Supporting Information for

Emergent ultrasmall multiferroics in paraelectric perovskite oxide by hole polarons

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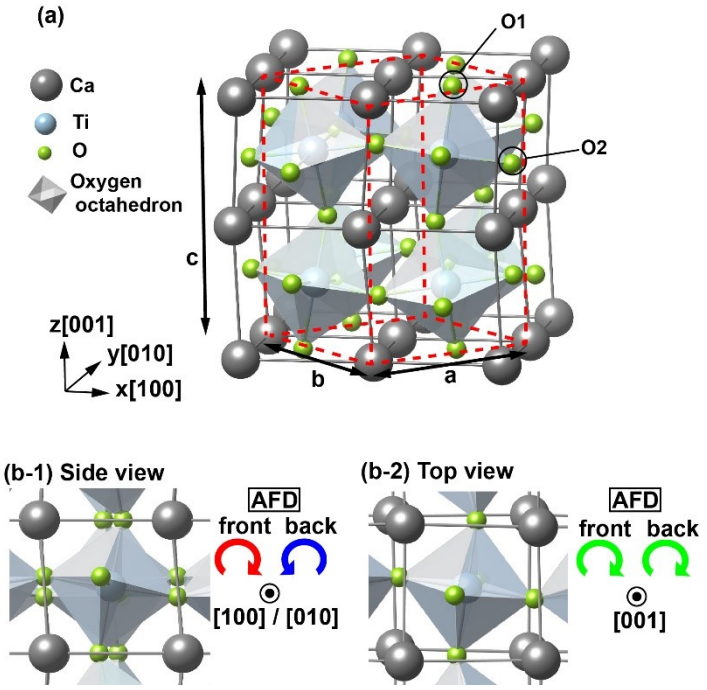

Fig. S1. (a)Crystal structure of orthorhombic $CaTiO_3$. The red dot box indicates the primitive cell. (b-1)(b-2)AFD displacement exist in this structure. The arrows indicate AFD displacement around each axis.

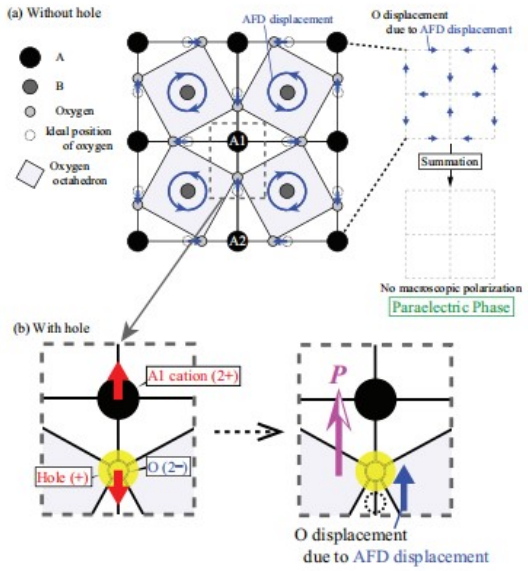

Fig. S2. (a)Schematic diagram of perovskite ABO_3, which has uniaxial AFD displacement. Blue arrows indicate the displacement of O atoms due to AFD displacement. (b)Schematic diagram of ABO_3 with hole polaron(yellow area). The red arrows indicate the displacement of A1 and O atoms due to the localization of hole. The pink and blue arrows indicate the direction of polarization and the displacement of O atom due to AFD displacement, respectively.

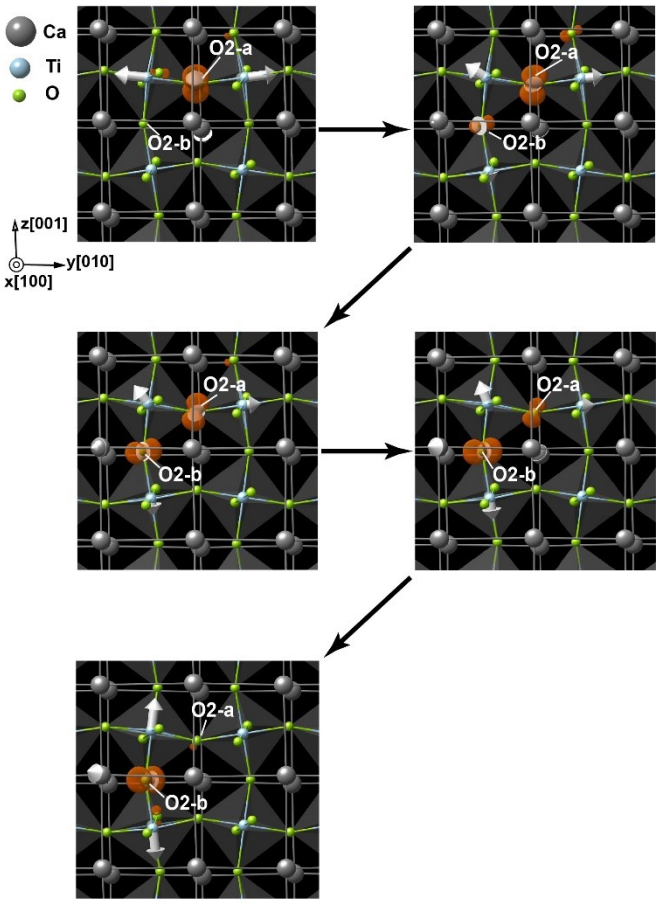

Fig. S3. The evolution of the squared wave function of the hole polaron in $CaTiO_3$ along the migration pathway. The yellow area represents the iso-surface of charge densities of 0.02 $Å^{-3}$. White arrows indicate the small displacement of atoms around the hole polaron.

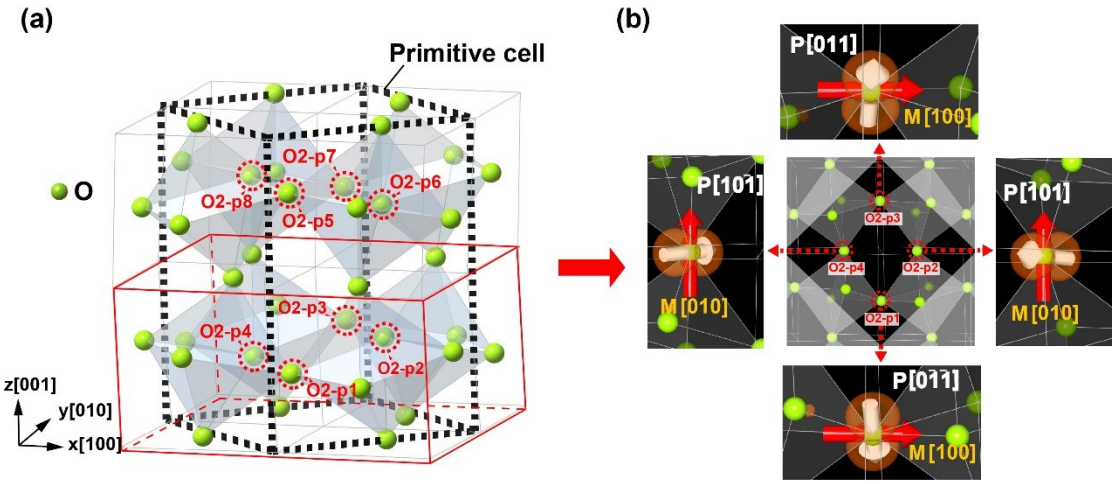

Fig. S4. (a)O2 atoms in primitive cell (black dot box) of orthorhombic $CaTiO_3$. (b)The direction of polarization (white arrows) and magnetic moment (red arrows) in the case of the hole polaron at each O2 atom.

Table S1. Band gap E_{gap}, lattice parameters *a*, *b,* and *c* of orthorhombic $CaTiO_3$ calculated using HSE06. The experimental values [1,2] are also shown for comparison.

	HSE06	Exp
E_{gap} (eV)	3.86	3.8 ~ 4.4
a (Å)	5.36	5.38
b (Å)	5.43	5.44
c (Å)	7.61	7.64

Table S2. Activation energy *Ea* and the hole polaron mobility μ for polaronic migration in $CaTiO_3$ from initial to the final structure.

Number of O2	O2-b,d	O2-c,e		
E_a (meV)	148.0	167.0		
$\mu(\times 10^{-3})(cm^2/Vs)$	2.52	1.19		
Number of O1	O1-a	O1-b	O1-c	O1-d
E_a (meV)	151.6	250.8	265.5	136.9
$\mu(\times 10^{-3})(cm^2/Vs)$	2.19	4.73×10^{-2}	2.69×10^{-2}	3.79

Reference

[1] A. R. Chakhmouradian, R. H. Mitchell, *J. Solid State Chem*., 1998, **138**, 272277.
[2] A. Krause, W. M. Weber, D. Pohl, B. Rellinghaus, A. Kersch, T. Mikolajick, *J. Phys. D: Appl. Phys*., 2015, **48**, 415304.