Design of ternary alkaline-earth metal Sn(II) oxides with potential good p-type conductivity

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Oxides with good p-type conductivity have been long sought after to achieve high performance all-oxide optoelectronic devices. Divalent Sn(II) based oxides are promising candidates because of their rather dispersive upper valence bands caused by the Sn-5s/O-2p anti-bonding hybridization. There are so far few known Sn(II) oxides being p-type conductive suitable for device applications. Here, we present via first-principles global optimization structure searches a material design study for a hitherto unexplored Sn(II)-based system, ternary alkaline-earth metal Sn(II) oxides in the stoichiometry of MSnO3 (M = Mg, Ca, Sr, Ba). We identify two stable compounds of SrSnO3 and BaSn2O3, which can be stabilized by Sn-rich conditions in phase stability diagrams. Their structures follow the Zintl behaviour and consist of basic structural motifs of SnO tetrahedra. Unexpectedly they show distinct electronic properties with band gaps ranging from 1.90 (BaSn2O3) to 3.15 (SrSn2O3) eV, and hole effective masses ranging from 0.87 (BaSn2O3) to above 6.0 (SrSn2O3) m0. Further exploration of metastable phases indicates a wide tunability of electronic properties controlled by the details of the bonding between the basic structural motifs. This suggests further exploration of alkaline-earth metal Sn(II) oxides for potential applications requiring good p-type conductivity such as transparent conductors and photovoltaic absorbers.

INTRODUCTION

Metal oxides promise to be an important class of optoelectronic semiconductors owing to their robust environmental stabilities, earth-abundance, low-cost processing, etc.1 Depending on specific band gaps, oxides can be applied in various devices such as emitters and detectors in blue and ultraviolet spectral regions,2 photocatalysts,3 transparent conductors4, photovoltaic absorbers5, etc. The most significant factor hindering further development of the oxides based optoelectronic devices is their generally low p-type conductivity. Taking transparent conducting oxides (TCO) as examples, the industry standard n-type TCO, Sn-doped indium oxide, has a conductivity of at least 1000 S/cm, whereas the best p-type TCO, Mg-doped CuCrO2 in delafossite, only exhibits a one-order lower conductivity of 220 S/cm.6

Design principles for achieving p-type conductivity in oxides. The low p-type conductivity in oxides originates predominately from the localized O-2p orbital dominated upper valence bands (VBs) at relatively deep binding energies. This results in low hole mobility and difficulty in finding suitable dopants to form shallow acceptor levels and create enough hole carriers.7 One strategy to overcome this issue is to take advantage of coupling/hybridization between the O-2p orbital and other orbitals. This can enhance dispersion of VBs and simultaneously raise their binding energies. The performance of the CuAlO2, a recognized good p-type TCO, is related to this design principle, i.e., the hybridization between O-2p and Cu-3d (in d10 configuration) states.8 In addition to the strategy of the p-d coupling, one may also make use of the s-p coupling between lone-pair M-s (in s2 configuration) orbital of some heavy metalloids of M in low-valence state (for instance Tl(I), Sn/Pb(II), Bi(III), etc.) and O-2p orbitals.4,9,10 The fact that s-orbitals are generally more delocalized than d-orbitals means that the s-p coupling scenario may basically lead to more dispersive VBs, and thus is more effective in rendering oxides p-type conductive. Meanwhile, since the d10 and s2 orbitals are filled, their derived VBs (by hybridizing with O-2p) are anti-bonding states. The anti-bonding feature of VBs usually causes defect tolerant behavior,11,12 i.e., bond breaking associated with the formation of defect states will produce but shallow rather than deep acceptor levels in the mid-gap region. This greatly facilitates p-type doping, giving rise to required ambipolar conductivity in photovoltaic materials of chalcopyrites13 and hybrid halide perovskites14. Besides these efforts on utilizing the hybridization between cationic states and O-2p, introduction of anionic (e.g., chalcogen) states to couple with O-2p has also been considered15,16; however the actual VBs usually derive from the introduced anions, rather than the mixtures with O-2p.17

Sn(II) based oxides as promising p-type conducting materials. Sn(II) oxides with s-p coupling in VBs are therefore of interest, both in view of the design rules as above, and because Sn is an abundant, non-toxic element suitable for practical device applications. Binary Sn monoxide (SnO) has been demonstrated to have good p-type conductivity18,20 up to 300 S/cm21, and was proposed as candidate p-type TCO22,23 and to realize ambipolar oxide devices.24,25
conducting behaviors are associated with its dispersive VBs, consisting of anti-bonding Sn–5s/O–2p states and Sn–5p2 states. It has a small indirect band gap of 0.7 eV (and a direct gap of 2.7 eV), but suffers from a highly anisotropic effective mass of holes owing to its layered structure and issues with stability. Allying SnO with other isoelectronic oxides to reduce its direct gap (to visible spectral region) has been suggested to render it efficient photovoltaic absorber. Ternary oxides containing Sn(II) have been less studied. The known materials of oxostannates, e.g., A₂Sn₂O₅ (A = Na, K, Rb and Cs), having rather low calculated hole effective mass and band gaps of 2.4–2.7 eV, were recently proposed as promising p-type TCO. However, the compounds containing alkaline metals are prone to hydrolysis on exposure to air, and are meanwhile may not be fully compatible with semiconductor based devices. Finding alternative ternary Sn(II) oxides that may offer good p-type conductivity is thus of current interest.

Here we investigate crystal structures and phase stability of hitherto unexplored ternary Sn(II) oxides containing alkaline-earth metals, i.e., MSn₂O₃ with M = Mg, Ca, Sr, Ba, with first-principles particle swarm optimization structure search calculations. The most challenging issue associated with this class of materials is whether they are thermodynamically stable relative to the strongly competing Sn(IV) compounds such as ternary perovskites of Ca/Mg/Sr/BaSnO₃. We find while the less electronegative cations of Mg and Ca do not lead to stable compounds, the more electronegative cations of Sr and Ba stabilize ternary Sn(II) oxides against decomposing into competing phases under Sn-rich conditions. The identified stable phases of SrSn₂O₃ and BaSn₂O₃ show remarkably different electronic properties. BaSn₂O₃ has highly dispersive VBs with a low hole effective mass comparable to that of electron, leading to an expectation of both high electron and high hole mobility for ambipolar conduction. This work offers useful guidance to further exploration of ternary alkaline-earth metal Sn(II) oxides for applications requiring good p-type conductivity such as p-type TCO and photovoltaic absorbers.

**COMPUTATIONAL METHODS**

Stable crystal structures of MSn₂O₃ are searched by first principles DFT energetic calculations guided by an in-house developed Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) methodology. The key feature of our structure search method is its capability of rapidly identifying ground-state and metastable structures of materials with the only knowledge of chemical composition through intelligent exploration of the potential energy landscape. The algorithm details and its successful application in a variety of functional material systems have been discussed elsewhere. We perform structure searches with 1, 2 and 4 formulas of MSn₂O₃ in the unit cell. For each search, the population size of each generation is chosen as 30 and around 50 generations are carried out (see Fig. 1) to guarantee convergence of the search. That is, ~1500 structures are explored for each search calculation.

The underlying DFT calculations are performed with the projector-augmented wave (PAW) method implemented in the VASP code. The 4d¹⁰5s²5p² (Sn), 2s²2p³ (O), 3s² (Mg), 3p³4s² (Ca), 4s²4p⁶5s² (Sr), 5s²5p⁶6s² (Ba) shells are treated as valence electrons of PAW pseudopotentials. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) is chosen as exchange-correlation functional. We employ medium quality computational parameters to evaluate relative energies of explored structures and accelerate structure searches. Then the low-lying energy structures are further optimized with more accurate computational parameters, e.g., kinetic energy cutoff of 520 eV and k-point meshes with grid spacing of 2π×0.037 Å⁻¹. These settings ensure convergence of total energies at the level of less than 1 meV/atom. The hybrid functional (HSE06) is used in band structure calculations to properly consider self-interaction correction and get correct band gaps. The average effective mass tensor that relates directly to carrier’s electrical conductivity, is calculated based on the DFT-GGA rendered eigenvalues at more dense k-points grid of 2π×0.016 Å⁻¹ through the semiclassical Boltzmann transport theory. This takes into account effects of non-parabolicity and anisotropy of bands, multiple minima and multiple bands, etc. on carrier transport. The unified carrier concentration of 1.0×10¹⁸ cm⁻³ and room temperature of 300 K are chosen for such calculations. The phonon dispersions of predicted stable SrSn₂O₃ and BaSn₂O₃ phases are calcu-
lated by the supercell finite difference method as implemented in the PHONOPY code. The absorption coefficients are evaluated via calculating the imaginary part of the dielectric tensor, i.e., through the sum over occupied and unoccupied bands of the dipole matrix elements, neglecting local field effects. 

RESULTS AND DISCUSSION

![Fig. 2](image-url)

**Fig. 2.** (Color online). The lowest-energy structures of MgSn₂O₃ (a), CaSn₂O₃ (b), SrSn₂O₃ (c) and BaSn₂O₃ (d) identified from structure searches. In (a), the pentahedrons formed by Sn atoms coordinated by four O are highlighted in purple.

**Ground-state structures and their thermodynamic stabilities.** We begin with the identification of stable compounds based on extensive structure searches. Fig. 1 depicts an evolution of typical structure search (for BaSn₂O₃) with generation. One sees that more energetically favorable structures continually emerge with generation and the lowest-energy structure appears at the 38th generation. The overwhelming majority of low-lying energy structures are found to contain Sn coordinated by four O atoms (in red). This resembles that of A₂Sn₂O₃ (A = Na, K, Rb and Cs), but is distinct from that of the litharge SnO where Sn is four-fold coordinated by O. The changes in local chemical bondings between Sn and O cause deviation of electronic structure in ternary Sn(II) oxides from that in binary SnO (see below).

| Material   | Lattice | Wyckoff | Atoms      | x    | y    | z    |
|------------|---------|---------|------------|------|------|------|
| MgSn₂O₃    | a = 6.4662 | 4c      | O1         | 0.5853 | 0.7500 | 0.5530 |
|            |         |         | O2         | 0.0047 | 0.7500 | 0.7340 |
|            |         |         | Sn         | 0.7500 | 0.7500 | 0.8319 |
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The lowest-energy structures of MSn₂O₃ (M = Mg, Ca, Sr, Ba) identified from structure searches.

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![Image](image-url)

**TABLE I. Structural data of the lowest-energy structures of MSn₂O₃ (M = Mg, Ca, Sr, Ba) identified from structure searches.**

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peting phases. To accurately evaluate $\Delta \mu_{M}$ to ensure MSn equilibrium growth, Eq. (2) is to prevent precipitation. In each case, each line represent a known competing phase; the stable region of MSnO$_3$ is indicated in green if there is.

### Electronic properties of stable compounds: SrSnO$_3$ and BaSnO$_3$

Figure 5 shows calculated band gaps and average effective masses for the predicted lowest-energy structures of MSnO$_3$ (M=Mg, Ca, Sr, Ba).

#### Figure 3

Phase stability diagrams of MgSnO$_3$ (a), CaSnO$_3$ (b), SrSnO$_3$ (c) and BaSnO$_3$ (d) respectively. In each case, each line represent a known competing phase; the stable region of MSnO$_3$ is indicated in green if there is.

#### Figure 4

Calculated phonon dispersion curves of (a) SrSnO$_3$ in the ground-state $P$ca structure and (b) BaSnO$_3$ in the ground-state $C2/c$ structure.

The chemical potential of the atomic specie $i$ during growth ($\mu_i$) from that of bulk elemental solid or gas phase ($\mu_i^0$), $\Delta H_f$ is heat of formation, and $M_n$, $Sn_{m}, O_q$ represent all the known $j$ competing phases. The Eq. (1) is for equilibrium growth, Eq. (2) is to prevent precipitation to elemental phases of atomic species, and Eq. (3) is to ensure MSnO$_3$ stable against the formation of competing phases. To accurately evaluate $\Delta H_f$, the fitted elemental-phase reference energies [46] ($i.e., \mu_i^0$) are used to improve the error cancellation when calculating the energy differences between the compound and its elemental constituents. Fig. 4 shows two-dimensional phase stability diagrams with two independent quantities of $\Delta \mu_M$ and $\Delta \mu_{Sn}$ as variables. For each case, all the competing phases of binary and ternary compounds are considered. As clearly seen, while no stable region exists for MgSnO$_3$ and CaSnO$_3$, SrSnO$_3$ and BaSnO$_3$ exhibit visible stability under Sn-rich conditions ($i.e., \Delta \mu_{Sn}$ close to zero). As expected the strongest competitions come from binary SnO and ternary Sn(IV) compounds, which provide limitation to broadening of the stable regions of Sr/BaSnO$_3$. In addition to the thermodynamic stability with respect to competing phases, we have also examined lattice dynamical stability of SrSnO$_3$ and BaSnO$_3$. Fig. 4 shows their phonon dispersion curves. Absence of any imaginary phonon mode in the whole Brillouin zone clearly reflects their lattice stabilities at ambient condition. These results indicate that by deliberately controlling chemical potentials of reactants, single-phases of Sr/BaSnO$_3$ can be experimentally grown.

Electronic properties of stable compounds: SrSnO$_3$ and BaSnO$_3$. Fig. 4 shows calculated band gaps and average effective masses for the predicted lowest-energy structures of MSnO$_3$. All the compounds show indirect band gaps, along with larger direct gaps above 2 eV. For the stable compounds of SrSnO$_3$ and BaSnO$_3$, the direct gaps are 3.31 and 2.37 eV, respectively. The direct gap of SrSnO$_3$ is higher than those
of SnO[21] and K$_2$Sn$_2$O$_3$[10], making it transparent for entire range of visible spectrum. Turning to the effective masses, both MgSn$_2$O$_3$ and BaSn$_2$O$_3$ show low effective masses of holes ($m_h^*$), 0.78 and 0.87 $m_0$, respectively, comparable to those of electrons. The low $m_h^*$ values are comparable to those of Na/K$_2$Sn$_2$O$_3$ and other p-type TCO candidates proposed in Ref[10]. This is, however, not the case for SrSn$_2$O$_3$, which exhibits an unexpected heavy $m_h^*$ (above 6.0 $m_0$) originating from its generally quite dispersionless VBs (as discussed below). Table II shows calculated electrical conductivities ($\sigma$) at the selected hole carrier concentration ($n$) for p-type SrSn$_2$O$_3$ and BaSn$_2$O$_3$, compared with the experimental values of typical p-type materials, CuAlO$_2$[8] and SnO[21].

| Material   | $n$ (cm$^{-3}$) | $\sigma$ (S/cm) |
|------------|----------------|-----------------|
| CuAlO$_2$  | $2.00 \times 10^3$ | 0.95 $\times 10^{-1}$ |
| SnO         | $2.00 \times 10^3$ | 3.00 $\times 10^2$ |
| SrSn$_2$O$_3$ | $2.00 \times 10^3$ | 0.96 $\times 10^2$ |
| BaSn$_2$O$_3$ | $2.00 \times 10^3$ | 4.50 $\times 10^2$ |

The remaining features are well consistent with previous calculations,

Figs. 6 and 7 show band structures and atomic orbital-projected density of states (DOS) for two stable compounds, SrSn$_2$O$_3$ (in red) and BaSn$_2$O$_3$ (in blue), compared with those of SnO (in black). The crystal orbital overlap population (COOP) results[48] for bonding-type analysis are shown in Supplementary Fig. S1. The electronic structure of SnO is calculated at experimental structural parameters, giving a slightly lower band gap of 0.44 eV than the experimental 0.7 eV[47]; the lower $n$), and comparable to the value (300 S/cm) of SnO. BaSn$_2$O$_3$ with the lighter $m_h^*$ exhibits even higher $\sigma$ than that of SnO.

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Theoretical $\sigma$ of SrSn$_2$O$_3$ (96 S/cm) and BaSn$_2$O$_3$ (450 S/cm) are much higher than that of CuAlO$_2$ (0.095 S/cm, at

FIG. 6. (Color online). Calculated band structures of (a) SnO, (b) SrSn$_2$O$_3$ and (c) BaSn$_2$O$_3$, respectively. Decomposed charge density for the VB maximum (indicated by red arrow) of each material is shown as right panel.

FIG. 7. (Color online). Projected density of states of SnO, SrSn$_2$O$_3$, and BaSn$_2$O$_3$ onto the atomic orbitals of (a) Sn−5s, (b) Sn−5p, and (c) O−2p, respectively. The VB maximum is set to energy zero.
For BaSn₂O₄, the dispersion of VBs is quite high, resembling that of SnO. This is responsible for its low $m_e^*$ as mentioned, and originates from the strong hybridization between Sn-5s and O-2p states in the region of -4~0 eV (Fig. 7). The anti-bonding feature of such hybridization is unambiguously indicated in the COOP results (with positive n(e) representing bonding and negative n(e) representing anti-bonding, see Supplementary Fig. S1a). In addition to the Sn-5s states, there appear substantial Sn-5p states in VBs (-4.7~0 eV in Fig. 7b), forming bonding states with O-2p orbitals. The decomposed charge density at the VB maximum shows an asymmetric distribution around each Sn atom with a "lobe" pointing to interstitial region. The involvement of the nominally unoccupied Sn-5p orbitals of Sn(II) in the VBs is essential to produce such an anisotropic charge distribution and contribute to stabilization of the structure. These electronic structure features are closely similar to those of SnO, though BaSn₂O₄ has one less coordination number of Sn.

By considering the usually similar properties of Ba and Sr oxides and the common motif of SnO₃ tetrahedron making up Sr/BaSn₂O₃, one may suppose that SrSn₂O₃ will show similar electronic properties. However, in fact, SrSn₂O₃ shows rather flat VBs (Fig. 6b) with a remark-ably heavy $m_e^*$. This is reflected in its decomposed charge density at VB maximum (right panel of Fig. 6b) where the charge is relatively symmetrically localized around Sn and O atoms. In contrast to the case of BaSn₂O₃ where the anti-bonding hybridization between Sn-5s and O-2p is spread over the energy range of -1~0 eV, the Sn-5s/O-2p anti-bonding states are mainly located within a narrow energy range of -1~0 eV (Fig. 7 and Supplementary Fig. S1a). Additionally in the same energy range there exists bonding hybridization between Sn-5p and O-2p states (Supplementary Fig. S1b). These two types of hybridizing states with strong localization cause the remarkably heavy VBs and a sharp DOS peak at VB edges of SrSn₂O₃. Such a large difference between chemically similar compounds is unusual, but does occur in some systems including Sn₄⁺ ternary oxides with perovskite based structures.

Wide tunability of optoelectronic properties in metastable materials. In addition to the lowest-energy ground-state structure, our structure searches have also identified metastable structures. These structures represent local minima of the potential energy landscape. If they are not so high in energy, there is the possibility that they could be stabilized under some particular conditions. It is also of interest to study the metastable structures to access the extent to which properties are likely to be tunable. Also, exploration of the metastable structures can provide understanding of structure-property relationships. Focusing on BaSn₂O₃, we first choose 11 low-lying metastable structures that can survive in the phase stability diagram of Fig. 3I, i.e., their energies are low enough to render the stable green region existing. The maximum difference in energy between them and the ground-state C2/c structure is 47 meV/atom. Their detailed structure information is listed in Supplementary Table S1. The results of their absorption spectra, as well as $m_e^*$ and $m_h^*$ are shown in Fig. S5 compared with those of the ground-state structure (solid line). One observes that the absorption thresholds of them span a wide energy range of more than 1 eV. Besides the ground-state structure, five of them (e.g., Imma, Pnn2, Pnma, C2/c[1] and Cmcm) show low $m_e^*$ below 1.0 m₀; the remaining ones have medium-low $m_e^*$ between 1.0 and 3.0 m₀. The C2 and Pcc2₁ structures with rather high thresholds of ~2.7 eV (just above the blue part of the visible spectrum) may be used as potential p-type TCOs depending on the exact optical window of interest. The particularly interesting case is the Imma structure, which is only 11 meV/atom higher in energy than the ground-state, starts absorbing visible light from a low threshold of ~1.6 eV. Also, it has simultaneously low $m_e^*$ (0.41 m₀) and low $m_h^*$ (0.62 m₀) favourable for ambipolar conductivity. Therefore it would be potentially good photovoltaic absorber if it can be made.

![FIG. 8. (Color online). Calculated absorption spectra of selected metastable BaSn₂O₃ compounds identified from structure searches (see text). The result of the ground-state C2/c structure is shown for comparison (in solid line). The values following space groups of materials are their $m_e^*$ and $m_h^*$ (highlighted in blue), respectively.](image-url)
Fig. 9, one can see a general trend that the larger band gap, the higher \( m^*_n \). This trend is in accord with the discipline derived from the \( k \cdot p \) theory for conventional semiconductors. Turning to \( m^*_n \), the data seems rather scattered without clear trend. For the structures with the smaller band gaps (< 2 eV), their \( m^*_n \) are also lower (< 2 \( m_0 \)), and only the wide-gap (> 2 eV) structures have chances to own high \( m^*_n \).

![Diagram](image)

**FIG. 9.** (Color online). Distribution map of the metastable compounds of BaSn\(_2\)O\(_3\) with energies of no more than 0.2 eV/atom higher than the ground-state \( C2/c \) structure, onto the variables of \( m^*_n \) vs band gaps (a) and \( m^*_n \) vs band gaps, respectively. The data in blue represent the structures with Sn 3-fold coordinated by O.

**SUMMARY AND FURTHER DISCUSSION**

With the aim of designing new-type oxides with the \( s - p \) hybridization in valence bands for achieving good \( p \)-type conductivity, we explore crystal structures and phase stability of ternary alkaline-earth metal Sn(II) oxides by using first-principles global optimization structure search calculations. We identify two stable compounds, SrSn\(_2\)O\(_3\) in the \( Pcca \) structure and BaSn\(_2\)O\(_3\) in the \( C2/c \) structure, exhibiting both lattice dynamical stabilities and thermodynamic stabilities with respect to competing phases. BaSn\(_2\)O\(_3\) shows a moderate band gap of 1.90 eV (with a direct gap of 2.37 eV), and quite dispersive valence bands with a low hole effective mass of 0.87 \( m_0 \). This originates mainly from the antibonding hybridization between Sn-5s and O-2p states in valence bands, resembling that of litharge SnO. In contrast, SrSn\(_2\)O\(_3\) have a wide band gap of 3.15 eV, and unexpected flat valence bands with a very heavy hole effective mass of above 6.0 \( m_0 \). Further analysis of low-lying metastable phases indicate that this class of materials show a wide range of change in electronic properties with respect to specific connection manners of the basic structural motifs of SnO\(_3\) tetrahedra. The remarkable differences in properties of the two newly identified stable compounds, BaSn\(_2\)O\(_3\) and SrSn\(_2\)O\(_3\) and the fact that this class of materials span ranges of applications requiring \( p \)-type conductivity such as transparent conductors and solar absorbers, suggests experimental investigation of these compounds as well as searches for quaternary Sn(II) oxide compounds and alloys with related compositions.

The family of ternary Sn(II) oxides containing alkaline/alkaline-earth metals follows Zintl behavior in that the cationic metals act only by providing electrons and supporting the lattices, and the structural framework is made up of connected SnO\(_3\) tetrahedra. The electronic properties of materials are to a large extent determined by the Sn-O framework. In this sense these materials can be viewed as stuffed, though very heavily distorted, SnO (e.g., with the change of Sn coordination number from 4 to 3). The breaking of ideal layered structure of SnO increases isotropy of transport-related properties. The tetrahedra connecting with each other within the Sn-O framework facilitates carriers band transport. The stabilization of Sr/BaSn\(_2\)O\(_3\) in the system can also be rationalized based on this Zintl concept. Compared with Mg/Ca, Sr and Ba have the lower electronegativities, 0.95 and 0.89 by Pauling scale, respectively, which are comparable to those of Na (0.93) and K (0.82). Such more electropositive cations correspond to the more complete charge transfer from cation sites to the Sn-O framework. The sufficient amount of electrons available for Sn-O bonding in the framework prevents Sn from being oxidized to Sn(IV) and thus stabilizes Sn(II) compounds. This underlines the important role of the electronegativity of metals in stabilizing relevant ternary or quaternary Sn(II) oxides. Furthermore the existence of alkaline-earth metals with +2 valence in the system is greatly beneficial to \( p \)-type doping, since partial substitution of alkaline-earth metals with alkali metals is a well established doping routine, as demonstrated for instance in Fe-based superconductor of Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\).[54] The possibility of existence of compensating intrinsic defects (i.e., hole killers) such as the Sn interstitial and oxygen vacancy[55, 56] should be considered in the context of doping studies if these compounds are successfully synthesized.

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Supporting Information for "Design of ternary alkaline-earth metal Sn(II) oxides with potential good p-type conductivity"

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FIG. S1. (Color online). Results of crystal orbital overlap population (COOP) between the (a) Sn-5s and O-2p and (b) Sn-5p and O-2p orbitals for SnO (black), SrSn$_2$O$_3$ (red) and BaSn$_2$O$_3$ (blue). The positive n(e) represents bonding states and the negative n(e) represent anti-bonding ones. The VB maximum is set to energy zero.

SUPPLEMENTARY INFORMATION
TABLE S1. Explicit structural data of the metastable phases of BaSn₂O₃ (shown in Fig. 8 of the main text) identified from structure searches. The differences in energy between these structures and the ground-state C2/c structure are indicated (as “Relative energy”).

| Relative energy | Lattice parameters (Å) | Wyckoff positions | Atoms | x     | y     | z     |
|-----------------|------------------------|-------------------|-------|-------|-------|-------|
| 47 meV/atom     | a = 6.3843             | 4c                | Ba    | 0.0000| 0.9990| 0.2500|
|                 | b = 9.8625             | 8m                | Sn    | 0.0000| 0.3368| 0.5035|
|                 | c = 8.2268             | 8e                | O1    | 0.7823| 0.5000| 0.5000|
|                 |                        | 4c                | O2    | 0.0000| 0.7138| 0.2500|
| Cmcm            |                        |                   |       |       |       |       |
|                 | a = 5.9318             |                   | Ba1   | 0.1855| 0.1412| 0.9022|
|                 | b = 6.0781             |                   | Sn1   | 0.1150| 0.2482| 0.3397|
|                 | c = 8.3409             | 2i                | Sn2   | 0.5599| 0.3984| 0.6883|
| P-1             | α = 98.2931°           |                   | O1    | 0.8206| 0.4305| 0.1886|
|                 | β = 88.3811°           |                   | O2    | 0.3550| 0.3243| 0.1906|
|                 | γ = 60.8210°           |                   | O3    | 0.2478| 0.8976| 0.1684|
|                 |                        |                   |       |       |       |       |
| 31 meV/atom     | a = 10.5842            |                   |       |       |       |       |
|                 | b = 5.9641             | 4c                | Sn2   | 0.2110| 0.1605| 0.8373|
|                 | c = 14.6972            |                   | O1    | 0.1505| 0.9507| 0.6865|
|                 | β = 145.4060°          |                   | O2    | 0.6025| 0.9328| 0.6907|
|                 | γ = 60.8210°           |                   | O3    | 0.8666| 0.1143| 0.6686|
|                 |                        |                   |       |       |       |       |
|                 | a = 10.8670            | 4e                | Ba    | 0.0000| 0.7222| 0.2500|
|                 | b = 5.9815             | 8f                | Sn    | 0.7222| 0.0754| 0.9962|
|                 | c = 13.8858            | 8f                | O1    | 0.6256| 0.8851| 0.0183|
|                 | β = 144.2090°          |                   | O2    | 0.0000| 0.5487| 0.7500|
|                |                        |                   |       |       |       |       |
| 23 meV/atom     | a = 6.0895             |                   | Sn2   | 0.3517| 0.2422| 0.8750|
|                 | b = 6.1125             |                   | Sn3   | 0.7443| 0.5338| 0.9435|
|                 | c = 8.1359             | 1a                | Sn4   | 0.6908| 0.5325| 0.4619|
| P1              | α = 91.7823°           |                   | O1    | 0.0519| 0.1684| 0.9493|
|                 | β = 87.3882°           |                   | O2    | 0.7662| 0.1577| 0.4004|
|                 | γ = 61.3076°           |                   | O3    | 0.3202| 0.6018| 0.4252|
|                 |                        |                   | O4    | 0.0440| 0.6143| 0.8960|
|                 |                        |                   | O5    | 0.6641| 0.4707| 0.7090|
|                 |                        |                   | O6    | 0.3357| 0.1376| 0.6311|
| Relative energy | Lattice parameters (Å) | Wyckoff positions | Atoms   | x       | y       | z       |
|-----------------|------------------------|-------------------|---------|---------|---------|---------|
| 20 meV/atom     | a = 10.8670            | 2a Ba1            | 0.0000  | 0.0040  | 0.0000  |
|                 |                        | 2b Ba2            | 0.5000  | 0.0037  | 0.5000  |
| 20 meV/atom     | b = 5.9815             | 4c Sn1            | 0.3930  | 0.0017  | 0.7196  |
| C2              | c = 13.8858            | 4c Sn2            | 0.6187  | 0.4672  | 0.7998  |
|                 | β = 144.2090°          | 4c O1             | 0.5903  | 0.1281  | 0.7338  |
|                 |                        | 4c O2             | 0.3927  | 0.3466  | 0.7576  |
|                 |                        | 4c O3             | 0.8859  | 0.3721  | 0.0463  |
|                 |                        | 2a Ba1            | 0.4035  | 0.9072  | 0.8406  |
| 20 meV/atom     | a = 9.7708             | 4a Sn2            | 0.6975  | 0.7327  | 0.5312  |
| Pca2₁           | b = 9.1720             | 4d O1             | 0.3690  | 0.7500  | 0.2500  |
|                 | c = 6.0581             | 8e O2             | 0.8955  | 0.0231  | 0.1251  |
| 16 meV/atom     | a = 11.2582            | 4e Ba             | 0.2359  | 0.2500  | 0.7500  |
|                 |                        | 2a Ba1            | 0.0000  | 0.0000  | 0.0652  |
|                 |                        | 2a Ba2            | 0.0000  | 0.0000  | 0.5559  |
| 16 meV/atom     | a = 10.9179            | 4c Sn1            | 0.1749  | 0.4638  | 0.7823  |
| Pnn2            | b = 5.9425             | 4c Sn2            | 0.6797  | 0.0072  | 0.8026  |
|                 | c = 8.2892             | 4e O1             | 0.8611  | 0.8611  | 0.8239  |
|                 |                        | 4e O2             | 0.1530  | 0.3988  | 0.5379  |
|                 |                        | 4e O3             | 0.1402  | 0.8458  | 0.3089  |
| 9 meV/atom      | a = 6.0678             | 4e Ba             | 0.5000  | 0.2500  | 0.8077  |
| Imma            | b = 6.2523             | 8i Sn             | 0.2549  | 0.2500  | 0.3998  |
|                 | c = 10.6876            | 4e O1             | 0.5000  | 0.2500  | 0.0640  |
|                 |                         | 8g O2             | 0.2500  | 0.5255  | 0.7500  |
|                 | a = 6.0678             | Ba                | 0.4619  | 0.4594  | 0.7543  |
|                 | b = 6.1860             | Sn1               | 0.1571  | 0.8544  | 0.0364  |
| 9 meV/atom      | c = 8.2778             | 2i Sn2            | 0.8547  | 0.2166  | 0.4317  |
| P-1             | α = 97.1624°            | O1                | 0.7782  | 0.5118  | 0.5240  |
|                 | β = 90.7640°            | O2                | 0.7805  | 0.7862  | 0.9974  |
|                 | γ = 115.5592°           | O3                | 0.7866  | 0.2698  | 0.1962  |