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Theoretical elucidation and design of local atomic structures and their colossal permittivity properties of doped TiO₂

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I. INTRODUCTION

Recently, colossal permittivity (CP) material continues to arouse considerable interest motivated by their myriad device miniaturization and high-energy-density storage applications. So far, capacitors using CP materials are mostly based on ferroelectrics such as BaTiO₃ [1]. Unfortunately, the high permittivity of this material is temperature sensitive and thus ferroelectric based capacitors are hampered by the poor temperature stability of their capacitance. A number of new materials with nearly temperature independent CP have been discovered and expected to become potentially useful capacitor materials. A prominent example is CaCu₃Ti₄O₁₂ which achieved a large dielectric constant above 10⁴ over a large range of temperature [2]. Other non-ferroelectric transition-metal oxides including La_{2-x}Sr_xNiO₄ with CP near room temperature are also viable [3]. However, their high dielectric loss severely prevents them from being used to realize actual devices. Achieving CP and low dielectric loss in a single material is, therefore, still an extremely challenging task, which becomes even more difficult when other desirable properties such as temperature- and frequency-stability are added to the mix. The difficulty in achieving such behavior has greatly impeded the practical application of CP materials.

Doped TiO₂ material has aroused as a potential material which can overcome the roadblock of other CP material. The donor substitution are chosen as ion with valance 5 (V⁵⁺, Nb⁵⁺, Ta⁵⁺). Experimentalist has found that at high temperature, the colossal permittivity of this material is due to the Maxwell-Wagner effect. In this case, electrons prefer to

accumulate at grain boundaries, leading to very high dielectric dipole. At low temperatures, even though the Maxwell-Wagner effect is suppressed, the permittivity of doped TiO₂ is still very high (about four-fold compared to the undoped case) [4]. Therefore, the mechanism of colossal permittivity of doped TiO₂ at this regime is still unclear. At low temperatures, where the Maxwell-Wagner effect is largely suppressed, our previous study has revealed that small polarons become the dominant contributors to the dielectric response in Nb-doped TiO₂ [5]. Polarons are quasiparticles originating from the coupling between charge carriers and lattice distortions [6]. In the presence of an external electric field, their flip-flop hopping via the dopant leads to an increase in polarization and, consequently, in permittivity. Since Nb doping significantly enhances the low-temperature permittivity of TiO₂, it is important to examine whether other pentavalent dopants, such as V and Ta, can produce similar effects. Understanding this might help clarify how different dopants influence polaron dynamics and dielectric properties.

Additionally, the external pressure may significantly influences the polaron hopping barrier in doped TiO₂. To explore the relationship between pressure and the polaron hopping barrier, I perform DFT calculations to determine the hopping energy barriers in V-, Nb- and Ta-doped TiO₂ under varying pressure conditions. By comprehensively understanding the migration mechanism of polarons, this study aims to provide valuable insights for designing novel atomic structures and enhancing the colossal permittivity properties of doped TiO₂-based

materials.

II. COMPUTATIONAL METHOD

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP)[7], employing the projector augmented-wave (PAW) method [8,9] to optimize both geometric and electronic structures. The hybrid HSEsol [10,11] functionals were used in combination with the following PAW potentials: Ti_pv ($3p^63d^34s^1$), V_pv($3p^63d^44s^1$), Nb_pv ($4p^64d^45s^1$), Ta_pv ($5p^65d^46s^1$), and O ($2s^22p^4$). This combination has proven to yield accurate calculations of both the polaronic nature of doped TiO_2 and the static dielectric constant of pure rutile TiO_2 [5]. Structural relaxations were conducted using a force convergence criterion of 10^{-3} eV/Å and a plane-wave energy cutoff of 550 eV. To study the stability of polaron in doped TiO_2 , a $2\sqrt{2} \times 2\sqrt{2} \times 4$ supercell was employed with a Γ -centered k-point mesh of $1 \times 1 \times 2$. The hopping of polaron in doped TiO_2 is investigated using a large supercell in the hopping direction of $2 \times 2 \times 6$ with the k-point mesh is chosen as $2 \times 2 \times 1$. To investigate polaron hopping barriers, the nudged elastic band (NEB) method [12] was applied, considering 5 intermediate images between each pair of localized polaron sites.

III. RESULTS AND DISCUSSION

A. Stability of polaron in V, and Ta - doped TiO_2

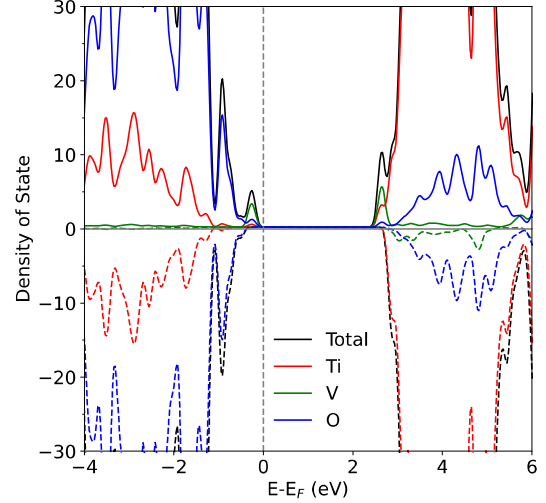


FIG. 1: Density of State of V-doped TiO_2

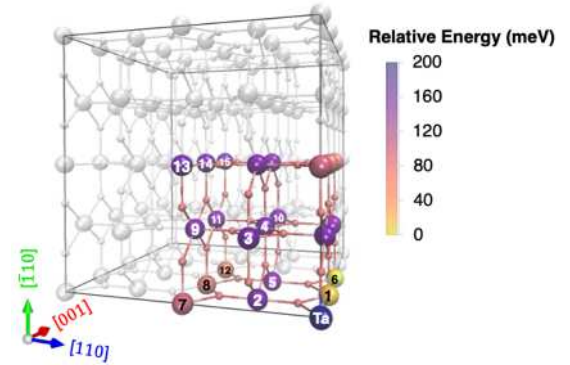


FIG. 2: The stability of polaron in Ta-doped TiO_2 . Numbers correspond to the proximity of Ti sites to the Ta dopant.

Fig.1 show the Density of State (DOS) of V-doped TiO_2 . In V-doped TiO_2 , the localization results in a mid-gap state of V^{4+} . The proximity of this state to the valence band maximum indicates that the excess electron is strongly bound to the V dopant, leading to the formation of V^{4+} . It is worth noting that, regardless of the initial localization (even when the excess electron is initially forced to localized on a Ti site), the electron ultimately relaxes to the V site after structural optimization. Since the potential energy surface of V-doped TiO_2 exhibits a single-well profile, polarization switching might not occur.

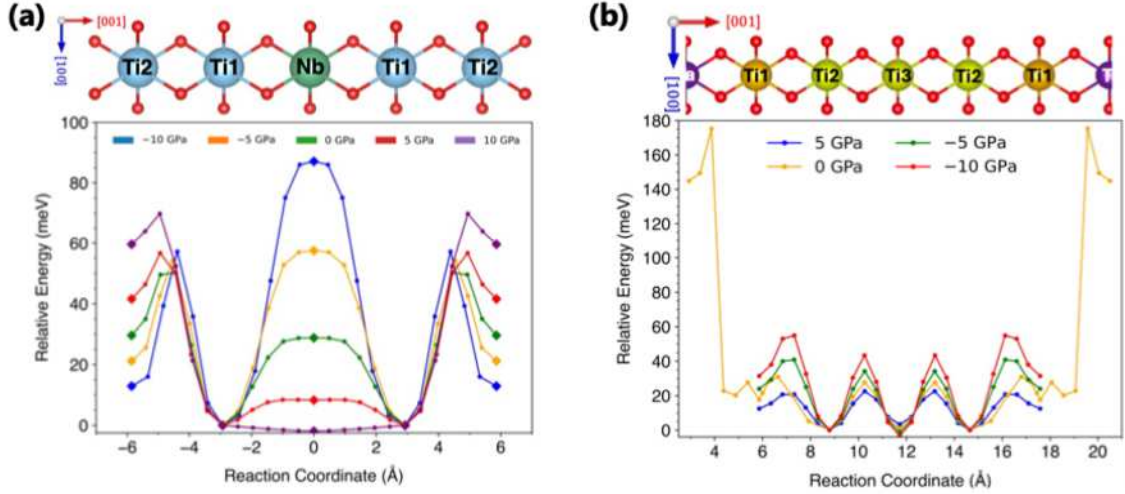


FIG. 3: The potential energy surface of polaron hopping in (a) Nb- and (b) Ta-doped TiO₂ under ambient, tensile and compressive pressure

As a result, polarons do not contribute to the enhancement of the dielectric response of this material at low temperatures.

In Nb-doped TiO₂, the polaron is most stable at the first nearest-neighbor Ti site to the dopant, followed by the second nearest-neighbor site in the [001] direction. In Ta-doped TiO₂, we find that the stability of polarons differs significantly from that in Nb-doped TiO₂. Figure 2 shows the relative energies of polaron localized at different sites in Ta-doped TiO₂, labeled according to their proximity to the dopant. The polaron is most stable when localized at the sixth nearest-neighbor Ti site (the second nearest neighbor in the [001] direction).

B. Polaron hopping in Ta doped TiO₂

Figure 3a shows the hopping path of polaron along the [001] direction and the hopping barrier when polaron hopping between these sites. The hopping path and activation energy of polaron in Nb-doped TiO₂ are shown in Fig. 3b as reference. From this figure, it is clear that Ta-doped TiO₂ is not only different from Nb-doped TiO₂ in the stability of polaron but also the polaron hopping behavior. In particular, the polaron does not hop through the dopant since the barrier for this hopping is very high of 175 meV. Instead, the polaron hopping between

Ti sites between Ta atoms is preferable since the barrier of this hopping is about 30 meV. Since Polaron in Ta-doped TiO₂ is confined between Ta dopants, at low doping concentration it is able to hop over longer distances and along more extended pathways than in Nb-doped TiO₂. This implies that Ta-doped TiO₂ exhibits a larger permittivity than Nb-doped TiO₂ at low temperature. Furthermore, the low hopping barrier of polarons in Ta-doped TiO₂ is comparable to that in pristine TiO₂ with an excess electron (TiO₂ + e⁻). This indicates that at sites sufficiently far from the dopant, polaron hopping is only weakly influenced by the presence of Ta and closely resembles that of a free polaron.

C. Polaron hopping in Nb- and Ta- doped TiO₂ under pressure

The polaron hopping barriers in Nb- and Ta-doped TiO₂ are also strongly influenced by hydrostatic pressure. To investigate the effect of pressure, the structure optimization calculations were first performed. The hydrostatic compressive (5 and 10 GPa) and tensile (-5 and -10 GPa) pressures were then applied to find the optimized structure and hopping barrier of polaron at these pressures. We find that tensile pressure increases the energy barrier for polaron hopping in every pathway,

whereas compressive pressure has the opposite effect, leading to a decrease in the barrier.

IV. CONCLUSION

Our findings suggest that the mechanism behind the colossal permittivity of doped TiO_2 at low temperatures involves the hopping of excess electrons within the material. Pentavalent ions such as V, Nb and Ta have an additional electron in their outer shell compared to Ti atoms. In V-doped TiO_2 , the excess electron is strongly bound to the V dopant, suppressing polaron hopping and dielectric dipole formation. When Ti is substituted with Nb or Ta, this excess electron can become localized, forming a quasi-particle known as a polaron. In Nb-doped TiO_2 , DFT calculations confirm that the excess electron from Nb localizes on the nearest titanium atom, resulting in a molecular polaron configuration. In contrast, in Ta-doped TiO_2 , the excess electron tends to localize on the second-nearest titanium atom along the [001] direction relative to the Ta atom.

This distinction also extends to the hopping mechanism. In Nb-doped TiO_2 , polaron hopping occurs via the dopant site, whereas in Ta-doped TiO_2 , hopping through the dopant is unfavorable. Instead, the polaron preferentially hops between Ti sites located between Ta dopants along the [001] direction. The more extended polaron hopping pathways are expected to enhance the permittivity than in Nb-doped TiO_2 , but also result in increased dielectric loss at low temperature. In both cases, the hopping barrier is increase under tensile pressure and decrease under compressive pressure.

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