Supplementary Information

Collective nonlinear electric polarization via defect-driven local symmetry breaking

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I. Characterizations

Structure and phase characterizations



Figure S1. Structure and phase characterization of Mg_xTi_{1-x}O_{2-δ} at different doping levels (a x=0.25 at%, b x=0.5 at%, c x=1 at%, and d x=5 at%). The black and red bars at the bottom of each graph are the standard diffraction patterns for rutile TiO₂ pattern (JCPDS No. 21-1276) and orthorhombic MgTi₂O₅ pattern (JCPDS No. 98-003-7232), respectively. All the figure shows the experimental XRD data and the calculated pattern by Jana2006, the negligible variation in the difference confirm the good calculation. For the sample presenting the single rutile phase, the unitcell parameters exhibit a small expansion with increasing the Mg content (a=4.5949(5) Å, c=2.9597(4) Å for x=0.25 at% and a=4.5963(5) Å, c=2.9606(5) Å for 0.5 at%), which is possibly due to the larger ionic radius of Mg²⁺ in comparison with Ti⁴⁺. Moreover, as the doping level increases, the relative intensity of some diffraction peaks change obviously. For example, the peak intensity $I_{(211)}$ at (211) and its ratio (i.e. $I_{(211)}/I_{(110)}=0.285$ for x=0.25 at%, and $I_{(211)}/I_{(110)}=0.474$ for x=0.5 at%) relative to the main peak increase obviously, suggesting the change of the atomic position or the preferred orientation after the introduction of Mg with larger ionic radius into the host rutile TiO₂ structure, which has been similarly observed in rutile TiO₂ doped with sterically mismatched In³⁺ ions. While, for sample with higher doping levels (1 at% to 5 at%), the pattern needs to be fitted by rutile TiO₂ phase and orthorhombic MgTi₂O₅ phase. Two characteristic peaks of the orthorhombic MgTi₂O₅ in the x=1 at% sample, including (110) and (023) indicated by asterisks, can be observable. And more characteristic peaks are significant in the 5 at% as shown in Figure S1d with asterisks and indexed as well. These XRD analyses suggest the doping limits of Mg into the rutile TiO2 is less than 1 at%, which is in a good agreement with the results reported previously^{1, 2}.



Figure S2. Four BSE images (up, from left to right) and corresponding SE images (down, from left to right) scanned in an area on surface of 0.5 at at% Mg-doped rutile TiO_2 where the areas were chosen so that each of the right-hand images partially overlaps with the image to the left, to depict a continuous scanning area.



Figure S3. Four BSE images (up, from left to right) and corresponding SE images (down, from left to right) scanned in an area on surface of 1 at% Mg-doped rutile TiO_2 where the areas were chosen so that each of the right-hand images partially overlaps with the image to the left, to depict a continuous scanning area.

Mg-doped rutile TiO₂ shows a pure rutile phase at low doping levels. The XRD patterns of the synthesized samples indicates that the Mg-doped rutile TiO₂ contains a second phase of MgTiO₃, as shown by the peaks within the blue rectangular regions at doping level beyond 1 at% (Figure S1). The main reason for this is that the ionic size of Mg²⁺ (86 pm) is much larger than that of the Ti⁴⁺ (74.5 pm). According to the bond valence sum (BVS) calculation,³ replacing the Ti⁴⁺ with Mg²⁺ in the rutile TiO₂ average structure gives a 30.6% over-bonded, apparent valence (AV) for the Mg²⁺ ion of +2.6121, which makes the structure instability index to be about 0.3119. The high

structure instability makes it hard for high concentration of Mg to be soluble in rutile TiO₂, thus resulting in secondary phase. Our results are also consistent with the reported literature that small amount of Mg can be doped into TiO₂.^{1, 2} To further confirm the Mg was doped into the rutile TiO₂, the pure phase of the Mg doped rutile TiO₂ at relatively low levels, e.g. 0.5 at%, microstructure, element distribution and chemical composition were determined by field emission scanning electron microscopy (SEM, Zeiss Ultraplus) in conjunction with an energy dispersive Xray spectrometer (INCA Energy 450 EDXA system), back scattered electron image (BSE) and secondary electron image (SE) were used to confirm the pure phase of the 0.5 at% Mg-doped rutile TiO₂, particularly, we randomly scanned four continued areas on 0.5 at% (Figure S2) and 1 at% (Figure S3) Mg-doped rutile TiO₂ for comparison. To prove the images from left to right are continuous, the images on the left partially overlap with the adjacent ones on the right. It is obvious from Figure 1b that there is no secondary phase within the grain or grain-boundary in 0.5 at% Mg doped rutile TiO₂, indicating a homogenous chemical composition distribution, while, in contrast, the 1 at% Mg doped rutile TiO₂ typically shows obvious secondary phase in each image as shown in Figure S3. Therefore, there is no secondary phase observable in the images in 0.5 at% Mg doped rutile TiO₂ while there is obvious secondary phase in the 1 at% Mg doped rutile TiO₂. These results are consistent with the XRD pattern that the 0.5 at% Mg doped rutile TiO₂ shows a pure rutile TiO₂ phase. In light of these considerations, we mainly focus on 0.25 at% and 0.5 at% Mg doped rutile TiO₂.



Figure S4 (a) EPR spectra of the blank quartz tube (black curve) as background and 0.5 at% Mg doped rutile TiO₂(red curve). (b) EPR spectrum of background (black curve), 0.5 at% Mg doped rutile TiO₂(red curve), and 0.5 at% In+Ta co-doped rutile TiO₂ (blue curve) with nominal composition $[(In_{0.5}Ta_{0.5})_{0.005}Ti_{0.995}O_2]^4$ where the signal of Ti³⁺ has been confirmed. Note: To make the comparison consistent, the weight of all the samples keeps ~0.1g and other

measurement conditions are also similar. As shown in Figure S4a, the quartz tubes did not have any EPR signal, demonstrating that they were well cleaned. When Mg doped TiO₂ with a doping level of 0.5 at% were added into the quartz tubes and also measured by the EPR instrument at 10 K, it almost presents the same EPR curve as that of quartz tube. Further comparing the EPR results of Mg doped TiO₂ with that of our other samples like In+Ta co-doped TiO₂ with nominal composition [(In_{0.5}Ta_{0.5})_{0.005}Ti_{0.995}O₂] (Figure S4b) confirmed,⁴ there is no obvious Ti³⁺ signal in the Mg doped TiO₂. In addition, we also did not find the EPR peak of V_0^{\bullet} (i.e., one electron is trapped on oxygen vacancy) at around g=2.004 as generally reported.⁵⁻⁷ Therefore, we claim that there were no Ti³⁺ and V_0^{\bullet} in Mg doped TiO₂.

Electric polarization characterization



Figure S5 Voltage dependent P-E and I-E loops of fresh 0.25 at% Mg doped rutile TiO_2 measured at 0.5 Hz (first loop without pre-poling). The maximum polarization value and current increase with the increasing electric field measured at 0.5 Hz, where two current peaks are nearly symmetrical about x axis.



Figure S6 I-E loops of fresh 0.25 at% Mg doped rutile TiO_2 measured with a triangle electric field at the frequency of 2 Hz, 50 Hz, 100 Hz, and 200 Hz. The current is presented using a normalized current (for comparison). For the I-E loops measured at different frequencies, their overall shapes are quite similar except the shift of the current peaks, suggesting that the increase of the switching field with the increase of frequency, not as the same as behavior observed in a normal ferroelectricity.



Figure S7 Temperature-dependent P-E loops selected at three temperature points at RT (black square), 325 K (red round), and 355 K (gree triangle) after the sample was negatively poled at room temperature. Increasing the temperature can reduce the internal bias and return to the fresh state once the temperature is sufficiently high.



Figure S8 The polarization fatigue of the positively poled polarization state, the evolution of P-E loops before fatigue and after fatigue. Inset image is the mean switching electric field $E_s=(E_{s+}+E_{s-})/2$ and negative remnant polarization P_{r-} as a function of the cumulative number of cycles. Poling electric field was set to be 2.5 kV/cm at RT. It is found that the electric-field-cycling also benefits the recovery of the internal field and the P-E loop shifts back to the origin after the electric-field cycled over 10^5 times. This suggests that such an internal field built in Mg-doped rutile TiO₂ is metastable.



Figure S9 Temperature-dependent dielectric spectra of 0.25 at% Mg doped rutile TiO₂ for fresh sample (a) and poled sample (c) measured from 20 Hz to 1 MHz over the temperature range 10 K to 450 K. A negatively electric field of 2.5 kV/cm is applied for poling at room temperature. (b) The complex permittivity (ϵ^*) plot of 0.25 at% Mg doped rutile TiO₂ fitted with Debye-derivative Havriliak-Negami relaxation (HN) model⁸ with respect to the relaxation peak just over 150 K. (d) The complex permittivity plot at selected temperature of 320 K for fresh sample (b) and with respect to the (d) as indicated by black and red dashed rectangle, respectively. The inset image in Figure S8b indicates an Arrhenius equation fitting on the thermal activated dielectric relaxation peak over 150 K corresponds to the blue dash circle in Figure S8a.

In the Debye-derivative Havriliak-Negami (HN) model,⁸ the $\varepsilon^*(\omega)$ can be expressed in a general form:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{\left(1 + \left(i\omega\tau_{HN}\right)^{\alpha}\right)^{\beta}} \tag{1}$$

where ε_s is the static permittivity, ε_{∞} the permittivity in the high frequency limit, ω the frequency, τ_{HN} the relaxation time, α the parameter for the peak breadth of the distribution of relaxation frequency and β the parameter for the symmetricity of the distributed function. Equation (1) reduces to an original Debye model when $\alpha = \beta = 1$. The equation also reduced to Cole-Davison equation when $\alpha = l$ and $0 < \beta < 1$.

It is obvious that the dielectric relaxation for the unpoled samples (Figure S9a) can be easily fitted quite well using Debye-like HN model with reasonable parameters (Figure S9b and Figure S8d), and the relaxation peak over 150 K and around 250 K was also analyzed by Arrhenius type fitting on f vs T to obtain an activation energy of 0.196 eV as shown in the inset image in Figure S8b. In contrast, the relaxation for the poled samples (Figure S9c) cannot be fitted by the Debye-like relaxation model as shown in Figure S9d, in which both the large value of relaxation time and value of β are non-physical.



Figure S10 (a)-(b) Non-linear polarization behavior in 0.25 at% Ni-doped rutile TiO₂. P-E and I-E loops measured using a triangle wave method with an ac field of 4 Hz for 0.5 at% Ni-doped rutile TiO₂. Though the non-linear polarization behavior is not as obvious as that observed in Mg-doped rutile TiO₂ as shown in the main article, it is confirmed from the I-E loop where similarly two current peaks observed which is attributed to domain-switching-like behavior. For the current as a function of time, it is obvious that the current reaches a maximum when the voltage is close to zero, which is significantly different from that observed in linear dielectric behavior like in pure rutile TiO₂ where the current is only proportional to the change of the voltage.

II. Model used to fit the additional thermal activated dielectric relaxation

The model was developed as proposed by Macedo et al.⁹ This model considers the relaxation act as the occurrence of two simultaneous events:

First, the molecule must attain sufficient energy to break away from its neighbors and change its orientation. Second, there must be a site with a defect in the vicinity of the moving molecule with sufficient local free volume for reorientation to occur. The probability of a transition from one orientation of the molecule to another is given by:

$$P = P_a P_d \tag{2}$$

where P_a is the probability of attaining sufficient energy to break the bonds and P_d is the probability that there is defect, i.e. oxygen vacancy moves to facilitate the reorientation of defect dipoles.

The probability P_a can be calculated on the basis of the activation energy theory of Eyring.¹⁰ In the modified form, it reads:

$$P_a \cong \exp[-E_a/k_B(T-T_0)] \tag{3}$$

where E_a the activation energy, k_B the Boltzmann constant, T_0 is called ideal glass temperature.

 P_d can be described within the framework of the Cohen and Turnbull approach.¹¹ In this approach, P_d can be calculated as the probability of finding the volume V^* of a defect necessary for a molecule reorientation to occur and is given by

$$P_d \cong \exp(-V^* N/V) \tag{4}$$

where V is the average free volume per defect. One should bear in mind that the value of the volume V^* is close to the volume of the molecule volume. The free volume concept deals with a constant number of molecules and considers the temperature dependences of the free volume. We assume that the temperature dependences of the number of defects N can be described by Boltzmann's law:

$$N = N_0 \exp(-E_d/k_B T) \tag{5}$$

where N_0 is the average number of reorientational molecules in the matrix, and E_d is the energy of the defect formation. By substitution Equation (3) to Equation (2) and taking into account that the V varies with temperature as a linear function, i.e. far less than the exponential term, we obtain

$$P_d \cong \exp(-C\exp(-E_d/k_B T)) \tag{6}$$

where $C = V^*N/V$. According to the definition, V^*/V stands for the maximum possible number of defects in the matrix. Therefore, *C* is a constant and is related to the defect concentration, and in the current case proportional to the capacitance of the measuring capacitor cell.

Assuming the dipole relaxation frequency is proportional to the transition probability, the relaxation frequency is obtained by

$$f = f_0 \exp\left[\frac{E_a}{k_B(T - T_0)} + C \exp(-\frac{E_d}{k_B T})\right]^{-1}$$
(7)

which describe the temperature dependences of the relaxation time corresponding to the relaxation process with simultaneous events of dipole reorientation and defect formation.

In our case, we treat the lattice polarization as the "reorienting molecule", with the defect transformation via oxygen vacancy movement taking the place of opening defects in the original theory. This facilitates alignment/de-alignment of defect-dipoles. E_a corresponds to the reorientation of the lattice in response to a defect transformation, and E_d corresponds to defect transformation (oxygen-vacancy move) during the alignment/de-alignment of defect-dipoles. The thermal activated behavior demonstrated in the frequency depend relaxation due to electrical poling was analyzed based on Equation (7). The best fitting gives reasonable parameters as follows: $f_0=1.91\times10^{12}$ Hz, $E_a=0.0438$ eV, $E_d=1.6$ eV, $T_0=321.47$ K, and $C=2.5\times10^{10}$. One should note, the E_d calculated here is within the mean activation energy range calculated by the DFT where both the equatorial position (four equilibrium sites) and axial position (two equilibrium sites) can be the site of the vacancy with different energy barriers between them (1.26 eV for equatorial position, and 1.77 eV for axial position). Therefore, the experimental results are quite consistent with the DFT calculation results.

We also further modified the fitting model by considering the different defect transformation energies. Following Equation (6), the temperature dependences of the number of defects N can be divided into two parts by $N=N_1+N_2$ where N_1 and N_2 corresponds to equatorial and axial position, respectively. Therefore, N can be written as:

$$N = N_{01} \exp(-E_{d1}/k_B T) + N_{02} \exp(-E_{d2}/k_B T)$$
(8)

where N_{01} and N_{02} are the average numbers of the two types of reorientational defect-dipoles corresponds to the two kinds of oxygen vacancy occupations, respectively, and their corresponding defect formation energy are E_{d1} and E_d , respectively. By substitution Equation (3) in to Equation (2) and taking into account that the V varies with temperature as a linear function, i.e. far less than the exponential term, we obtain

$$P_d \cong \exp[-C_1 \exp(-E_{d1}/k_B T) + C_2 \exp((-E_{d2}/k_B T)]$$
(9)

where C_1 and C_2 are defect concentrations corresponds to the two type of oxygen vacancy occupations.

Therefore, Equation (7) is modified as

$$f = f_0 \exp\left[\frac{E_a}{k_B(T - T_0)} + C1 \exp\left(-\frac{E_{d1}}{k_B T}\right) + C2 \exp\left(-\frac{E_{d2}}{k_B T}\right)\right]^{-1}$$
(10)

(1.0)

The poling induced relaxation process was analyzed based on both Equation (7) and Equation (10) as shown in Table S1. The best fitting results by equation (10) are shown in Figure 2e in the text. Table S1: The parameters obtained from best fitting the experimental data using Equation (7) and Equation (10).

	f_0	E_a	E_d	E_{dl}	E_{d2}	T_{0}	χ^2
	(Hz)	(eV)	(eV)	(eV)	(eV)	(K)	
Equation (7)	1.91×10 ¹²	0.0438	1.6			321.469	788.91
Equation (10)	2.64×10 ¹²	0.0435		1.26	1.769	321.58	668.99

Both equations can give a good fitting with reasonable fitting parameters. By fitting using Equation (7) we obtained a mean energy ~1.6 eV for defect formation, while using Equation (10) leads to slightly better fitting results with two activation energies of 1.26 eV and 1.77 eV, which are consistent with the results calculated by DFT of 1.3 eV and 1.8 eV, respectively. All the parameters are reasonable within the framework of ionic polarization¹² The eigen frequency is around 10^{12} Hz, which is within the THz range and reasonable for general ionic displacement. T_0 is quite close to the temperature corresponding to the relaxation peak ~328 K measured at 100 Hz. The relaxation behavior on the basis of the simple model developed is thus very consistent with the theoretical calculation results and other data. The dielectric relaxation analysis based on this model and

theoretical calculation providing robust evidence for the nonlinear polarization behavior and abnormal electric polarization. The model can be applied to the interpretation of the dynamic of defect-dipole distributed in the metal oxides.

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