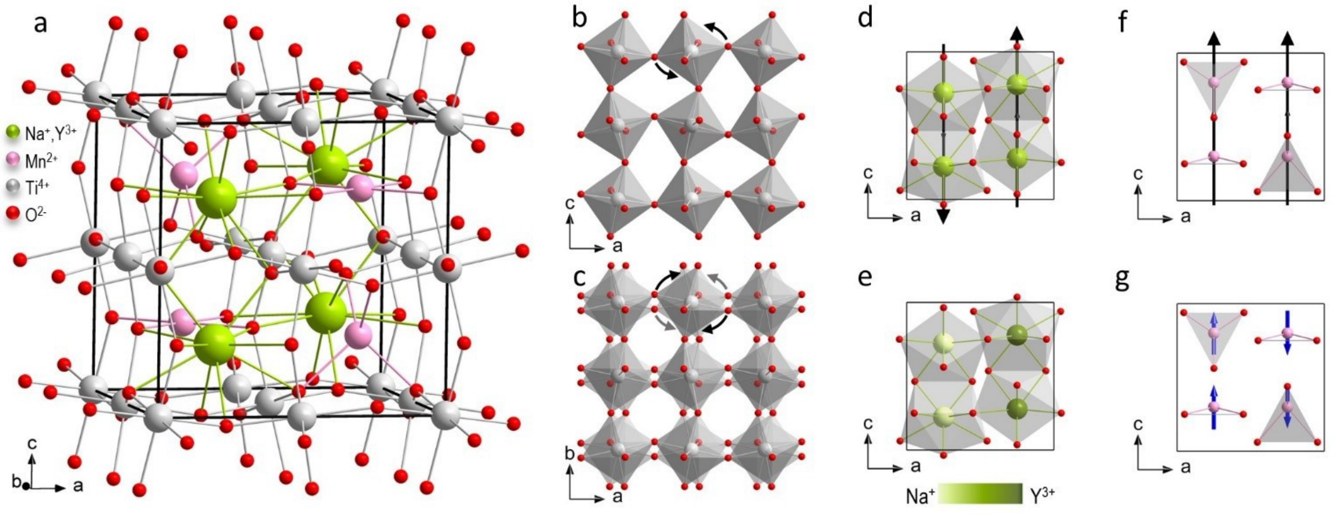

Figure 1. Crystal structure of $(NaY)MnMnTi_4O_{12}$, (b) $(a^+,a^+,0)$ octahedra tilts (A4+ irrep), (c) (0,0,c-) octahedra tilts (Z2- irrep), (d) columnar shifts (M3- irrep), (e) cation ordering (M1+ irrep), (f) proper polar distortions (Γ3- irrep) and (g) C-type magnetic structure.

[1] S. Mallick, S., Fortes, A. D., Zhang, W., Halasyamani, P. S. & Hayward, M. A. (2021) *Chem. Mater.* **33**, 2666–2672.

[2] Benedek, N. A. (2014) Inorg. Chem. **53**, 3769–3777.