



Effects of epitaxial strains on spontaneous polarizations and band gaps of alkaline-earth-metal oxides MO (M = Mg, Ca, Sr, Ba)



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ABSTRACT

The spontaneous polarization and band gap of the alkaline-earth-metal binary oxides MgO, CaO, SrO and BaO under epitaxial strain are investigated using a first principles density functional theory. The main findings are summarized as follows: (1) the polarization can reach up to $\sim 100 \mu\text{C}/\text{cm}^2$ at the compressive strain of $\epsilon_s = -8\%$, which is much larger than those of most typical ferroelectric perovskite oxides. For all the studied four systems, the variation of the polarization displays the extremely similar behavior that the polarization value increases almost linearly under the compressive or tensile strain. (2) For MgO, the optical band gap increases remarkably under the compression, and reaches its maximum at $\epsilon_s = -10.74\%$. Beyond this range, the band gap gradually decreases. For the other three heaviest oxides, the band gaps undergo a decrease for both types of strain. Our calculated results are in good agreement with the available experimental and other theoretical data.

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1. Introduction

Strain engineering has been adopted widely to alter the structural and electronic properties of various functional materials to obtain the desired physical and electronic properties by introducing intrinsic strain through lattice mismatching in epitaxial films, heterostructure superlattices, or core/shell nanowires [1–7]. Recently, as a powerful promoter of ferroelectric materials, strain has been applied to induce ferroelectricity in some nonferroelectric compounds such as the alkaline-earth-metal oxide MO (M = Mg, Ca, Sr, Ba) [1], the nitride GdN [8] and the quantum paraelectric perovskite oxide SrTiO₃ [9,10], due to the rearrangement of electrons along with the lack of centrosymmetry. Engineering ferroelectricity through epitaxial strains was also considered to be a promising route to convert paraelectric magnets to multiferroics [11], for instance, in perovskite CaMnO₃ [12,13] and in binary oxide EuO [1]. Also, the strong amplification of ferroelectricity in strained BaTiO₃ has been demonstrated [14].

The alkaline-earth-metal binary oxides MgO, CaO, SrO and BaO have attracted much attention because of their potential use in a wide range of technological applications [15,16]. MgO and CaO are widely employed as catalysts, optical materials or microelectronics. As a potential gate dielectric material, BaO is also

considered to replace SiO₂ in metal–oxide–semiconductor field-effect transistors (MOSFET's) [17]. SrO and BaO exhibit important as a buffer layer in the epitaxial growth of multifunctional perovskite oxides directly on silicon [18]. MO (M = Mg, Ca, Sr, Ba) oxides have large band gaps due to their high ionicity. It is possible to adjust the band gap by epitaxial strain, since the strain-induced variations of the interatomic distances and relative positions of atoms have a strong bearing on the band structure. For example, the effects of strain on the structural and electronic properties of ZnX (X = O, S, Se, and Te) and XN (X = Al, Ga) have been studied using density functional theory (DFT) [19–21]. Studying the band gap modulations under strains is necessary in order to tailor materials for use in specific devices.

In this paper, the aim is to illustrate how epitaxial strain affects the spontaneous polarization and band gap of the alkaline-earth-metal oxides MO (M = Mg, Ca, Sr, Ba) by performing an extensive first-principles calculation. Our study differs from the previous works in two main aspects. (1) Previous searches have just predicted the existence of ferroelectricity in the simple rock-salt binary oxides under epitaxial strain according to the condensation of polar optical soft phonon mode [1]. However, the relations between the spontaneous polarization and epitaxial strain for MO (M = Mg, Ca, Sr, Ba) oxides have not systematically been described. In this work, we illustrate the clear trends in the dependence of the spontaneous polarization on the strain, and reveal the structural and electronic driving forces from ionic displacements and Born effective charge tensors. (2) Strain-induced band gap

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tuning of the alkaline-earth-metal oxides MO (M = Mg, Ca, Sr, Ba) can be used for their practical application. However, such systematic studies have not been executed in previous work. Thus, another focus of our research is to explore the effects of epitaxial strain on the band gap of MO (M = Mg, Ca, Sr, Ba), and trends in band gap value changes are well predicted. Our results may be helpful in better revealing the underlying mechanisms of their giant ferroelectricity and in broadening the opportunities for their new applications.

2. Computational method

To calculate the structure, band gap and Born effective charges of the alkaline-earth oxides MO (M = Mg, Ca, Sr, Ba), we use DFT within the generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) [22], as implemented in the Cambridge Serial Total Energy Package (CASTEP) code [23]. The plane-wave pseudopotential method is adopted by treating the valence electron configurations of oxygen, Mg, Ca, Sr and Ba atoms as $2s^2 2p^4$, $2p^6 3s^2$, $3p^6 4s^2$, $4p^6 5s^2$ and $5p^6 6s^2$ respectively. For structural relaxation and total energy calculations, a plane-wave cut-off energy of 475 eV and a Monkhorst-Pack k -point mesh of $6 \times 6 \times 6$ are required to obtain well-converged results.

The epitaxial strain can be produced by the lattice mismatch between the equilibrium thin film MO and the underlying substrate with a different lattice constant. We define the strain by $\varepsilon_s = (a - a_0)/a_0 \times 100\%$, where a_0 corresponds to the equilibrium lattice constant and a the strain-induced lattice constant in the {110} plane. The substrate with a larger (smaller) lattice constant results in tensile (compressive) strain which means $\varepsilon_s > 0$ (< 0). Given a compression or tension upon the unit cell, the sufficient relaxation of the lattice parameters a in the {110} plane and c along the [001] axis are performed until the lowest total energy of the fully optimized unit cell is reached up. We have examined the accuracy of our calculations by comparing strain-free structure parameters with experimental and other theoretical data. As summarized in Table 1, good agreement between theoretical and experimental methods is achieved. In addition, the band gap E_g of the equilibrium MO can be found in Table 1. However, E_g is typically underestimated in comparison with the experimental value. Although it has been suggested in Refs. [46] and [47] that the time-intensive beyond DFT calculations involving exact-exchange functionals can reproduce the experimental value, the relatively simpler GGA is employed in our work because we focus mainly on the trends in the dependence of E_g on epitaxial strains rather than its absolute value [20].

3. Results and discussion

The strain-induced electric polarization (P) in the simple rock-salt MO oxides originates from the lack of centrosymmetry which has a strong influence on the Born effective charge. First, Table 2 gives the Born effective charge Z^* of cation ($Z_M^* = -Z_O^*$) for the series of alkaline-earth oxides under strain-free situation. We obtain values of 2.74, 2.44, 2.27, and 1.99 for BaO, SrO, CaO, and MgO respectively, which deviate from the corresponding normal charge of +2. For the whole series the agreement of our results with the experimental and other theoretical ones is very good. Except for MgO ($Z^* < 2$), the deviations of Z^* from the normal value are caused by the strong hybridizations between O $2p$ orbitals and unoccupied cation d states [49], which are similar to what has been reported, for example, between Ti and O in perovskite compound BaTiO₃ [50]. In Fig. 1, our calculation shows the sensitivity of Z^* to the lattice strain. Under the epitaxial strain, the lattice symmetry is lowered to the tetragonal one and the space group changes from

Table 1

Calculated strain-free lattice constant a and energy band gap E_g for the series of alkaline-earth oxides, together with the available experimental and computational data for comparison.

Compound		Lattice constant a (Å)	Energy band gap (eV)
MgO	This work	4.283	4.35
	Expt.	4.213 ^a , 4.212 ^b	6.4 ^g , 7.8 ^h , 7.83 ⁱ , 8.7 ^j
	Other cal.	4.259 ^c , 4.247 ^d , 4.260 ^e , 4.261 ^f	4.8 ^g
CaO	This work	4.834	3.65
	Expt.	4.811 ^k	7.09 ^l
	Other cal.	4.810 ^l , 4.820 ^m , 4.834 ⁿ , 4.838 ^o , 4.714 ^c	3.7 ^g , 7.72 ^p
SrO	This work	5.195	3.33
	Expt.	5.16 ^q	5.9 ^f
	Other cal.	5.196 ^e , 5.197 ^c	4.1 ^s , 3.4 ^g
BaO	This work	5.594	2.08
	Expt.	5.539 ^q	4.8 ^u
	Other cal.	5.579 ^t , 5.465 ^t	1.75 ^v , 2.0 ^g , 5 ^w

^a Ref. [24].

^b Ref. [25].

^c Ref. [26].

^d Ref. [27].

^e Ref. [28].

^f Ref. [29].

^g Ref. [30].

^h Ref. [31].

ⁱ Ref. [32].

^j Ref. [33].

^k Ref. [34].

^l Ref. [35].

^m Ref. [36].

ⁿ Ref. [37].

^o Ref. [38].

^p Ref. [39].

^q Ref. [40].

^r Ref. [41].

^s Ref. [42].

^t Ref. [43].

^u Ref. [44].

^v Ref. [45].

^w Ref. [18].

Table 2

The Born effective charge Z^* of cation for the series of alkaline-earth oxides under strain-free situation. The experimental results are from [48] and other calculated results are from [1,49].

Compound	Born effective charge Z^*		
	This work	Expt.	Other cal.
MgO	1.99	1.96/2.02	1.98, 1.96
CaO	2.27	2.26/2.30	2.35, 2.39
SrO	2.44	2.34/2.47	2.44, 2.49
BaO	2.74	2.69/2.97	2.72, 2.81

$Fm\bar{3}m$ to $I4/mmm$. Therefore, the Born effective charge tensors of cation Z_{xx}^* ($= Z_{yy}^*$) is not equal to Z_{zz}^* . The tensors of O ion are always the negative values of those of cation, which implies the same roles of the opposite charged ions as driving force of the ferroelectric distortion. The compressive or tensile strain drives Z_{xx}^* and Z_{zz}^* to deviate gradually from the equilibrium value (the intersection point of the black and red lines). The tensor Z_{xx}^* increases

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