Hybrid functional band gap calculation of SnO_6 containing perovskites and their derived structures

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We have studied the properties of SnO_6 octahedra-containing perovskites and their derived structures using ab initio calculations with different density functionals. In order to predict the correct band gap of the materials, we have used B3LYP hybrid density functional, and the results of B3LYP were compared with those obtained using the local density approximation and generalized gradient approximation data. The calculations have been conducted for the orthorhombic ground state of the SnO_6 containing perovskites. We also have expended the hybrid density functional calculation to the $\text{ASnO}_3/\text{A}'\text{SnO}_3$ system with different cation ordering. We propose an empirical relationship between the tolerance factor and the band gap of SnO_6 containing oxide materials based on first principles calculation.

Keywords: Transparent conducting oxide; $\text{ASnO}_3/\text{A}'\text{SnO}_3$ system; Electronic structure and band gap; Hybrid functional calculation

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I. Introduction

Recently, there has been considerable interest in new transparent conducting oxides (TCO), not only for technological issues, such as cost-saving and environmental issues, but also for their scientific importance [1-6]. One of most promising next candidates for TCO is perovskite oxides, in which SnO_6 octahedra form the 3D network of a corner sharing structure [5-18]. The unique optical properties of Sn-O bonding with the recent developments in thin oxide film synthesis by layer-by-layer epitaxial growth on different substrates open many unknown possibilities of SnO_6 -containing perovskites [19, 20]. A theoretical understanding of various phases of SnO_6 -containing perovskites is essential for understanding the nature of TCOs as well as designing new materials with engineering potential [5-7, 12, 13].

One of the most important properties of SnO_6 -containing perovskites is the band gap, which determines the transparent energy window of the materials [5-10, 12, 13, 17]. A large amount of experimental data for the band gap of $\text{A}_{1-x}\text{A}'_x\text{SnO}_3$ exists, which in principle, can be determined by optical absorption experiments [21-25]. On the other hand, a first principle calculation of the band gap is far from perfect [7-14]. Local density approximation (LDA) [26] and generalized gradient approximation (GGA) [27], which are two variations of common density functional theory, severely underestimate the band gap of oxide perovskites [28]. There are many approaches to overcome the band gap issue of LDA and GGA in density functional theory, including meta GGA method such as TB-mBJ [29-30], a GW approximation [30], and hybrid density functional theory [31]. The three methods have been quite successful in solving the semiconductor problem of the band gap. Note that TB-mBJ method is successfully applied to the band gap problem of parent ASnO_3 compounds [17].

It is generally believed that the computation cost to perform a GW approximation and hybrid density functional prevents the application of those theories to general perovskite oxides [13, 14, 32]. In a hybrid functional calculation, the most time consuming part is the calculation of Hartree - Fock

exact exchange term in plane wave pseudopotential approach because a four wave function integral needs to be done in real space while the plane wave theory is designed to be performed effectively in reciprocal space. An alternative approach to the plane wave is the extension of atomic orbital (AO) theory, such as the Gaussian type orbit (GTO) or Slater type orbit (STO), which has achieved quite successful results in many quantum chemical problems [34, 35]. Note that many density functional forms were originally developed in quantum chemistry based on GTO and STO [34-35]. In an extension of the atomic orbital theory, the computational cost to calculate the Hartree-Fock exact exchange term is in the same order of magnitude as other potential integral term in the Kohn Sham Hamiltonian.

This paper reports the hybrid density functional determination of the band gap of a SnO_6 -containing perovskite oxide. In this approach, we have evaluated the band gaps of the orthorhombic phase of ASnO_3 and $\text{ASnO}_3/\text{A}'\text{SnO}_3$ superlattices, which has a primitive cell of 20 atoms. These types of calculations using the plane wave (PW) approach are too expensive in terms of the computational cost. The results of the hybrid density functional calculation using AO have been compared with those of GGA using the PW approach. We have found that our calculation reproduces the experimental band gap data of the ASnO_3 materials quite well. We also have extended our calculation to $\text{ASnO}_3/\text{A}'\text{SnO}_3$ superlattices and analyzed the band gap as a function of the tolerance factor of SnO_6 -containing perovskite oxide. We finally propose an empirical relationship between the band gap and the tolerance factor of SnO_6 containing perovskite oxide.

II. Calculation Details

We have performed first principles density functional calculations of SnO_6 -containing oxides with two different methods. The first approach is density functional calculations with the PBEsol generalized gradient approximation (GGA) [36] and the projector-augmented-wave method as implemented in VASP [37, 38]. We considered the following valence electron configuration: $5s^2 6s^2 5p^6 5d^1$ for Ba, $4s^2 5s^2 4p^6 4d^1$ for Sr, $3s^2 3p^6 4s^2 3d^0$ for Ca, $4d^{10} 5s^2 5p^2$ for Sn, and $2s^2 2p^4$ for O. The

electronic wave functions were expanded with plane waves up to a kinetic-energy cutoff of 400 eV except for structural optimization, where a kinetic energy cutoff of 520 eV has been applied to reduce the effects of Pulay stress. The momentum space integrations were performed using a $4 \times 5 \times 5$ Γ -centered Monkhorst-Pack k -mesh [39]. For the various symmetries examined, the lattice constants and internal coordinates were fully optimized until the residual Hellmann-Feynman forces became smaller than 10^{-1} meV/Å. In the PBEsol calculation, the correct band gap could not be obtained, as noted by previous researchers [11-14], because of ignoring the Hartree-Fock exact exchange part. In addition, the plane wave approach for the hybrid functional calculation incurs considerable computational cost for low symmetry structural optimization. Therefore, we have applied the hybrid density functional calculation of CRYSTAL09 [40] to study the electronic structure of SnO₆-containing oxides for a systematic band gap prediction with B3LYP hybrid functional [41]. For the oxygen atom, we have used all electrons Gaussian Type Function (GTF) and the Hay–Wadt pseudo-potential for the core electron has been used for the Ba, Sr, and Ca atoms [42]. We have applied the Durand 21G type pseudo-potential for Sn atoms [42]. For each given system, we have performed the independent structural optimization using the B3LYP hybrid functional [32, 41] and also LDA-PZ [26] and PBE-GGA [27] functional. The total energy calculations have been performed in the momentum space integrations using an $8 \times 8 \times 8$ Γ -centered Monkhorst-Pack k -mesh [39] for the CRYSTAL09 calculation. After each structural optimization starting from experimental values, structural parameters have been summarized based on the optimized structure and the band diagrams have been obtained to check the band gap obtained from the density of state calculation. We would like to emphasize that our B3LYP hybrid density functional calculation is done with independent optimized structure. Details of the structural parameters have been converted to CIF file format for GGA and B3LYP hybrid density functional and can be downloaded from the supplementary section for all 9 compounds [41].

III. Results and Discussions

A. Bulk Phases

One of the most important physics of SnO_6 -containing oxide perovskite is octahedral tilting and its consequence to the change in space group [7-14]. The low temperature stable structure of SnO_6 -containing oxide perovskite is determined by the octahedral tilting pattern and the common low symmetry phase of the orthorhombic phase can be identified by the Glazer classification [44-46]. The octahedral tilting pattern in the orthorhombic phase is summarized in Fig. 1. The Glazer classification of octahedral tilting can be described using the symbol, $a^{\#}b^{\#}c^{\#}$, in which the literals refer to the tilting magnitudes and tilting directions of the cubic perovskite, and the superscript can be 0, +, or -, indicating no tilting, tilting of the successive octahedral in the same direction or that in the opposite direction, respectively. The positive tilting and negative tilting is depicted in Figs. 1(a) and 1(b). It is important that the tilting sign can be identified easily when the tilting is viewed from the plane normal to the tilting, as shown in Figs. 1(a) and 1(b). The tilting angle can be calculated from the structural parameters, such as the lattice constants and atomic positions, especially the Sn and O positions. The perovskite without tilting is represented by the cubic structure, as shown in Fig. 1(c). The low temperature experimental structure of the SnO_6 -containing oxide perovskite is represented by $a^-a^-c^+$ tilting [7-14], which means negative tilting of the same amount (a) in two directions and positive tilting of a different amount (c) in one unique axis. The space group of the $a^-a^-c^+$ tilting pattern is the $Pnma$ structure, as shown in Fig. 1(d). The tilting pattern is related to the tolerance factor of perovskite defined by the ionic size of A, Sn and O atoms in the ASnO_3 perovskites [44-46].

The band structures of ASnO_3 ($A = \text{Ba}, \text{Sr}, \text{Ca}$) are depicted in Fig. 2 as a function of the density functional and Brillouine Zone directions. In these figures, we have used three different density functionals (B3LYP [32, 41], LDA-PZ [26], and PBE-GGA [27]), and each band structure is obtained in the optimized structure of each density functional. Fig. 2(a) shows the band structure of cubic BaSnO_3 . The experimental structure of BaSnO_3 is reported as cubic and the total energy difference

between the cubic and orthorhombic phase is small; therefore, we have shown the band structure of cubic space group without any tilting. The valence band top is located in the R point, whereas the conduction band minimum is located in the Γ point, which means the indirect band gap. The band gaps of PBE GGA and LDA-PZ is calculated to be ~ 1.175 eV and ~ 1.738 eV, respectively. When B3LYP is used, the band gap is calculated to be ~ 3.140 eV. The previous report of GGA [8] band gap is about 0.9 eV and that of TB-mBJ [17, 47] is about 2.82 eV $\sim$ 3.00 eV. As shown clearly in band diagram and density of state (DOS) data [48], the band shape of BaSnO_3 does not change significantly when a different density functional is used, meaning that the effective mass of an electron and hole does not change significantly depending on the choice of density functional. When Ba is replaced with smaller ions, such as Sr and Ca, the orthorhombic structure becomes the ground state [7-14, 17, 44]. The band structure of orthorhombic SrSnO_3 and CaSnO_3 is depicted in Fig. 2(b) and 2(c), respectively. The conduction band minimum is located in the Γ point, but the valence band maximum is located in the U point of the orthorhombic Brillouine zone. The dependency to the density functional of the orthorhombic phase is the same as that of the cubic phase: the indirect gap position does not change according to the choice of the density functional and the band shape does not change significantly [47]. On the other hand, the band gap value depends strongly on the choice of density functional [8, 17, 47]. The dependency of the band gap on the choice of density functional is summarized in the Fig. 2(d). In this figure, we have plotted the band gap of ASnO_3 as a function of the tolerance factor. The tolerance factor of ASnO_3 for Ba, Sr and Ca compounds is 1.0184, 0.9609 and 0.9270, respectively [49]. The experimental band gaps are plotted as green pentagons [21-25]. First of all, the band gap of ASnO_3 decreases as the tolerance factor increases as the previous reports noted [8, 17, 47]. Secondly, there is linear relationship between the tolerance factor and the band gap. These results are related to the overlap between Sn-O determined by tolerance factor, and as tolerance factor decreases, the overlap integral becomes larger and the band repulsion becomes stronger [8].

Finally, the B3LYP reproduces experimental value quite well, except for the small error in CaSnO_3 . In CaSnO_3 , the experimental value is scattered between 4.2 eV and 4.5 eV, which is very difficult range for determining the precise band gap from simple UV-VIS experiment. In addition, the band gap is quite sensitive to the structural parameters, especially the lattice volume [17]. Therefore, the zero temperature calculation overestimates the room temperature experimental data. It is worthwhile to note that our GGA results are consistent with previous GGA results [8] and our B3LYP results are also consistent but slightly larger than those of TB-mBJ calculation on bulk materials [17]. Tables 1 and 2 summarize the calculated values for the structural and electronic parameters. The CIF files are also presented both GGA and B3LYP for the optimized structure as a supplementary material.

B. Superlattice Structure

The simplest extension of ASnO_3 is the superlattice of ASnO_3 and A'SnO_3 , and there are three superlattices depending on the growth direction: [001] layered, [110] columnar and [111] rocksalt structures (see suppl. Fig. S2). Since previous reports indicate the non-centrosymmetric phase in the [001] and [111] superlattices [13, 50-52], we extended our hybrid functional calculation to these two structures. Figure 3(a) depicts the [001] layered superlattice. Again, because of the tolerance factor, the low temperature structure is the orthorhombic phase of the $Pmc2_1$ space group. We considered Ba/Ca, Sr/Ca and Ba/Sr configuration in the orthorhombic phase. The results of the Ba/Sr superlattice with B3LYP hybrid functional are plotted in the Fig. 3(b). A direct band gap of 3.50 eV can be observed between the Γ and Γ point. Fig. 3(c) depicts the [111] rock salt superlattice of the $Pmn2_1$ space group. The band structure of the Ba/Sr [111] superlattice is plotted in the Fig. 3(d). Note that the same Brillouine zone path is used for the [111] superlattice, as in the [001] superlattice, even though the symmetry of the two orthorhombic phases is different ($Pmc2_1$ for the [001] superlattice, $Pmn2_1$ for the [111] superlattices). First of all, the band structure from the [111] superlattice (Fig. 3(d)) is similar to that from the [001] superlattice (Fig. 3(b)). Secondly, the band gap (3.50 eV vs.

3.52 eV) is similar for two different superlattices, even though two layering gives a completely different space group and cation ordering pattern. The band structure of the other two compositions (Ba/Ca and Sr/Ca) shows similar behavior (see supplementary Fig. S3 for the detailed data).

C. Tolerance factor and band gap

To discuss the band gap of superlattices and parent compounds in a unified way, it is important to define effective tolerance factor [49] of superlattices. As shown in the previous Figures, the band gap of each superlattice is insensitive to the growth direction. Therefore, the effective tolerance factor of the superlattice can be defined as the average value of the parent compound. For example, the effective tolerance factor of $\text{BaSnO}_3/\text{CaSnO}_3$ is the average value of the tolerance factors of BaSnO_3 (1.0184) and CaSnO_3 (0.9270). We have plotted the band gap of the superlattices as a function of the effective tolerance factor for the [001] and [111] superlattice in Fig. 4(a) and 4(b), respectively. Since there are no experimental values for superlattices, only the calculated band gaps of B3LYP hybrid functional and GGA density functional have been plotted. As noted in the figure, the band gap of the GGA density functional was calculated using VASP and that of the B3LYP hybrid functional was calculated using CRYSTAL09. The band gap of the superlattices decreases as the effective tolerance factor increases and the GGA results are only ~ 50 % of the B3LYP results. It has similar trend with bulk material [8, 17, 47]. In addition, the band gap is almost independent of the growth directions, as discussed previously. Moreover, the band gap is an almost linear function of the effective tolerance factor. To investigate the generic behavior, we have plotted the band gap data (our B3LYP hybrid functional data) of the parent compounds and superlattices in Fig. 4(c). The band gap data of the parent compound (ASnO_3) are denoted as red circles. The band gap data of the [001] and [111] superlattices are denoted as green square and blue triangles, respectively. As shown clearly in figure 4(c), the band gap is almost a linear function of the effective tolerance factor and can be fitted by,

$$E_g = 3.416 + 20.038(1 - t) ,$$

where t is the effective tolerance factor and E_g is the band gap of SnO_6 containing perovskite oxide.

From this generic formula, the band gap of complicated artificial structure of SnO_6 containing perovskite oxide can be estimated. First of all, the band gap of SnO_6 -containing perovskite oxide can be fitted by this linear formula for such a large tolerance factor range ($0.92 < t < 1.02$). Secondly, the band structure itself is a detailed function of cation ordering and the local structure, but the value of band gap is a generic function of the tolerance factor, which is also noted earlier [8]. In ref. 17, there are descriptions about the strain effects on the band gap and optical properties of SrSnO_3 and BaSnO_3 [17]. They have fitted the band gap variation of strained condition ($a=b$ and c vary over 5-6 %), having different volume with the optimization of internal degree of freedom. Even though their fitting is intended for the volume variation under stained condition for single bulk compound, we have checked the applicability of such equation to our B3LYP data of 9 different compounds with the their independent optimized structures and results are summarized in supplementary Fig. S4. It is also interesting to note that, from partial DOS analysis, the maximum of the valence band is determined by O, and the minimum of the conduction band is determined by the hybridization between O and Sn. The band gap is determined by the Sn and O wave function and the overlap is determined by the size of the A site cation. Therefore, the tolerance factor can be considered one of the most important parameters for the value of band gap. On the other hand, further experimental and theoretical efforts will be needed to better understand linear relationship between the band gap and the tolerance factor.

IV. Conclusion

In conclusion, we have studied the electronic and structural properties of SnO_6 -containing perovskite oxides using the B3LYP hybrid density functional. As the most common ground state is

the orthorhombic structure, it is a quite challenge to calculate the correct band gap using the B3LYP hybrid functional. The hybrid density functional calculation reproduces the experimental band gap as well as the band structure of the ASnO_3 parent compounds. We also have extended our calculation to $\text{ASnO}_3/\text{A}'\text{SnO}_3$ superlattices with two different cation ordering ([001] layered and [111] rock salt). The band gap data of 9 compounds can be explained using the effective tolerance factor, which is the geometric average value of the parent compounds. The band gap decreases as the tolerance factor increases and it is because this behavior is related to the bonding nature of the SnO_6 network. Moreover, we formulated the band gap as a linear function of the effective tolerance factor. We believe that our hybrid density functional data of the band gap, especially the numerical formula of the band gap, can be the experimental keystone for identifying new engineering applications of SnO_6 -containing perovskites.

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Figure Captions

Figure 1. Structure of perovskite with two types of octahedral tilting. (a) positive tilting and (b) negative tilting viewed from the plane normal to the tilting. The tilting angle is denoted as ϕ . (c) Cubic structure of perovskite without tilting. (d) Orthorhombic structure of perovskite with $a^-a^-c^+$ tilting.

Figure 2. (a) Band structure of cubic BaSnO_3 with the LDA (black solid line), GGA (black dashed line), and B3LYP (red thick solid line) hybrid functional. Band structure of orthorhombic (b) SrSnO_3 and (c) CaSnO_3 with three different density functionals. Note the difference in the Brillouine zone for cubic and orthorhombic structure. (d) Band gap of ASnO_3 as a function of the tolerance factor for different density functionals. The experimental values of the band gap are marked as green pentagons. The blue squares are the GGA results from VASP. Red circles, black diamonds, and black triangles are the band gap of B3LYP, LDA, and GGA, respectively.

Figure 3. (a) [001] layered ordering of A-site cation in $\text{ASnO}_3/\text{A}'\text{SnO}_3$ superlattice. (b) Band structure of $\text{BaSnO}_3/\text{SrSnO}_3$ [001] ordered superlattice of the orthorhombic structure with the B3LYP hybrid functional. (c) [111] rock salt ordering of A-site cation in $\text{ASnO}_3/\text{A}'\text{SnO}_3$ superlattice. (d) Band structure of the $\text{BaSnO}_3/\text{SrSnO}_3$ [111] ordered superlattice with an orthorhombic structure using the B3LYP hybrid functional.

Figure 4. (a) Band gap of [001] cation ordered superlattices as a function of the effective tolerance factor. The red circles are the band gaps of the B3LYP hybrid functional and the black triangles are those of GGA. The effective tolerance factor was calculated from the average value of ASnO_3 and $\text{A}'\text{SnO}_3$. (b) Band gap of [111] cation ordered superlattices as a function of the effective tolerance factor. (c) B3LYP hybrid functional band gap of ASnO_3 , [001] ordered superlattices, [111] ordered superlattices of $\text{ASnO}_3/\text{A}'\text{SnO}_3$ as a function of the effective tolerance factor. Note the empirical linear relationship between the band gap and effective tolerance factor.

Figure 1 (Color online) Lee *et al.*

Figure 2 (Color online) Lee *et al.*

(a) [001] layered

(b) [001] Ba/Sr

(c) [111] rocksalt

(d) [111] Ba/Sr

Figure 3 (Color online) Lee *et al.*

Figure 4 (Color online) Lee *et al.*

Table 1. Structural properties of ASnO_3 perovskites and $\text{ASnO}_3/\text{A}'\text{SnO}_3$ ($\text{A}, \text{A}' = \text{Ca}, \text{Sr}, \text{Ba}$) superlattices with cation ordering: [001] layered ordering and [111] rocksalt ordering. The experimental data was obtained from ref. 21-25. The values in parentheses below are the difference between the calculated and the experimentally determined lattice properties. ΔV of the superlattices means the difference between the values calculated by the hybrid functional and those by the GGA density functional.

B3LYP(Hybrid functional)						GGA(VASP)			
Structure	Space group	Lattice parameter (Å)			Volume (Å ³ / f.u.)	Lattice parameter (Å)			Volume (Å ³ / f.u.)
		a	b	c		a	b	C	
CaSnO ₃	Pnma	5.521 (+0.1%)	5.657 (-0.1%)	7.855 (-0.3%)	61.333 (-0.3%)	5.437 (-1.4%)	5.639 (-0.4%)	7.803 (-1.0%)	59.817 (-2.8%)
SrSnO ₃	Pnma	5.673 (-0.6%)	5.688 (-0.3%)	8.082 (+0.2%)	65.198 (-0.6%)	5.663 (-0.8%)	5.693 (-0.2%)	8.011 (-0.7%)	64.568 (-1.6%)
BaSnO ₃	Pm $\bar{3}$ m	4.100 (-0.4%)	4.100 (-0.4%)	4.100 (-0.4%)	68.921 (-1.2%)	4.096 (-0.5%)	4.096 (-0.5%)	4.096 (-0.5%)	68.699 (-1.5%)
Experimental value									
CaSnO ₃	Pnma	5.514	5.663	7.882	61.534				
SrSnO ₃	Pnma	5.708	5.704	8.066	65.650				
BaSnO ₃	Pm $\bar{3}$ m	4.116	4.116	4.116	69.731				

B3LYP(Hybrid functional)						GGA(VASP)				ΔV (%)	
Structure	Space group	Lattice parameter (Å)			Volume (Å ³ / f.u.)	Lattice parameter (Å)			Volume (Å ³ / f.u.)		
		a	b	c		a	b	c			
[001]	Sr/Ca	Pmc2 ₁	5.610	5.673	7.960	126.675	5.614	5.725	8.005	128.632	+1.521
	Ba/Ca	Pmc2 ₁	5.714	5.764	8.140	134.048	5.714	5.764	8.140	134.048	0.000
	Ba/Sr	Pmc2 ₁	5.735	5.737	8.184	134.643	5.784	5.810	8.168	137.229	+1.885
[111]	Sr/Ca	Pmn2 ₁	5.615	5.674	7.947	126.587	5.620	5.732	7.991	128.724	+1.660
	Ba/Ca	Pmn2 ₁	5.706	5.748	8.041	131.864	5.724	5.798	8.080	134.083	+1.655
	Ba/Sr	Pmn2 ₁	5.735	5.736	8.197	134.818	5.797	5.809	8.170	137.569	+2.000

Table 2. Octahedral tilting angles and band gaps of the ASnO_3 perovskites and $\text{ASnO}_3/\text{A}'\text{SnO}_3$ ($\text{A}, \text{A}' = \text{Ca}, \text{Sr}, \text{Ba}$) superlattices with two different calculations.

Structure	Space group	B3LYP(Hybrid functional)			GGA(VASP)		
		E_g	Tilting angle (°)		E_g	Tilting angle (°)	
			a^-	c^+		a^-	c^+
CaSnO_3	Pnma	4.991	15.743	14.458	2.730	18.153	17.124
SrSnO_3	Pnma	4.158	8.617	9.096	2.123	12.172	11.957
BaSnO_3	$\text{Pm}\bar{3}\text{m}$	3.140	-	-	0.970	-	-

	Structure	Space group	B3LYP(Hybrid functional)			GGA(VASP)		
			E_g	Tilting angle (°)		E_g	Tilting angle (°)	
				a^-	c^+		a^-	c^+
[001]	Sr/Ca	$\text{Pmc}2_1$	4.501	12.790	12.056	2.214	15.274	15.143
	Ba/Ca	$\text{Pmc}2_1$	3.929	11.388	11.733	1.918	11.409	11.825
	Ba/Sr	$\text{Pmc}2_1$	3.500	0.396	4.936	1.494	8.863	7.243
[111]	Sr/Ca	$\text{Pmn}2_1$	4.541	13.192	12.048	2.227	15.301	14.536
	Ba/Ca	$\text{Pmn}2_1$	3.994	10.095	8.603	1.751	12.567	10.933
	Ba/Sr	$\text{Pmn}2_1$	3.524	0.339	5.419	1.484	8.990	7.737

Graphical Abstract Legend

(a) Structure of ASnO_3 for orthorhombic ground state. The green ball is A (Ba, Sr, Ca) cation and the small (red) ball on edge is oxygen. SnO_6 octahedrons are plotted as polyhedron. (b) Band gap of ASnO_3 as a function of the tolerance factor for different density functionals. The experimental values of the band gap are marked as green pentagons. (c) $\text{ASnO}_3/\text{A}'\text{SnO}_3$ superlattices with two types cation arrangement: [001] layered structure and [111] rocksalt structure, respectively. (d) B3LYP hybrid functional band gaps of ASnO_3 , [001] ordered superlattices, and [111] ordered superlattices of $\text{ASnO}_3/\text{A}'\text{SnO}_3$ as a function of the effective tolerance factor. Note that empirical linear relationship between the band gap and effective tolerance factor.