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First principles study on InP (001)-(2 × 4) surface oxidation

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First-principles study of antisite defects in perovskite stannates

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ABSTRACT

The perovskite stannates BaSnO₃ and SrSnO₃ are being actively explored for applications as transparent conductors, in power or high-frequency electronics, and as channel materials in epitaxial integration with functional perovskites. Realizing these applications requires controlled *n*-type doping, i.e., avoiding the formation of compensating acceptor-type defects. Here, we use density-functional theory to examine the formation of cation antisite defects. Our results indicate that antisites are not a problem in BaSnO₃; however, in SrSnO₃, Sr_{Sn} antisites may act as compensating centers.

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I. INTRODUCTION

Wide-bandgap semiconductors that can be heavily doped are attracting significant interest for applications as transparent conducting oxides (TCOs) and for power or high-frequency electronics.¹ One such material, BaSnO₃ (BSO), exhibits room-temperature mobility of $\sim 300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when doped with La.^{2–4} It can be integrated with other perovskite oxides for functional devices that can exploit ferroelectricity or strong correlations. The conduction-band offsets between BSO and other oxides^{5,6} allow electron confinement on the BSO side, enabling its use as a channel material.

SrSnO₃ (SSO) has a larger bandgap than BSO⁷ and can be alloyed with BSO, enabling the tuning of both the lattice constant and the bandgap.⁸ SSO is better lattice-matched to SrTiO₃ (STO), a commonly used substrate:⁹ the lattice parameters are $\sim 4.12 \text{ Å}$ for BSO (cubic),⁹ $\sim 4.04 \text{ Å}$ for SSO (pseudocubic),¹⁰ and $\sim 3.91 \text{ Å}$ for STO.¹¹ A large lattice mismatch with the underlying substrate can lead to the formation of extended defects and a reduction of electron mobility;⁷ therefore, better lattice-matching is desired. SSO is also being explored as an electronic material in its own right, with prospective applications in metal/semiconductor field effect transistors¹² and in electrostatic control of metal-insulator transitions.¹³

Lanthanum is the donor dopant most commonly used for *n*-type doping of BSO^{14–16} and SSO.^{7,17} While high levels of *n*-type doping have been achieved in BSO, doping of SSO has proven to be

more difficult. First-principles calculations based on density-functional theory (DFT) can provide detailed information about compensation mechanisms; studies on the point defects in BSO and SSO have been particularly insightful in this regard.^{18,19} Weston *et al.*¹⁹ studied La as an impurity and found that, while La_{Ba} and La_{Sr} act as shallow donors in BSO and SSO, La can also incorporate as a compensating acceptor on Sn sites. The authors also investigated compensation by vacancy- and interstitial-type point defects, identifying Ba and Sr vacancies as the primary compensating species.¹⁹ It was also found that the formation of compensating acceptors can be suppressed under oxygen-poor conditions, and that compensation is more problematic for SSO than for BSO, which is consistent with experimental observations.^{7,14,20}

The present study focuses on cation antisite defects, {Ba/Sr}_{Sn} and Sn_{Ba/Sr}, which have not yet been investigated in SSO but could act as compensating centers. Previous computational studies on the stannates have shown that the use of a hybrid functional in DFT is necessary to accurately calculate their structural and electronic properties. We use the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE),^{21,22} which has been extensively tested and demonstrated to provide reliable results.^{6,18,19,23,24} We examine the formation of antisite defects under various conditions in BSO and SSO in order to provide a systematic comparison and to identify their impact on *n*-type doping. Our results indicate that the antisite

defects do not impact n -type doping in BSO (consistent with Ref. 18), but that Sr_{Sn} acceptors could cause compensation in SSO. We identify synthesis conditions that are optimal for avoiding compensation and achieving high n -type electronic conductivity.

II. COMPUTATIONAL METHODS

We conduct first-principles calculations based on DFT^{25,26} with the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE),^{21,22} as implemented in the Vienna *Ab initio* Simulation Package (VASP).²⁷ The core electrons are described with projector-augmented plane wave (PAW) potentials,^{28,29} with Ba $5s^2 5p^6 6s^2$, Sr $4s^2 4p^6 5s^2$, Sn $5s^2 5p^2$, and O $2s^2 2p^4$ electrons treated as valence. The use of the hybrid functional, in which the short-range exchange potential is calculated by mixing a fraction of nonlocal Hartree-Fock exchange with the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE),³⁰ ensures a reliable description of both atomic and electronic structures.³¹ The standard mixing parameter of $\alpha = 0.25$ (corresponding to the fraction of Hartree-Fock exchange) is used, along with an energy cutoff of 500 eV for the plane wave basis set. Spin polarization is included.

The crystal structure of BSO is cubic (5-atom perovskite unit cell), while that of SSO is orthorhombic (20-atom unit cell). For our defect calculations, we use comparable 160-atom orthorhombic supercells (a $2 \times 2 \times 2$ multiple of the orthorhombic primitive cell) for both BSO and SSO. For BSO, doing so requires us to rotate and enlarge the standard cubic unit cell. A single special k -point is used. The lattice parameters of the supercells are fixed to their corresponding bulk values, and the internal coordinates are relaxed until the Hellman-Feynman forces are less than 0.01 eV/Å.

The formation energy, $E^f[D^q]$, for a defect in charge state q is calculated as³²

$$E^f[D^q] = E_{\text{tot}}[D^q] - E_{\text{tot}}[\text{bulk}] - \sum_{i=1}^n n_i \mu_i + qE_F + \Delta^q, \quad (1)$$

where $E_{\text{tot}}[D^q]$ is the total energy of a supercell containing defect D^q , $E_{\text{tot}}[\text{bulk}]$ is the total energy of the defect-free supercell, n_i is the number of atoms of element i ($i = \text{Ba}, \text{Sr}, \text{Sn}$) added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell to form the defect,

μ_i are the chemical potentials of the corresponding species i , E_F is the Fermi level referenced to the valence-band maximum (VBM), and Δ^q is a correction term³² that accounts for finite-size effects on the total energies of charged defects.

The chemical potentials are defined as

$$\mu_i = E_i + \Delta\mu_i, \quad (2)$$

where E_i refers to the energy of species i in its elemental phase. We refer to element-“rich” conditions as those for which $\Delta\mu_i = 0$. Correspondingly, we consider element-“poor” conditions for which $\Delta\mu_i$ is minimized. To determine the range of the $\Delta\mu_i$, we require thermodynamic stability of the host compounds,

$$\Delta\mu_{\{\text{Ba/Sr}\}} + \Delta\mu_{\text{Sn}} + 3\Delta\mu_{\text{O}} = \Delta H^f(\{\text{Ba/Sr}\}\text{SnO}_3). \quad (3)$$

We also consider the potential formation of other phases, namely, $\{\text{Ba/Sr}\}_2\text{SnO}_4$, $\{\text{Ba/Sr}\}\text{O}$, and SnO_2 ,¹⁹

$$2\Delta\mu_{\{\text{Ba/Sr}\}} + \Delta\mu_{\text{Sn}} + 4\Delta\mu_{\text{O}} \leq \Delta H^f(\{\text{Ba/Sr}\}_2\text{SnO}_4), \quad (4)$$

$$\Delta\mu_{\{\text{Ba/Sr}\}} + \Delta\mu_{\text{O}} \leq \Delta H^f(\{\text{Ba/Sr}\}\text{O}), \quad (5)$$

$$\Delta\mu_{\text{Sn}} + 2\Delta\mu_{\text{O}} \leq \Delta H^f(\text{SnO}_2). \quad (6)$$

From these expressions, we can derive phase stability regions for BSO and SSO, which we plot in Fig. 1 in the $\Delta\mu_{\text{O}} - \Delta\mu_{\text{Sn}}$ phase space.

We will plot results for different possible choices of chemical potentials (corresponding to growth or annealing conditions). By tuning $\Delta\mu_{\text{O}}$, we can separately consider O-rich (more positive $\Delta\mu_{\text{O}}$) and O-poor conditions (more negative $\Delta\mu_{\text{O}}$). For a particular choice of $\Delta\mu_{\text{O}}$, the chemical potentials of Ba/Sr and Sn can vary between $\{\text{Ba/Sr}\}$ -rich and Sn-rich. To examine this dependence on cation chemical potentials, we will plot the formation energy for the conditions indicated on the plots in Fig. 1 as A (O-rich, $\{\text{Ba/Sr}\}$ -rich), B (O-rich, Sn-rich), C (O-poor, $\{\text{Ba/Sr}\}$ -rich), and D (O-poor, Sn-rich).

When considering La impurities, we also need to take into account limiting phases for La. In this case, $\Delta\mu_{\text{La}}$ is subject to the

FIG. 1. Phase stability regions (shaded in gray) for (a) BaSnO_3 and (b) SrSnO_3 . Labels refer to various conditions: A (O-rich, $\{\text{Ba/Sr}\}$ -rich), B (O-rich, Sn-rich), C (O-poor, $\{\text{Ba/Sr}\}$ -rich), and D (O-poor, Sn-rich).

constraint

$$2\Delta\mu_{\text{La}} + 3\Delta\mu_{\text{O}} \leq \Delta H_f(\text{La}_2\text{O}_3). \quad (7)$$

We set $\Delta\mu_{\text{La}}$ to the maximum allowed value for a given $\Delta\mu_{\text{O}}$, i.e., $\Delta\mu_{\text{La}} = (\Delta H_f(\text{La}_2\text{O}_3) - 3\Delta\mu_{\text{O}})/2$, which corresponds to the most favorable conditions for La incorporation (i.e., the solubility limit).

III. RESULTS AND DISCUSSION

A. Atomic structure

The relaxed atomic structures for the antisite defects are shown in Fig. 2 for the 2+ and 2− charge states, which we will see are most relevant. The $\{\text{Ba}/\text{Sr}\}_{\text{Sn}}$ antisites remain most stable on the Sn sites in the perovskite lattice, where they adopt a sixfold coordination with O atoms. Bond lengths between $\{\text{Ba}/\text{Sr}\}$ and O in these configurations increase by 15% in BSO and 12% in SSO on average compared with Sn–O bond lengths in the pristine SnO_6 octahedra. Bond angles also experience distortion on these octahedral sites, which we can quantify in part by calculating the variance in O– $\{\text{Ba}/\text{Sr}\}$ –O angles and comparing with the variance of O–Sn–O angles in the pristine structures. In BSO, the variance increases from zero in the pristine cell (in which all O–Sn–O angles are 90°) to 0.10° , and in SSO, the variance increases from 0.45° (evidencing the lower symmetry of the orthorhombic perovskite lattice) to 1.68° . $\text{Sn}_{\{\text{Ba}/\text{Sr}\}}$, on the other hand, causes greater lattice distortions, moving off the nominal Ba/Sr sites (by about $0.5 \text{ \AA}$) and adopting a sixfold coordination with O atoms.

FIG. 2. Optimized atomic structures of the cation antisite defects (a) $\text{Ba}_{\text{Sn}}^{2-}$ and (b) $\text{Sn}_{\text{Ba}}^{2+}$ in BaSnO_3 , and (c) $\text{Sr}_{\text{Sn}}^{2-}$ and (d) $\text{Sn}_{\text{Sr}}^{2+}$ in SrSnO_3 . The circles and arrows indicate the location of the antisite defects. Ba atoms are shown in brown, Sr in green, Sn in gray, and O in red.

In this way, the Sn atoms prefer to maintain the same octahedral coordination as that of lattice Sn atoms, with $\text{Sn}_{\{\text{Ba}/\text{Sr}\}}\text{--O}$ bond lengths that are similar to but slightly longer in length than Sn–O bonds in the lattice SnO_6 octahedra, approximately 7% longer in BSO and 6% longer in SSO.

B. Formation energies

Formation energies of cation antisites in BSO and SSO are shown in Fig. 3 for the chemical potential conditions (A, B, C, D) defined in Sec. II and Fig. 1. We plot these formation energies alongside the energies of the dopant species $\text{La}_{\{\text{Ba}/\text{Sr}\}}$ and La_{Sn} and the cation vacancy point defects, which have been found to be the most pertinent compensating defects in previous work.¹⁹ The minor differences we find in formation energies compared to those in Ref. 19 can be attributed to the larger supercell size we use for BSO (160-atom vs 135-atom).

We focus first on the $\text{Sn}_{\{\text{Ba}/\text{Sr}\}}$ antisite, which is expected to behave as a donor. Indeed, we see that over much of the bandgap, this defect is present in the 2+ charge state, with the neutral charge state being favored closer to the conduction-band minimum (CBM). The formation energies of the $\text{Sn}_{\{\text{Ba}/\text{Sr}\}}$ antisites are in all cases higher than those of the $\text{La}_{\{\text{Ba}/\text{Sr}\}}$ donor, meaning that they will not impact doping.

The $\{\text{Ba}/\text{Sr}\}_{\text{Sn}}$ antisites, on the other hand, are expected to behave as acceptors, and, indeed, they appear principally in a 2− charge state over most of the bandgap. We note that the formation energy of Ba_{Sn} is significantly higher than the formation energy of Sr_{Sn} ; this observation is consistent with the atomic size of Ba being significantly larger than that of Sn, while Sr and Sn are more similar in size.

In BSO, the formation energy of the Ba_{Sn} acceptor is high, and it will not play any role in compensation. As already noted in Ref. 19, compensation in BSO can be attributed to V_{Ba} and La_{Sn} and will occur only under relatively O-rich conditions, which should, therefore, be avoided.

Compensation is more of an issue in SSO, and again, O-rich conditions are most problematic. Figures 3(e) and 3(f) show that strong compensation due to cation vacancies will occur; under Sr-rich conditions [Fig. 3(e)], Sr_{Sn} antisites may also contribute to the compensation. To avoid compensation in SSO, O-poor conditions are, therefore, preferred. In the extreme O-poor limit [Figs. 3(g) and 3(h)], no compensation of the La_{Sr} donor would occur; however, for intermediate oxygen pressures, Sr_{Sn} antisites are the dominant compensating native defects under Sr-rich conditions. This fact may not be immediately obvious from Fig. 3; to illustrate it more clearly, we performed a more detailed analysis as a function of oxygen chemical potential, as detailed in Sec. III C.

C. Role of antisites in compensation in SrSnO_3

In Sec. III B, we concluded based on an analysis of formation energies that compensation is not a concern in BSO. In SSO, compensation will strongly depend on the abundance of oxygen in the environment. We now examine to what extent Sr_{Sn} antisites play a role in this compensation, focusing on the Sr-rich conditions that would favor the formation of such antisites.

FIG. 3. Formation energies of defects in (a)–(d) BaSnO₃ and (e)–(h) SrSnO₃ as a function of Fermi level under the chemical potential conditions defined in Fig. 1: (a) and (e) correspond to point A (O-rich, Ba/Sr-rich), (b) and (f) to B (O-rich, Sn-rich), (c) and (g) to C (O-poor, Ba/Sr-rich), and (d) and (h) to D (O-poor, Sn-rich).

Detailed insight is provided by evaluating the actual concentration of impurities, native point defects, and electrons in the conduction band. In Fig. 4, we plot these concentrations as a function of oxygen chemical potential, for Sr-rich and Sn-rich conditions. We assume that La is incorporated at the solubility limit, as explained in Sec. II. Each choice of chemical potentials determines a set of formation energies [see Eq. (1) and Fig. 3], and the formation energies, in turn, yield concentrations. Assuming thermodynamic equilibrium, the concentration (c) of a defect is determined

by the formation energy according to a Boltzmann expression,

$$c = N_{\text{sites}} \exp \left(\frac{-E^f[D^q]}{k_B T} \right), \quad (8)$$

where N_{sites} is the concentration of sites on which the defect can form, $E^f[D^q]$ is the formation energy [Eq. (1)], k_B is the Boltzmann constant, and T is the temperature. We set $T = 1100$ K, which is within the typical range of growth temperatures for epitaxial deposition.^{8,12–16} The formation energies of charged species depend on the Fermi level, and the value of E_F in the system is determined by the overall charge neutrality. For a doped n -type semiconductor, charge neutrality corresponds to setting to zero the net charge contributed by positively charged donors, negatively charged acceptors, and carriers in the conduction band. This value of the Fermi level (at $T = 1100$ K) is also included in Fig. 4. The concentration of electrons in the conduction band is determined based on the Fermi-Dirac distribution and a conduction-band density of states, as in Ref. 19.

Figure 4 makes clear that, under Sn-rich (Sr-poor) conditions [panel (b)], V_{Sr} is the dominant compensating defect, while under Sr-rich conditions [panel (a)], the Sr_{Sn} antisite is the dominant compensating defect (except under extreme O-poor conditions). The prevalence of Sr_{Sn} may seem counterintuitive, given that, in Fig. 3, V_{Sn} appears to have the lowest formation energy as one moves toward O-rich conditions when E_F is at the CBM. The explanation is that when severe compensation sets in, the Fermi level is actually well below the CBM and close to the point where the formation energies of the dominant donor and compensating acceptor cross. At that point, V_{Sn} always has higher formation

FIG. 4. Equilibrium concentrations of impurities, native defects and electrons (e^-) at $T = 1100$ K as a function of the oxygen chemical potential μ_O , for SrSnO₃ under (a) Sr-rich and (b) Sn-rich conditions. The corresponding values of the Fermi level (referenced to the CBM) are also included (dotted line, right axis).

energies than any of the other defects; thus, it will not contribute in a significant fashion to compensation, as Fig. 4 clearly shows.

Our results shed light on the experiments of Wang *et al.*,¹⁷ who found that deviations in the cation stoichiometry lead to a significant reduction in the *n*-type carrier concentration and mobility, consistent with charge compensation. The authors interpreted their results in terms of formation of Sn and Sr vacancies. Our results confirm that, under Sr-poor conditions, V_{Sr} will be the dominant defect; however, under Sn-poor (Sr-rich) conditions, the dominant defects are not Sn vacancies but rather Sr antisites, Sr_{Sn} .

IV. CONCLUSION

In summary, we have studied cation antisite defects in BSO and SSO. $\text{Sn}_{\{\text{Ba}/\text{Sr}\}}$ antisites behave as deep donors and are not expected to play any role due to their high formation energies. $\{\text{Ba}/\text{Sr}\}_{\text{Sn}}$ antisites act as acceptors and may compensate *n*-type materials. The antisite formation is not a concern for BSO, but it could be important in SSO. In particular, Sr_{Sn} antisites have lower formation energies than V_{Sr} vacancies under Sr-rich conditions. Compensation can be suppressed by moving toward more O-poor and Sn-rich conditions.

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