A New Piezoelectric Layered Oxides Family, Na*R*TiO_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 Na*R*TiO_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 P-42_1*m*, which is piezoelectric. This study suggests that other A-site-ordered n=1 layered phases including A*R*TiO_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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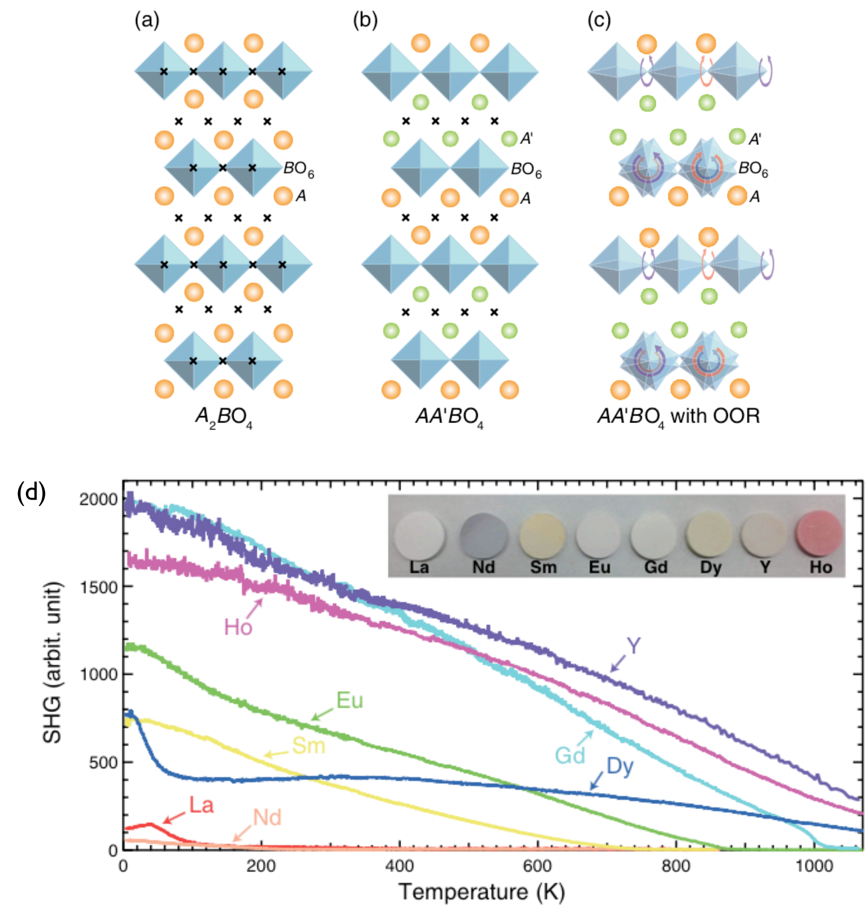

Discovery of a Family of Improper Acentric Oxides: Na*R*TiO_4: Top (a) An n=1 RP phase A_2BO_4 [I4/mmm], (b) an n=1 RP phase with layered A-site-cation ordering AA'BO [P4/nmm], and (c) $AA'BO_4$ with $a^-b^0c^0/b^0a^-c^0$-type octahedral rotations [P-42_1m]. The cross symbols indicate the locations of inversion centers. (Below) Temperature dependence of SHG intensity for Na*R*TiO_4 with R = La, Nd, Sm, Eu, Gd, Dy, Y, Ho. The inset shows the Na*R*TiO_4 pellet samples.