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Band-gap engineering in TiO$_2$-based ternary oxides
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Phys. Rev. B 85, 195201 — Published 4 May 2012
DOI: 10.1103/PhysRevB.85.195201
The electronic structure of several ternary oxides (Sn\(_2\)TiO\(_4\), PbTiO\(_3\), Bi\(_2\)Ti\(_4\)O\(_11\) and Bi\(_4\)Ti\(_3\)O\(_12\)) based on binary lone pair oxides (SnO, PbO, and Bi\(_2\)O\(_3\)) and a \(d^0\) oxide (TiO\(_2\)) is investigated using soft X-ray spectroscopy and electronic structure calculations. We find that the valence band of these ternary oxides is bounded by bonding (at the bottom of the valence band) and antibonding (at the top of the valence band) O\(_{2p}\) lone pair \(ns\) (Sn\(5s\), Pb\(6s\), Bi\(6s\)) hybridized states, while the conduction band is dominated by unoccupied Ti\(3d\) states. The existence of these two features is found to be independent of crystal structure or stoichiometry. The calculated hybridization in the bonding O\(_{2p}\) lone pair \(ns\) states is in reasonable agreement with the relative intensity of this feature in the measured X-ray emission spectra. The dominant influence on the conduction and the valence bands in the ternary oxides is due to different aspects of the electronic structure in the parent binary oxides, and we consequently find that the band gap of the ternary oxide is found to be a stoichiometric-weighted addition of the band gaps of the parent oxides.
I. INTRODUCTION

The search for more efficient host materials for solar-driven hydrogen production has brought metal oxides (such as TiO$_2$, ZnO, and Fe$_2$O$_3$) into the light of renewed scientific attention in the last few years$^1$. Of these binary metal oxides, TiO$_2$ is one of the most promising photoanode materials for water splitting using solar radiation because of its suitable band structure — including a band gap straddling the reduction and oxidation potential of water — and low cost and high corrosion resistance in a wide variety of aqueous electrolytes$^2$. However the band gap of TiO$_2$ is too large (3.03 eV for rutile$^3$ and 3.2 eV for anatase$^4$) to absorb a significant part of the visible spectrum. Only UV radiation, which is about 4-5% of the solar spectrum, can drive photoconversion in TiO$_2$. To achieve an acceptable hydrogen conversion efficiency (i.e. 15% or more) the band gap must be reduced below 2.2 eV$^5$. Therefore, the band gap reduction of TiO$_2$ is a key requirement for effective utilization of solar radiation. One way of reducing the bandgap for the next generation of TiO$_2$-based photocatalysts is to combine multiple anions or cations to form ternary (or even more complex) oxides. Of all the possible ways of forming ternary oxides, four areas of research are of immediate promise for band gap reduction:

1. Doping TiO$_2$ by replacing oxygen atoms with anions having higher 2$p$ orbital energy (such as B, C and N), creating bands$^7,8$ or defect states within the nominal band gap$^9-12$.

2. Replacing Ti ($d^0$) with 3$d^n$ and 4$d^n$ cations (such as V, Cr, Nb, or Mo) introducing $d$-character to the valence band$^{13,14}$.

3. Replacing Ti atoms with 3$d^{10}$ cations (such as Zn, Cd, or Ga) inducing 3$d^{10}$ - O 2$p$ repulsion$^{15}$.

4. Replacing Ti atoms with heavy metal ns$^2$ cations (such as Sn, Sb, Pb, or Bi) because of participation of 5$s$ or 6$s$ lone pairs in chemical bonding with O 2$p$ states$^{16,17}$.

Of course a combination of these approaches is also possible$^{18,19}$.

The focus of the present paper is to explore the last possibility. We study the electronic structure of ternary oxides formed by the precursors TiO$_2$ and SnO, PbO or Bi$_2$O$_3$. Soft X-ray spectroscopy measurements and electronic structure calculations of TiO$_2$, SnO, PbO, Bi$_2$O$_3$ and ternary Sn$_2$TiO$_4$, PbTiO$_3$, Bi$_4$Ti$_3$O$_{12}$ and Bi$_2$Ti$_4$O$_{11}$ are presented and the driving factors behind the reduction in band gap of the ternary oxides from that of pure TiO$_2$ are examined.

II. SYNTHESIS, MEASUREMENT, AND CALCULATION DETAILS

Synthesis: Single crystals of Sn$_2$TiO$_4$ were prepared by heating a mixture of K$_2$CO$_3$ and TiO$_2$ with a molar ratio of 1:1 in air at 600 - 700 °C for 6 h. The product was then mixed with SnCl$_2$ with a molar ratio of Sn/Ti = 1 - 2. This mixture was then put into a quartz tube and dehydrated at 200 °C for 1 h in vacuum. The tube was then sealed and heated at 700 °C for 24 h. The product was washed with distilled water to remove chlorides and dried at 50 °C. The full details of the preparation and structural characterization of this material are published elsewhere.$^{20}$

The Bi$_4$Ti$_3$O$_{12}$ powder sample was prepared from a stoichiometric mixture of Bi$_2$O$_3$ (Alfa Aesar, 99.9999 %) and TiO$_2$ (Alfa Aesar, 99.99 %) by annealing in air at 850 °C for 50 h with two intermediate grindings. The phase purity was checked with XRD, our results were the same as those available in the literature.$^{21}$ PbTiO$_3$ and Bi$_2$Ti$_4$O$_{11}$ were both commercially available powders (Alfa Aesar, 99.9%). Rutile TiO$_2$, SnO, litharge PbO, and Bi$_2$O$_3$ powders were also commercially available (Alfa Aesar, 99.9%).

Spectroscopy Measurements: The X-ray emission spectroscopy (XES) measurements were performed at Beamline 8.0.1 of the Advanced light Source (ALS) at Lawrence Berkeley National Laboratory. The endstation uses a Rowland circle geometry X-ray spectrometer with spherical gratings and an area sensitive multichannel detector$^{22}$. The O K XES were excited near the O 1$s$ ionization threshold ($\sim$ 540 eV) to suppress the high-energy satellite structure$^{23}$. The spectrometer resolving power ($E/\Delta E$) for emission measurements was about 10$^3$.

The X-ray absorption spectroscopy (XAS) measurements were performed at the Spherical Grating Monochromator (SGM) beamline of the Canadian Light Source (CLS) at the University of Saskatchewon. The absorption measurements were acquired in total fluorescence mode (TFY) using a channel plate fluorescence detector$^{24}$. The monochromator resolving power ($E/\Delta E$) for absorption measurements was 2$\times$10$^3$. All absorption spectra were normalized to the incident photon current using a highly transparent gold mesh in front of the sample to correct for intensity fluctuations in the incident photon beam. For all X-ray measurements the above samples were pressed into clean indium foil and measured in ultrahigh vacuum ($\sim$10$^{-7}$ - 10$^{-8}$ torr).
FIG. 1. (Color online) Crystal structures of the oxides studied herein. (a) PbTiO$_3$, (b) Bi$_4$Ti$_3$O$_{12}$, (c) SnO or PbO, (d) TiO$_2$, (e) Bi$_2$O$_3$, (f) Sn$_2$TiO$_4$, (g) Bi$_2$Ti$_4$O$_{11}$. In the case of Bi$_4$Ti$_3$O$_{12}$ only half of the unit cell is shown, the full unit cell is formed by mirroring the shown atoms upwards in the plane of the page. In the other cases slightly more than a single unit cell is shown to emphasize the site symmetry of the cations. These crystal structure diagrams were produced using VESTA 2.1.0.

Electronic Structure Calculations: Density functional theory (DFT) calculations for the experimentally determined crystal structures of ternary oxides Sn$_2$TiO$_4$ (space group $P4_2/mbc$), PbTiO$_3$ (space group $P4mm$), Bi$_4$Ti$_3$O$_{12}$ (space group $B2cb$), Bi$_2$Ti$_4$O$_{11}$ (a phase, space group $C2/c$), TiO$_2$ (rutile, space group $P4_2/mmc$), SnO (space group $P4/nmm$), PbO (litharge, space group $P/nmm$), and Bi$_2$O$_3$ (a phase, space group $P2_1/c$) based on the full-potential augmented plane-wave method with scalar-relativistic corrections were performed using the WIEN2k code. For the exchange-correlational functional the Perdew-Burke-Ernzerhof (PBE) variant of the generalized gradient approximation was used. To improve the calculated band gaps, we have also added a calculation cycle to the PBE calculation using the modified Becke Johnson (mBJ) exchange potential. The atomic sphere radii (used to determine whether plane waves or spherical harmonics will be used in the expansion of the wavefunction) for all cases were chosen such that they were nearly touching, and $R_{MT} K_{max} = 7$ (the product of the smallest of the atomic sphere radii $R_{MT}$ and the plane wave cutoff parameter $K_{max}$) was used for the expansion of the basis set. The Brillouin zone integrations were performed on a $k$-point grid of up to 1000 points (the exact number of $k$-points depends on the symmetry of the unit cell). In all cases the energy convergence was better than $10^{-4}$ Ry/unit cell and the charge convergence was better than $10^{-3}$ e/atom.

The oxygen $K$ XES and $L_s$ XAS was calculated from the ground state bandstructure using the “XSPEC” package included with WIEN2k, which simulates the measured spectra by multiplying the partial density of states with a dipole transition matrix and a radial transition probability. The calculated XES and XAS were broadened with a Lorentzian function (with an energy dependent width varying quadratically from 0.1 eV at the upper band edge to 0.5 eV at the lower band edge) to mimic the core hole lifetime broadening, and a Gaussian function (with an energy dependent width based on the aforementioned experimental resolving power) to mimic the instrumental resolution.

The energy scale of the calculated XES spectra were shifted so the main spectral peak was aligned with the main spectral peak in the measured XES spectra. The calculated XAS spectra were shifted by the same amount; in this manner the energy of the most intense measured and calculated XES spectral feature coincides for each material by design, any agreement between other calculated and measured XES or XAS features may be regarded as an indication of the accuracy of the calculation.

III. RESULTS AND DISCUSSION

The crystal structure of the ternary oxides Sn$_2$TiO$_4$, PbTiO$_3$, Bi$_4$Ti$_3$O$_{12}$ and Bi$_2$Ti$_4$O$_{11}$, in particular the local symmetry of the constituent atoms, bears some similarity to their precursor binary oxides. As shown in Figure 1, we may separate the ternary oxides into two groups: those consisting of alternating layers of TiO$_6$ octahedra and cation - oxygen planes (namely, PbTiO$_3$ and Bi$_4$Ti$_3$O$_{12}$), and those consisting of groups of TiO$_6$ octahedra separated by cation - oxygen channels (namely Sn$_2$TiO$_4$ and Bi$_2$Ti$_4$O$_{11}$).

To what degree does the similarity in local structure between the ternary oxides and their precursor binary oxides indicate a similarity in electronic structure? For an arbitrary material we may not expect any general similarity, but for these ternary oxides there are two key factors to keep in mind:
FIG. 2. (Color online) Calculated DOS of the materials studied herein. The top of the valence band is at 0 eV. The calculations predict all materials have a band gap, although the gap for SnO is quite small. The conduction band Ti $3d$ states have been reduced in amplitude by a factor of 3. Note how the lone pair cation states (Sn $5s$, Pb and Bi $6s$) are split into bonding and antibonding states at the bottom and top of the valence band, respectively.

a For brevity, we will call the top of the valence band the “Fermi level”, even though technically the Fermi level is undefined for band gap materials.

1. We expect the conduction band to be dominated by Ti $3d$ states (since in all cases the Ti is nominally in a $3d^0$ state), and

2. We expect the lone pair Sn $5s$, Pb/Bi $6s$ states to strongly affect the valence band.

In regard to the former point, the distribution of transition metal $3d$ states is strongly driven by the local symmetry$^{37,38}$, and since in all cases the Ti atoms are in distorted octahedra we may expect the distribution of these states in all ternary oxides considered herein to be similar to those of the precursor TiO$_2$. With regard to the latter point, because the lone pair Sn $5s$, Pb/Bi $6s$ states are nominally directed away from the ligands, and all stereochemical activity is confined to the same species of ligand, we may expect some similarity in the distribution of these states in the ternary oxides compared to the precursor binary oxides.

To examine these qualitative predictions in more detail, we turn to our X-ray spectroscopy measurements and DFT calculations of the materials in question. XES measurements involve the transitions from occupied electron states to core levels, while XAS measurements involve the transitions from core levels to unoccupied states. This process is dominated by dipole selection rules, and XES measurements involving a core level with angular momentum $\ell$ therefore probe the local $\ell \pm 1$ projected character of the valence band, and XAS measurements probe the local $\ell \pm 1$ projected character of the conduction band. Note that the conduction band probed by XAS is distorted from the true ground state conduction band by the presence of a local core hole in the final state of the absorption process.

Oxygen $K$ XES measurements (probing the $2p \to 1s$ transition) provide a good experimental probe of the ground state oxygen $2p$ valence band. The oxygen states strongly hybridize with bonding cation states$^{39-41}$ and consequently these measurements can provide insight into the cation electronic structure. Further, although the presence of an O $1s$ core hole in oxygen $1s$ XAS measurements (probing the $1s \to 2p$ transition) distorts the shape of the local conduction band, when oxygen is bonded to heavy cations the core hole does not usually shift the measured XAS in energy relative to the ground state conduction band$^{41}$. Therefore the combination of O $K$ XES and $1s$ XAS can provide an estimation of the band gap (be it direct or indirect).
Electronic Structure: The calculated density of states (DOS) for the ternary oxides and their precursors is shown in Figure 2. It is immediately clear that the electronic structures of these materials have many aspects in common. As we expect, the valence band in all of these materials is dominated by O 2p states. Where Ti 3d states are present, they are hybridized with the O 2p states, primarily at 4-5 eV below the Fermi level. These Ti 3d states dominate the onset of the conduction band as well, and typically are separated into two different features (although the separation is weak for Bi$_2$Ti$_4$O$_{11}$): a rather sharp feature directly at the onset of the conduction band, and a somewhat less intense feature at 2 - 3 eV higher in the conduction band. Since the Ti sites are almost octahedral, the low and high energy Ti 3d - O 2p conduction band hybridization regions are often referred to as $e_g$ and $t_2g$ bands, respectively.$^{42,43}$ The heavy cation $p$ states (Sn $5p$, Pb and Bi $6p$) have an almost negligible contribution to the conduction band, and only make a significant contribution to the conduction band at about 5 eV above the Fermi level.

The lone pair cation states (Sn $5s$, Pb and Bi $6s$) provide a significant contribution to the valence band. These states are also hybridized with O 2p states, and bonding between O and the heavy cation create a O 2p - cation ns band at the bottom of the valence band. This band is actually separate from the main valence band for materials with Bi and to a lesser extent, Pb. There is also a weaker, but still significant, O 2p - cation ns antibonding region at the Fermi level. This lone-pair hybridization is consistent with previous studies.$^{44-46}$ It is worth noting that one can qualitatively see the effects of combining the lone-pair oxides with TiO$_2$ octahedra in the DOS of the ternary oxides. In all cases the bonding O 2p - cation ns states of the ternary oxides are shifted to slightly higher energies than the corresponding states in the binary oxides. Similarly, the Ti 3d states at the onset of the conduction band are shifted towards the onset of the conduction band in the lone pair oxide. This is easiest to see in the case of Sn$_2$TiO$_4$: SnO is calculated to have a very narrow band gap, and the conduction Ti 3d states in Sn$_2$TiO$_4$ are about 2 eV lower in energy than the corresponding states in TiO$_2$. This trend also occurs in PbTiO$_3$, Bi$_2$Ti$_4$O$_{11}$, and Bi$_4$Ti$_3$O$_{12}$, although it is harder to see (the Ti 3d conduction states in PbTiO$_3$ start ~ 0.4 eV lower in energy than in TiO$_2$, while the corresponding states in Bi$_2$Ti$_4$O$_{11}$ and Bi$_4$Ti$_3$O$_{12}$ are ~ 0.2 eV higher in energy). Finally, in the case of PbTiO$_3$ and Sn$_2$TiO$_4$, the antibonding cation ns states at the Fermi level are more localized in energy, this is probably due to the greater concentration of states at the Fermi level in the TiO$_6$ octahedra (relative to pure SnO and PbO) limiting the curvature of the band structure. These observations suggest there is some merit to our initial hypothesis that the electronic structure of a $d^5$-lone pair ternary oxide may be described in terms of the electronic structure of both binary precursors.

X-ray Spectroscopy: The measured and calculated O K XES and 1s XAS spectra are shown in Figure 3. The calculated O K XES spectra generally agree quite well with the measured ones. There is also reasonable agreement between the calculated and measured O 1s XAS spectra, although since our calculations did not include a core hole we do not expect the agreement to be perfect. In fact, since the XES measurements agree with the calculations, we can attribute the differences between the measured and calculated XAS spectra to the influence of the O 1s core hole. We have previously found that the main influence of a O 1s core hole is to increase the intensity of the XAS at the bottom of the conduction band,$^{41}$ this seems to be true for the ternary and binary oxides studied herein as well, although the O 1s core hole seems to shift the XAS to lower energies in Bi$_2$O$_3$ (by about 1 eV), and to a lesser extent, in Bi$_2$Ti$_3$O$_{12}$ (by about 0.5 eV). In contrast, the O 1s core hole seems to have a minor effect on the XAS of Sn$_2$TiO$_4$ and SnO.

The measured spectra have several features in common. The TiO$_2$ XES spectrum shows two clear features (labelled $A$ and $B$ in Figure 3), which we can attribute to O 2p - Ti$3d$ hybridization for $A$, and O 2p states for $B$ with the help of the DOS calculations shown in Figure 2. The TiO$_2$ XAS spectrum also has two clear near edge features, labeled $C$ and $D$, these can be attributed to O 2p hybridization with the Ti 3d $e_g$ and $t_2g$ bands. The ternary and binary oxides containing lone pairs also show low energy structure in their XES spectrum that is related to bonding O 2p - cation ns states, labelled $S_1$ in Figure 3. There is also high energy structure in the O XES spectrum of SnO, Sn$_2$TiO$_4$, PbO, and Bi$_2$O$_3$ that is related to antibonding O 2p - cation ns states (labelled $S_2$). This identification of the $S_1$ and $S_2$ features follows from analysis of the calculated DOS discussed previously. Identifying $S_2$ in the XES spectrum of PbTiO$_3$, Bi$_2$Ti$_4$O$_{11}$ and Bi$_4$Ti$_3$O$_{12}$ is difficult, and not unambiguous. However since the calculated XES spectra for these materials do not suggest any discontinuous behaviour from the main O 2p states at B to the Fermi level, this is not unexpected. Small vertical bars in Figure 3 denote the features $S_1$, $A$, $B$, $S_2$, $C$, and $D$ in the XES and XAS for each compound. Note that in the binary oxides SnO, PbO, and Bi$_2$O$_3$, we attribute feature $B$ to O 2p - cation np hybridization, as suggested by the DOS in Figure 2.

There are two general observations one may make about the measured compared to the calculated XES spectra. The main peak $B$ is typically sharper and more intense relative to the other spectral features in the measured spectrum than predicted by the calculated spectrum. This is likely due to lattice defects in the materials destroying the perfect crystalline periodicity assumed by the calculations, and consequently introducing a greater localization of states. The other general observation is that, save for PbO and perhaps SnO, the $S_1$ spectral feature is at lower energies than predicted by the calculated spectrum. This may be due to the calculation underestimating O 2p - cation np bonding affinity. We also note that $S_1$ in the ternary oxides Sn$_2$TiO$_4$ and PbTiO$_3$ is closer in energy to $S_1$ in their parent
binary oxides (SnO and PbO, respectively), than suggested by the calculation, this indicates that the calculation may overestimate the influence of TiO$_6$ octahedra on the bonding structure. Despite these differences, however, the basic agreement in features, relative intensities, and energy spacings of the calculated and measured XES and XAS spectra suggest that our calculated DOS is accurate for these systems.

**O 2p Hybridization with Cations:** We can use our experimental XES spectra to quantitatively estimate the strength of the O 2p-cation ns bonding by taking the ratio of the integrated intensity of the $S_1$ XES feature $I_{S_1}$ to the integrated intensity of the total XES spectrum $I_{tot}$, and dividing by the ratio of the number of cation atoms $n$ and the number of electron pairs $p$ per formula unit of the lone pair binary oxide. This analysis for Bi$_2$O$_3$ and PbO is available in the literature, and is commonly called the $f_{O2p}$ value:

$$ f_{O2p} = \frac{I_{S_1}}{I_{tot}} \left( \frac{p}{n} \right) $$

Our estimates for $f_{O2p}$ are shown in Figure 4(a). These empirical values can be compared directly to the ratio of the total O 2p states to the total O 2p and cation ns states in this region (using the calculated DOS).

The technique of using $f_{O2p}$ to estimate the degree of O 2p-cation ns hybridization is justified, given the agreement shown in Figure 4(a). Importantly, we can also estimate whether $f_{O2p}$ will over- or underestimate the hybridization by a qualitative inspection of the XES. Referring back to Figure 3, we see that in the case of SnO and Sn$_2$TiO$_4$ the $S_1$ feature is relatively intense and is more of a shoulder to the main XES emission than a separate feature. We can therefore predict that $f_{O2p}$ will be an underestimate of the true hybridization, since the the $S_1$ feature probably extends somewhat into the main XES. On the other hand, for Bi$_2$O$_3$ and Bi$_2$Ti$_4$O$_{11}$ the $S_1$ feature is relatively quite weak. We can therefore predict that $f_{O2p}$ will be an overestimate of the true hybridization, since the broadened emission from the main DOS region will extend into $S_1$, providing a significant contribution to the weak hybridization emission. Bi$_3$Ti$_2$O$_{12}$ has lowest intensity $S_1$ feature, but this feature is also quite low in energy. The separation of this feature from the emission band minimizes the amount of “leakage” that can occur through broadening. We therefore expect that $f_{O2p}$ will be quite close to the true DOS hybridization, as indeed it is.

Indeed, the impact of spectral broadening on $f_{O2p}$ is evident in Bi$_3$Ti$_3$O$_{12}$: the calculated XES has roughly double the $S_1$ intensity as the measured XES (refer back to Figure 3), although $f_{O2p}$ is in excellent agreement with the
DOS hybridization (refer to Figure 4(a)). Note that $S_1$ in the calculated XES is also about 1.5 higher in energy; it is therefore likely that the broadening of the main $A$ and $B$ features into $S_1$ is responsible for the larger intensity (this also probably applies to PbTiO$_3$, where a similar situation occurs). Finally, we should mention that the broadening applied to the calculated spectra was merely a “best guess”, it could easily have been somewhat too large.

**Band Gap Estimates:** In our previous research on binary and ternary oxides, we have shown that the separation between the local maxima in the second derivatives of the O $K$ XES and $1s$ XAS spectra provides a reasonably consistent method for estimating the band gap. This is not a particularly rigorous method of determining the band edges, indeed it is only correct for DOSes which exhibit a limited range of behaviours near the band edge (here “near” means within the effective range of the spectral broadening), such as being linear or parabolic in energy. Looking back at Figure 2, we may anticipate that the second derivative method will provide reasonable estimates of the band gap for TiO$_2$ and the Bi-based compounds, since they all have relatively sharp and smooth behaviour near the Fermi level and the bottom of the conduction band. In the Sn-based materials, however, the valence band and (and conduction band for SnO) have very gradual onsets, it is unlikely that a single second derivative maximum can be unambiguously determined at the band edges. Note also that even if the DOS is shaped appropriately for the second derivative method, the aforementioned core hole shift will cause the X-ray “spectral gap” to be less than the true ground state band gap.

With these caveats in mind, it is worthwhile mentioning the estimated gap ($\Delta_{\text{exp}}$) for these materials to compare with the calculated band gap ($G_{\text{mBJ}}$) and values obtained from previous studies. These values are shown in Table I. As we expected, the $\Delta_{\text{exp}}$ spectral gap for SnO is considerably larger than both our calculated gap and those obtained from optical measurements, because of the extremely gradual onset of both the valence and the conduction bands, we expect this value to be an over estimate. Indeed, the second derivative maximum of the SnO $O K$ XES is at 527.2 eV, which is above the $S_2$ antibonding feature, and therefore clearly not at the Fermi level. In the same sense the Fermi level of Sn$_2$TiO$_4$ is also not accurately estimated by the XES second derivative maximum (this is at 526.9 eV, again above $S_2$), although the XAS second derivative maximum is within 0.1 eV of the calculated conduction band onset. For TiO$_2$, PbO, PbTiO$_3$, and Bi$_2$Ti$_3$O$_11$, the spectral gaps $\Delta_{\text{exp}}$ are quite similar to the calculated gaps. If we add the estimated core hole shifts for Bi$_2$O$_3$ and Bi$_2$Ti$_3$O$_12$ mentioned above to $\Delta_{\text{exp}}$ then we again get good agreement, but since the core hole shifts here were estimated by comparing the calculated and measured XAS the agreement is admittedly a bit contrived.

The band gaps reported from the literature in Table I are all derived from optical measurements, most of which were only probing the direct band gap. For SnO, the indirect gap was estimated as $\sim$0.7 eV from the optical data,
the lone pair parent oxide (x = 0). A similar trend in the gap between the peaks in the second derivative of the \( \text{O}_2 \) gap of a ternary oxide with a TiO₂ computation is a computationally intensive task. A particular parent oxide may have complicated crystal structures and make calculating their properties directly a

but this analysis is not available for the other lone pair oxides Bi₂O₃ and PbO. Calculated band structures suggest these are all indirect band gap materials, so we may expect the literature values for PbO and Bi₂O₃ in Table I to overestimate the gap. For Bi₂O₃, this perhaps suggests that our larger calculated gap may be a rare overestimate of a band gap by DFT (it is well known that DFT underestimates band gaps).

**Trends in Electronic Structure:** Due to the previously discussed features in the electronic structure particular to these binary and ternary oxides, namely the lone pair ns states bounding the valence band and the Ti 3d states defining the bottom of the conduction band, if we treat the ternary oxides as a mixture of the two precursor binary oxides (i.e. Sn₂TiO₄ is treated as (SnO)\(_{2/3}\)(TiO₂)\(_{1/3}\) the calculated band gaps show an almost linear dependence on the mixing fraction, as shown in Figure 4(b). Interestingly, the estimated spectral gaps \( \Delta_{\exp} \) for the Sn- and Pb-based compounds also show an almost linear dependence — despite the aforementioned inaccuracy of \( \Delta_{\exp} \) as an estimate of the band gap for SnO and Sn₂TiO₄. There is no linear trend in \( \Delta_{\exp} \) for the Bi-based compounds, but this is perhaps due to the anomalous core-hole effect on Bi₂O₃, as discussed above ("anomalous" in the fact that it appears to disproportionally affect Bi₂O₃ over any of the other Bi-based compounds).

Further, while \( \Delta_{\exp} \) does not necessarily indicate the band gap of a compound with lone pair s states, it can be used to determine whether a ternary oxide abides by this rule. If the \( \Delta_{\exp} \) of the ternary compound obtained from O K XES and 1s XAS is close to the "ideal" value (again by stoichiometry-weighted addition of \( \Delta_{\exp} \) of the parent oxides), then the band gap of the ternary compound may be inferred to be the stoichiometry-weighted addition of the band gaps of the parent oxides. This is useful because ternary oxides with a dilute stoichiometric addition of a particular parent oxide may have complicated crystal structures and make calculating their properties directly a computationally intensive task.

This is demonstrated by the energies of the XES spectral features, shown in Figure 3 and summarized in Figure 4(c). In Figure 4(c) we see how the TiO₂ content gradually lowers the energy of the antibonding S₂ feature at the top of the valence band (note that the dotted lines in Figure 4(c) show the band edges estimated using the second derivative maxima, here the problem with using the method for SnO and Sn₂TiO₄ is clear since S₂ is at higher energies than the second derivative maxima). Conversely, the presence of TiO₂ seems to stabilize the conduction band (features C and D).

This simple agreement in both calculated and measured data suggests that the true band gap of a ternary oxide formed from lone pair and a \( d^0 \) binary oxide is directly related to the stoichiometry-weighted addition of the band gaps of the precursors: in the examples studied herein the conduction band is qualitatively defined by the Ti 3d\(^0\) states, but increasing the stoichiometric content of lone pair oxides is responsible for progressively “dragging” of the conduction band edge to energies closer to that of the pure lone pair oxide. The same argument applies to the valence band edge; while it is qualitatively defined by antibonding \( s^2 \) states, increasing stoichiometric content of TiO₂ can “drag” the valence band edge closer to that of pure TiO₂.

**Conclusions:** To summarize, we have probed the electronic structure of ternary oxides Sn₂TiO₄, PbTiO₃, Bi₄Ti₃O₁₂ and Bi₂Ti₄O₁₁ using O K XES, 1s XAS, and DFT calculations. These ternary oxides are formed from precursor binary lone pair oxides (SnO, PbO, and Bi₂O₃) and the \( d^0 \) oxide TiO₂. We find that key features in the electronic structure of the precursor oxides, such as the valence band being bounded by bonding and antibonding Sn 5s, Pb 6s, or Bi 6s states hybridized with O 2p states in SnO, PbO, and Bi₂O₃, and the conduction band being primarily defined by Ti 3d states in TiO₂, are preserved in the ternary oxides. Importantly we find that the band gap of a ternary oxide with a TiO₂ fraction of x basically falls on the straight line between that of TiO₂ (x = 1) and the lone pair parent oxide (x = 0). A similar trend in the gap between the peaks in the second derivative of the O K XES and 1s XAS of these oxides suggests that this trend is a property of the general electronic structure, and

<table>
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<th>Compound</th>
<th>( \Delta_{\exp} ) ± 0.2 eV</th>
<th>( G_{\text{mBJ}} ) [eV]</th>
<th>Literature [eV]</th>
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<td>2.6</td>
<td>2.336</td>
<td>3.4(^{41})</td>
</tr>
<tr>
<td>PbO</td>
<td>2.5</td>
<td>2.116</td>
<td>2.75(^{52})</td>
</tr>
<tr>
<td>Bi₄Ti₃O₁₂</td>
<td>2.8</td>
<td>2.887</td>
<td>3.75(^{53})</td>
</tr>
<tr>
<td>Bi₂Ti₃O₁₂</td>
<td>2.4</td>
<td>2.919</td>
<td>3.08(^{54})</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>2.2</td>
<td>3.388</td>
<td>2.91(^{55})</td>
</tr>
</tbody>
</table>

**TABLE I.** Measured, calculated, and previously reported band gaps for all materials studied herein. The measured gaps are denoted by \( \Delta_{\exp} \) and the calculated band gaps are denoted by \( G_{\text{mBJ}} \). The literature band gaps are all based on optical measurements save for Sn₂TiO₄, which is exclusively based on a calculation. The second value for SnO is the estimated indirect gap, from the measurement of 2.7 eV for the direct gap.
that O K XES and Is XAS spectroscopy can be an experimental way of testing the idea that the band gap of a lone pair, $d^0$ ternary oxide is the stoichiometry-weighted addition of the band gaps of the parent lone pair and $d^0$ binary oxides. These findings can be used to predict the band gap of new ternary oxides if the band gaps of the parent lone pair and $d^0$ binary oxides are known.

ACKNOWLEDGMENTS

We acknowledge support of the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Research Chair program, and the Russian Foundation for Basic Research (Projects 11-02-00022). The Canadian Light Source is supported by the NSERC, the National Research Council (NSC) Canada, the Canadian Institutes of Health Research (CIHR), the Province of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.
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 While Bi\textsubscript{2}Ti\textsubscript{4}O\textsubscript{12} was recently reported to have B2c\textsubscript{h} symmetry\cite{57}, there are a few earlier reports that Bi\textsubscript{2}Ti\textsubscript{4}O\textsubscript{12} is best represented by the B1a1 spacegroup at ambient conditions\cite{58, 59}. Since other studies have noted that there is very little difference between the two structures\cite{60, 61}, and \textit{ab initio} calculations reveal little difference in the energy stability\cite{62} between the two phases, we feel justified in using the B2c\textsubscript{h} phase herein. Indeed, there is little difference in the bulk electronic structure of the B1a1 phase and the higher symmetry I\textit{a}m\textsubscript{3}m phase (realized above 700\degree C)\cite{21}.


