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The contribution of doped-Al on the colossal permittivity properties of $Al_xNb_{0.03}Ti_{0.97-x}O_2$ rutile ceramics

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Supplementary information:

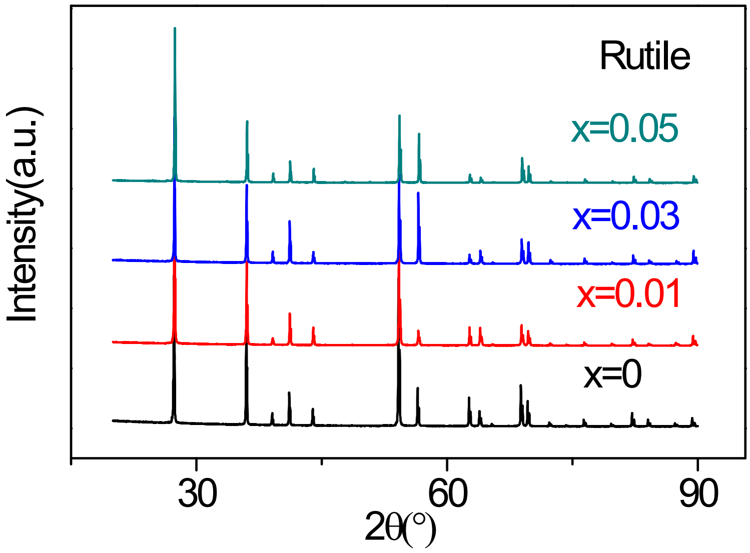

Figure S1 XRD patterns of Al+Nb co-doped rutile TiO_2 with different co-doping levels. The results indicate that all compositions have a pure phase rutile structure in average.

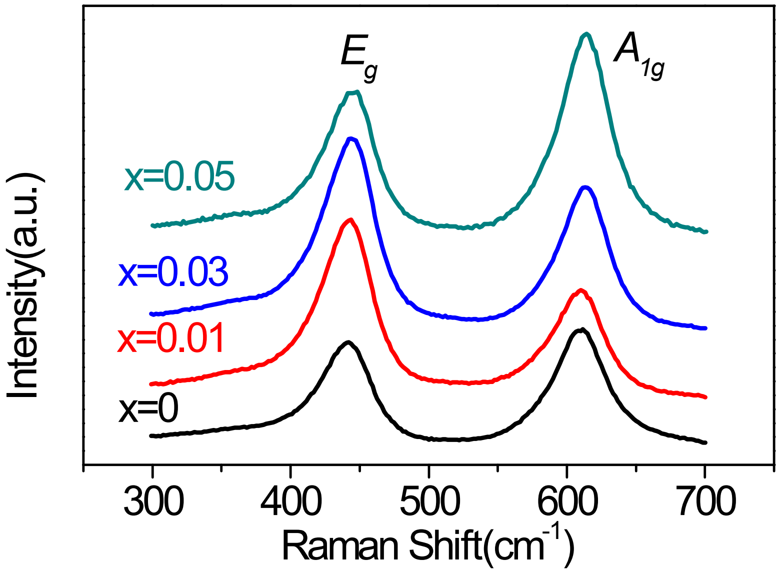

Figure S2. Raman spectroscopy of Al+Nb co-doped rutile TiO_2. Two strongest E_g and A_{1g} modes[1] at ~445 cm^{-1} and ~618 cm^{-1} were detected, which also indicate the pure rutile TiO_2 were synthesis

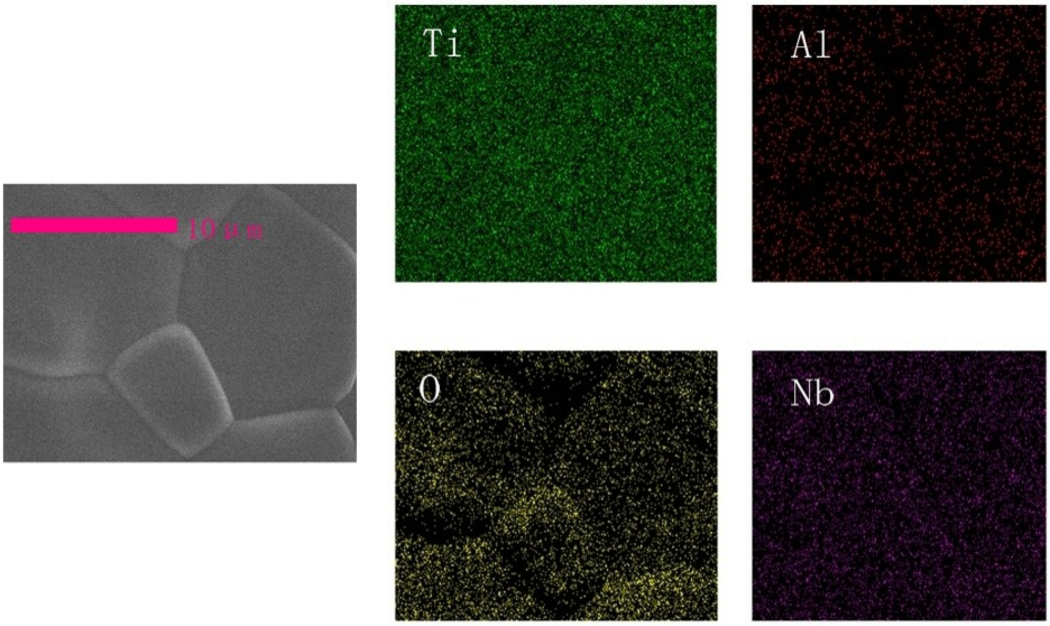

Figure S3. Element mapping of $Al_{0.03}Nb_{0.03}Ti_{0.94}O_2$ ceramics. The size of grain is about 10μm and all of the dopants are homogeneously distributed through the ceramics.

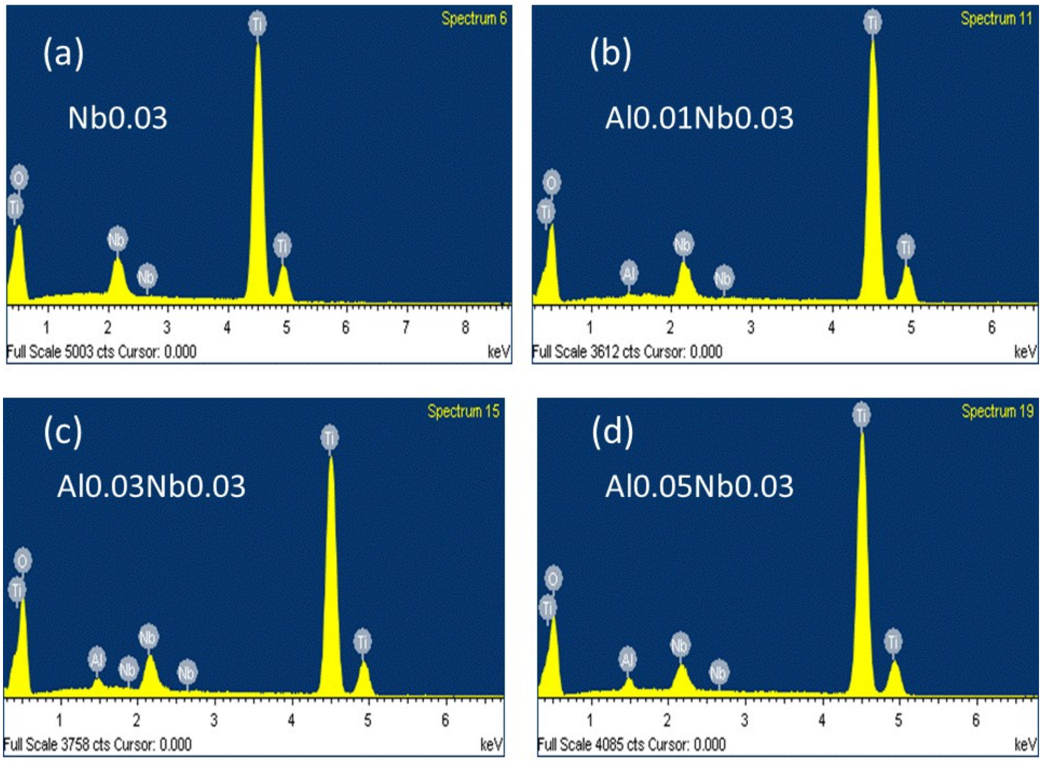

Figure S4. EDX of $Al_xNb_{0.03}Ti_{0.97-x}O_2$ (x= 0.01, 0.03, 0.05) ceramics, (a) x=0, (b) x=0.01, (c) x=0.03, (d) x=0.05. The doping amount of Al element increased with increasing Al-doping.

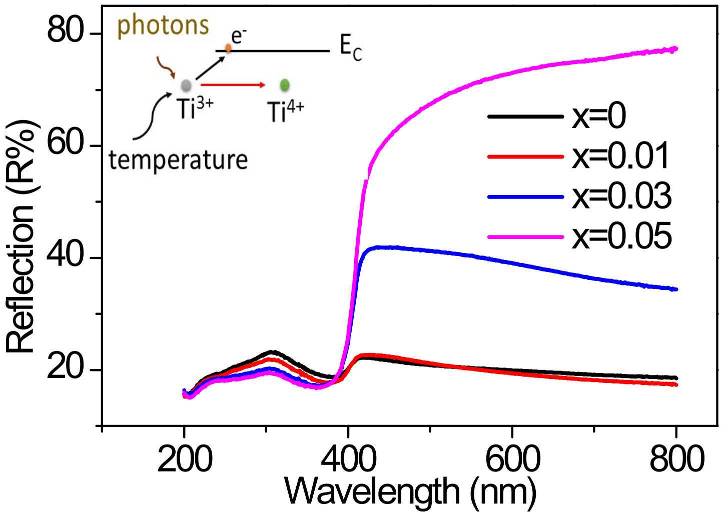

Figure S5. Reflectance spectra of $Al_xNb_{0.03}Ti_{0.97-x}O_2$ (x= 0, 0.01, 0.03, 0.05) ceramics.

Reflection spectrum is a powerful evidence for the hypothesis, the electrons of Ti^{3+} introduced by doped Nb can be easily be excited by probe light and show a low value in reflection spectrum, as shown in the insert. The reflection spectrum of all the samples have a sharply drop in the spectral region of λ~400 nm, which is attributed to the band gap ~3 eV of rutile TiO_2. In the spectral region of λ>400 nm, $Nb_{0.03}Ti_{0.97}O_2$ ceramics and $Al_{0.01}Nb_{0.03}Ti_{0.96}O_2$ ceramics have a similar reflection valve ~ 20%. With the increase of Al doping amount to 3%, the valve of reflection spectrum grow to 40%. When Al is excessive doping, the reflection valve is as high as 80%. For $Nb_{0.03}Ti_{0.97}O_2$ and $Al_{0.01}Nb_{0.03}Ti_{0.96}O_2$ ceramics, a lot of Ti^{3+} can absorb photons and result in a very low reflectivity. For $Al_{0.03}Nb_{0.03}Ti_{0.94}O_2$ ceramics, the remaining few Ti^{3+} can absorb a small amount of photons and show a moderate reflectivity about 40%. When the amount of doped Al is more than that of Nb, there is almost no Ti^{3+} left, so high reflectivity can be achieved.

Relationship between relaxation τ time and R_b: the reason for the larger bulk activation energy calculated by dielectric permittivity measurements at different temperature than real value

The relaxation time τ associated with the dielectric permittivity depends on the frequency can be described by the following equations:[S1]

$$\tau = \frac{\tau_{gb} R_b + \tau_b R_{gb}}{R_b + R_{gb}} \tag{S1}$$

Here, $\tau_b = C_b R_b$, $\tau_{gb} = C_{gb} R_{gb}$, R_b and R_{gb} are the resistance of the bulk and grain boundary, respectively. C_b and C_{gb} are the capacitance of the bulk and at the grain boundary, with $C_{gb} \gg C_b$, $R_{gb} \gg R_b$.[S1] Therefore, Eq (S1) can be formulated as

$$\tau = kR_b \tag{S2}$$

Here, k=R_{gb}/(R_{gb}+R_b) C_{gb} is a value closed to C_{gb} in view of that R_{gb} is much larger than R_b. So, the activation energy of bulk can be calculated by the following formula，and the dielectric relaxation time τ becomes smaller with increasing temperature due to the reduction of R_b.

$$\tau = \tau_0 exp(E_a / k_B T) \tag{S3}$$

But actually, k should slowly become larger as the temperature increases base on that the conductive activation energy of R_{gb} is much larger than that of R_b. So the activation energy of bulk is larger than real value.

S1. M. R. Shen, S. B. Ge and W. W. Cao, *J. Phys. D: Appl. Phys*, 2001, **34**, 2935.