A New Piezoelectric Layered Oxides Family, NaRTiO$_4$

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Rotations of oxygen octahedra are ubiquitous in ABO$_3$ perovskites, but they cannot break inversion symmetry in simple perovskites. However, in a layered oxide structure, this is possible, as we demonstrate here in A-site ordered Ruddlesden-Popper NaRTiO$_4$ (RE; rare earth), previously believed to be centric. As shown in panel (a), a simple $n=1$ RP phase $A_2BO_4$ possesses inversion centers (marked as $x$'s). These inversion centers at the B sites are removed in the A-site-ordered structure with P4/nmm space group in panel (b). The remaining inversion centers can be removed by oxygen octahedral rotations as shown in panel (c). By revisiting this series via synchrotron x-ray diffraction, optical second-harmonic generation (panel (d)), piezoresponse force microscopy, and first principles phonon calculations, we find that the low-temperature phase belongs to the acentric space group $P42_{1}m$, which is piezoelectric. This study suggests that other A-site-ordered $n=1$ layered phases including ARTiO$_4$ (A=H, Li, Na, K, Ag; R=rare earth) could be piezoelectric, where we predict a similar mechanism to be active.

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Discovery of a Family of Improper Acentric Oxides: NaRTiO$_4$: Top (a) An $n=1$ RP phase $A_2BO_4$ [I4/mmm], (b) an $n=1$ RP phase with layered A-site-cation ordering AA’BO$_4$ [P4/nmm], and (c) AA’BO$_4$ with $a$–$b_0^0c_0^0$-$b_0^0a_0^0$-type octahedral rotations [P-42$_1$m]. The cross symbols indicate the locations of inversion centers. (Below) Temperature dependence of SHG intensity for NaRTiO$_4$ with R = La, Nd, Sm, Eu, Gd, Dy, Y, Ho. The inset shows the NaRTiO$_4$ pellet samples.