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Band gap engineering strategy via polarization rotation in perovskite ferroelectrics

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We propose a strategy to engineer the band gaps of perovskite oxide ferroelectrics, supported by first principles calculations. We find that the band gaps of perovskites can be substantially reduced by as much as 1.2 eV through local rhombohedral-to-tetragonal structural transition. Furthermore, the strong polarization of the rhombohedral perovskite is largely preserved by its tetragonal counterpart. The *B*-cation off-center displacements and the resulting enhancement of the antibonding character in the conduction band give rise to the wider band gaps of the rhombohedral perovskites. The correlation between the structure, polarization orientation, and electronic structure lays a good foundation for understanding the physics of more complex perovskite solid solutions and provides a route for the design of photovoltaic perovskite ferroelectrics. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4871707]

Solar energy is widely viewed as a long term substitution of the traditional fossil fuels because it is clean, abundant, and renewable.[1] In the past few decades, considerable efforts have been made to design and optimize materials for photocatalytic or photovoltaic use with the aim of efficiently converting light to electrical energy. This requires sufficient absorption of the solar radiation, efficient separation of the photo-excited charge carriers, and a low charge recombination rate. Ferroelectrics (FEs) provide a route to separate charge by the bulk photovoltaic effect, where charge carriers are separated spontaneously by a single phase material.[2–4] However, most of the current FE oxides have wide band gaps ($E_g > 2.7$ eV for $BiFeO_3$, $E_g > 3.5$ eV for PZT) that are beyond the visible-light range and thus allow the use of only 8%–20% of the solar spectrum. Very recently, visible-light absorbing FEs have been reported,[5,6] and materials design of FEs with low band gaps in the visible-light range is still of crucial importance for their use in solar energy applications.

Perovskites (ABO_3) are the most well-studied class of ferroelectrics for solar energy and other applications. They are not only capable of hosting above 90% of the natural metallic elements, but are also highly tunable through substitution and/or mixed oxidation states. As a result, they can exhibit a variety of interesting bulk and interfacial properties, ranging from the ferroelectric, magnetic, superconducting, and catalytic properties to the two dimensional electron gas.[7,8] Understanding the underlying physical properties of perovskites especially the correlation between the composition, structure, and electronic properties is highly desired for the design of efficient solar energy absorbers and bulk photovoltaics. There have been several studies demonstrating that O_6 tilting distortions from the ideal high-symmetry cubic ABO_3 structure have a strong impact on the band gaps of perovskites.[9,10] On the other hand, the impact of ferroelectric cation off-center displacements on E_g has been largely ignored. Here, we find that the BO_6 octahedral distortions induced by the *B*-cation off-center displacements have a strong effect on the band gap and propose a strategy to reduce the band gaps of perovskites while maintaining their polarizations by rhombohedral (*R*)-to-tetragonal (*T*) structural transitions.

We performed first principles plane-wave density functional theory (DFT) calculations within the generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) approach,[11,12] as implemented in the QUANTUM-ESPRESSO code.[13,14] All elements are represented by norm-conserving, optimized nonlocal pseudopotentials with a cutoff energy of 50 Ry, generated with the OPIUM package.[15] The polarization was calculated following the Berry-phase approach[16,17] by choosing an adiabatic path from the centrosymmetric reference state to the equilibrium polarized state. $8 \times 8 \times 8$ Monkhorst-Pack *k*-point grids were used to sample the Brillouin zone, while the polarization was calculated with $6 \times 6 \times 20$ *k*-point grids, where the denser grids are for the polarization direction.[18] We also used two hybrid functionals: HSE06 and PBE0, to corroborate the band gap change trend that we find.[11,19–21] Note that the band gap here was estimated using the single-particle Kohn-Sham eigenvalues, which, although theoretically not fully justified, can be compared to the fundamental band gap obtained by photoemission or electrochemical mesurements.[22] We adopted a five-atom unit cell for both the *R* and *T* phase perovskites and fully relaxed the structures. For some perovskites (e.g., $BaTiO_3$), the experimentally found *T* phase is due to the averaging of local *R* cation displacements.[23] For these cases, the *T* phase studied in our five-atom calculations should be thought of as a local *T* phase that does not correspond to the experimental *T* phase but can be achieved in epitaxially strained thin films. For other perovskites (e.g., $BaZrO_3$), the ground state structure involves octahedral rotations that cannot be represented in a five-atom unit cell. Nevertheless, we used the simple five-atom cells on purpose to isolate the effects of *B*-cation displacements from the effects of other ABO_3 distortions.

Table I shows the calculated band gaps and polarizations of the *T* and *R* phases of various ABO_3 perovskites using three different methods. The electronic structure of typical

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TABLE I. The band gaps E_g (eV) of various rhombohedral (R) and tetragonal (T) oxides calculated with various functionals. The polarization (C/m^2) calculated at the GGA level is also shown. $LaScO_3$, $BaTiO_3$, $PbTiO_3$, $KNbO_3$, and WO_3 are from fully relaxed structures while $BaZrO_3$ and $KTaO_3$ are relaxed starting from the $BaTiO_3$ and $KNbO_3$ structures.

	E_g^{GGA}		E_g^{HSE06}		E_g^{PBE0}		P^{GGA}	
Composition	R	T	R	T	R	T	R	T
$LaScO_3$	3.49	3.36	5.16	5.08	5.89	5.82	0.29	0.20
$BaTiO_3$	2.30	1.74	3.72	3.12	4.46	3.86	0.40	0.28
$BaZrO_3$	3.56	3.04	5.04	4.51	5.77	5.24	0.32	0.22
$PbTiO_3$	2.29	1.70	3.51	2.92	4.19	3.63	0.72	0.97
$KTaO_3$	3.29	2.32	4.73	3.72	5.47	4.45	0.51	0.46
$KNbO_3$	2.40	1.39	3.68	2.60	4.42	3.32	0.56	0.50
WO_3	1.92	0.76	3.13	1.86	3.87	2.59	0.64	0.54

ABO_3 perovskites depends on the fundamental characteristics of the metal-oxygen chemical bonds. Because of the large electronegativity difference between oxygen and the metals, the band gap of a perovskite can be as large as >5 eV (e.g., 5.72 eV for $LaScO_3$). Basically, the top of the valence band (VB) arises mainly from the O 2p orbitals, while the bottom of the conduction band (CB) is essentially set by the B-cation d orbitals. Compared to the A-cation, the B-cation has a much more significant effect on fixing the band gaps. For example, the GGA band gap of rhombohedral $BaZrO_3$ is 1.3 eV larger than that of $BaTiO_3$ because Zr is less electronegative than Ti. Similarly, the band gap of $KTaO_3$ is around 0.9 eV larger than that of $KNbO_3$. Nevertheless, $BaTiO_3$ and $PbTiO_3$ have similar band gaps even though the electronegativity of Pb is much higher than that of Ba, suggesting a minor role of A-O chemical bonds in determining the band gaps.

Additionally, the band gaps of different phases of perovskites with the same composition can be quite different, indicating a more complex picture of the crystal structure and electronic structure in perovskites. Specifically, we find that the R perovskite phase always exhibits a larger band gap than its T counterpart irrespective of the composition (Fig. 1). The band gap difference between the R and T perovskites ranges from 0.1 eV for $LaScO_3$ to 1.2 eV for WO_3 using GGA (Table II). This trend is very robust and further corroborated by the hybrid functional calculations using HSE06 and PBE0. The HSE06 band gaps are 1.1–1.5 eV larger than the GGA gaps, while PBE0 increases the band gaps further by about 0.7 eV. However, the band gap differences change by less than 0.15 eV as the functional is varied. Fig. 1(b)

TABLE II. The band gap difference $E_g^R - E_g^T$ between R and T perovskite oxides with various functionals.

	$LaScO_3$	$BaTiO_3$	$BaZrO_3$	$PbTiO_3$	$KTaO_3$	$KNbO_3$	WO_3
GGA	0.13	0.56	0.59	0.68	0.97	1.01	1.18
HSE06	0.08	0.60	0.59	0.68	1.01	1.08	1.29
PBE0	0.07	0.60	0.56	0.65	1.02	1.10	1.30

shows the band gap difference as a function of the B-cation valence. As the B-cation valence increases from +3 to +6, the band gap difference is also substantially enlarged. Furthermore, the polarizations of the R perovskites are also uniformly enhanced except for $PbTiO_3$ (Fig. 1). Thus, the band gaps of perovskite oxides can be reduced by a large amount while the polarizations are still largely retained as they undergo the local R–to–T phase transitions.

To further investigate the origin of the large band gap difference between R and T perovskites, we plot the band structure and density of states (DOS) of $BaTiO_3$ (Fig. 2). Clearly, the band gap reduction from R to T phase arises from the down-shift of the CB since the VB is essentially unchanged. As shown in Fig. 2(a), the bottom of the CB in a perovskite oxide falls at the Γ point due to the essentially nonbonding B-O interaction constrained by the translational symmetry. At the A point, the B-O interaction is mainly antibonding. The contrast of the orbital character between the Γ and A points determines the CB width and the resulting band gap. As the B-cations move further off-center in the R phase, long *vs.* short bond length differences become significant along all the three crystallographic directions. Simultaneously, both O-B-O and B-O-B angles deviate severely from 180° and more antibonding character is induced at Γ-point by the distortion of the O-B orbital overlap.[9] Therefore, the bottom of the CB shifts up due to the enhanced antibonding interaction. This enhancement of the antibonding O-B interaction is increased as the valence of the B-cation increases. This is because when the B-cation changes from Sc^{3+} to W^{6+}, the electronegativity of the B-metal rises, leading to more covalent B-O bonds. Overall, the band gaps are substantially increased as the CB involves more antibonding character in the R phase.

To elucidate the connections between structural distortions and polarization, we carefully analyze the BO_6 distortions in perovskites. Basically, there are two kinds of BO_6 octahedral distortions: octahedral tilting and B-cation off-center displacement. In some materials (such as monoclinic WO_3), both BO_6 octahedral tilting and B-cation

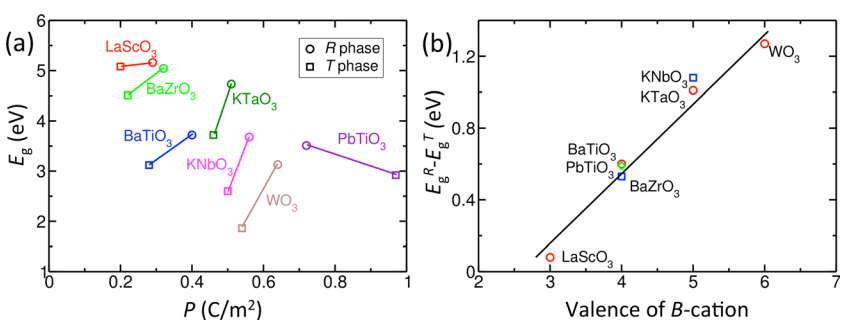

FIG. 1. (a) The HSE06 band gap (eV) as a function of the polarization (C/m^2) in T and R perovskite oxides and (b) the band gap difference $E_g^R - E_g^T$ as a function of the valence of the B-cation.

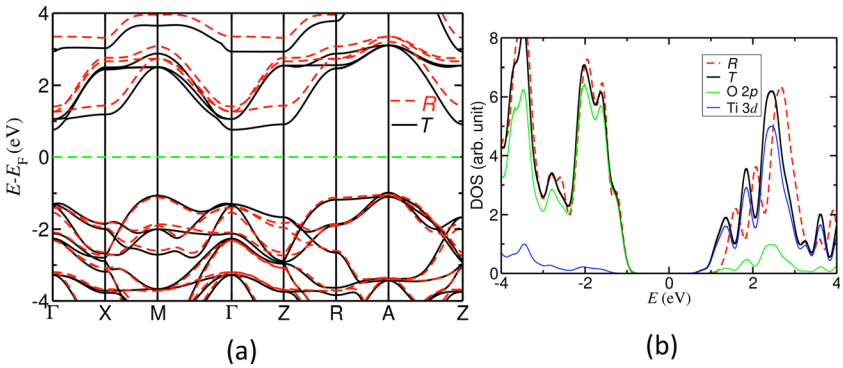

FIG. 2. The band structure and DOS of tetragonal (T) and rhombohedral (R) $BaTiO_3$.

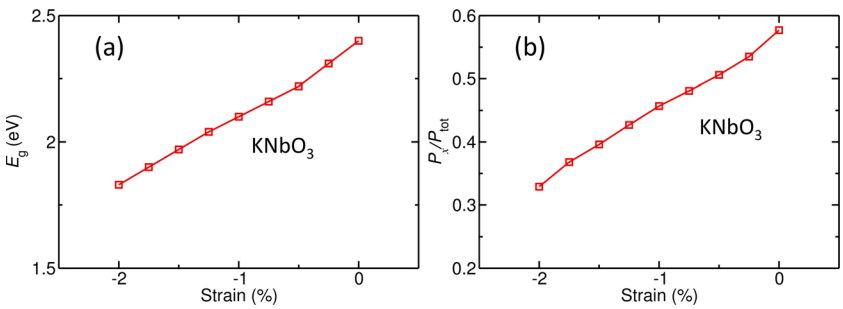

FIG. 3. The (a) band gap E_g (eV) and (b) ratio between the x-component of P and the total P (P_x/P_{tot}) as a function of the in-plane strain.

off-center displacements can exist.[22] Octahedral tiltings with deviation of the B-O-B angles from 180° can substantially affect the electronic structure of perovskites, even though they induce no polarization in simple ABO_3. On the other hand, B-cation off-center displacements could lead to long and short bond length differences, deviations of both O-B-O and B-O-B angles from 180°, and significant polarization. In T phase perovskites, the B-cations are displaced along the [001] direction while in the R phase the off-centering is along all the three Cartesian directions. Correspondingly, in the T phase both the O-B-O and B-O-B angles are still 180° along the [001] direction while in the R phase they deviate from 180° along all the three crystallographic directions. This leads to smaller band gaps in the T phase.

The local T phase displacements necessary for lower E_g could be achieved by strain, doping,[24] or by mixing with locally tetragonal materials such as $PbTiO_3$ in a solid solution. Here, we examine the effect of strain. As shown in Fig. 3, as the in-plane compressive strain increases, the band gap of $KNbO_3$ decreases, and the proportion of the in-plane component to the total polarization also decreases. This verifies the feasibility of our proposed band gap engineering strategy using the R-to- T phase transition.

In summary, we propose a way to engineer the band gap of perovskites from first principles. Through R-to-T phase transitions, the band gaps can be significantly reduced by up to 1.2 eV without significantly affecting the magnitude of polarizations. The BO_6 distortions, especially the B-cation off-center displacements, enhance the antibonding character of the CB, leading to wider band gaps in the R phase. The clear correlation between the structure, electronic structure, and polarization provides a route for the design of photovoltaic perovskite FEs.

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