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A photoactive titanate with a stereochemically active Sn lone pair: Electronic and crystal structure of Sn_2TiO_4 from computational chemistry

Lee A. Burton, Aron Walsh*

Centre for Sustainable Chemical Technologies and Department of Chemistry, University of Bath, UK

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ABSTRACT

TiO_2 remains the most widely studied metal oxide for photocatalytic reactions. The standard approach to reduce the band gap of titania, for increasing the absorption of visible light, is anion modification. For example the formation of an oxynitride compound, where the nitrogen 2p states decrease the binding energy of the valence band. We demonstrate that cation modification can produce a similar effect through the formation of a ternary oxide combining Ti and an ns^2 cation, Sn(II). In Sn_2TiO_4, the underlying Ti 3d conduction states remain largely unmodified and an electronic band gap of 2.1 eV (590 nm) is predicted by hybrid density functional theory. Our analysis indicates a strong potential for Sn_2TiO_4 in visible-light driven photocatalysis, which should prove superior to the alternative $(SnO_2)_{1-x}(TiO_2)_x$ solid-solution.

1. Introduction

Metal oxides are widely studied for solar harvesting applications, despite the fact that the majority of metal oxides have optical band gaps that transmit a large fraction of the terrestrial solar spectrum. Indeed, while the most studied material titanium dioxide (TiO_2) is catalytically active for the water-splitting reaction [1], the theoretical maximum solar-to-H_2 conversion efficiency is only of the order of 1%, given its large optical band gap of ca. 3.2 eV [2]. One major challenge in the field of energy materials is to design, or discover, new metal oxide systems that can absorb significant fractions of visible light in order to make commercial devices economically viable in a competitive market place [3–5].

TiO_2 has been studied for applications ranging from heterogeneous catalysis to dye sensitized solar cells [6–8]. Despite its large optical band gap, partially reduced TiO_2 conducts electrons, i.e., $TiO_{2-\delta}$ is an n-type wide band gap semiconductor. Ti(IV) has a valence electronic configuration of $3d^0$, with the unoccupied 3d states forming the conduction band. In the presence of excess electrons, paramagnetic Ti(III) $3d^1$ species can also be formed, and in significant concentrations they can change the color of the material from white to black, with the limiting compound Ti_2O_3 being a Mott-insulator [9]. The defect chemistry and physics of TiO_2 has resulted in a substantial amount of literature in recent years [10–18]. The most promising progress towards obtaining a higher-efficiency TiO_2 based photocatalyst has involved: (i) the incorporation of nitrogen [19]; (ii) co-doping of multiple anions [20]; (iii) the application of epitaxial or uniaxial strain [21]. An alternative approach is to introduce post-transition metal oxides with filled low binding energy s states.

In comparison to TiO_2, stannous oxide (SnO) features a smaller and indirect band gap (0.7–1.3 eV), and has been the subject of recent attention owing to its hole mediated electrical conductivity (p-type conduction) [22]. Sn(II) has an occupied $5s^2$ state around 7 eV below the top of the valence band, which hybridizes with O 2p, and nominally empty Sn 5p states, to produce a local distortion in the Sn electron distribution and coordination environment, resulting in the layered litharge structure [23–25]. The oxide of tetravalent tin (SnO_2) adopts the rutile crystal structure, similar to TiO_2, and exhibits a wider band gap (3.6 eV) as well as electron mediated conductivity (n-type conduction) [26,27].

The combination of Sn(II) and Ti(IV) cations in a single material could be desirable for numerous reasons including the potential for the coexistence of p-type and n-type conductivity for oxide-based electronic applications (e.g., oxide p–n homo-junctions), and a relatively low optical band gap for photocatalysis. Unfortunately, attempts to grow the ternary Sn/Ti oxide system have resulted in anatase or rutile solid solutions containing the Sn(IV) species [28–30], without the presence of the occupied Sn $5s^2$ orbitals. However, Kumada et al. reported the successful synthesis of Sn_2TiO_4 single crystals from TiO_2 and $SnCl_2$ precursors [31], with a more recent report of microwave assisted synthesis by Ohara et al. [32]. The electrical or optical properties of Sn_2TiO_4 have not yet been reported to our knowledge.

In this paper, we report a study of the structural and electronic properties of tin titanate, using an electronic structure approach

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* Corresponding author.
E-mail address: a.walsh@bath.ac.uk (A. Walsh).

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based on Density Functional Theory (DFT). Preliminary results were reported as part of a perspective on the computational study of energy materials [33], but this work has been extended to include thermodynamic and vibrational properties, in addition to the electronic band structure and alignments. The results compare well to the limited experimental data available to date, including the recently measured vibrational spectrum. We call for further studies on the topic in order to verify our predictions in relation to the electronic and optical properties of the material, and to assess its photocatalytic activity.

2. Computational methodology

Total energy electronic structure calculations were performed within the framework of DFT [34,35], using periodic boundary conditions to represent the perfect solid [36]. The all-electron FHI-AIMS code [37,38] was employed, which constructs the electronic wavefunction using a basis set composed of numeric atom-centered orbitals. In this study, a “Tier-2” basis set was employed with a $6\times6\times8$ special k-point grid, and scalar-relativistic effects treated at the scaled ZORA level [39]. Relativistic corrections were found to be important in the correct description of the Sn 5s band energy, which for an atomic calculation increases the binding energy by 0.75 eV. Exchange–correlation effects were described through the generalized gradient approximation, with the semi-local Perdew–Burke–Ernzerhof functional revised for solids (PBEsol) [40].

In order to obtain a more quantitative band gap prediction, hybrid-DFT calculations were also performed in which 25% of the short-range semi-local exchange functional was replaced with exact non-local Hartree–Fock exchange, and screening ($\omega = 0.11$ Bohr^{-1}) was applied to partition the Coulomb potential in short-range (SR) and long-range (LR) components: the HSE06 functional [41–43]. This functional is known to perform well for the parent compound TiO_2 [44]. All hybrid functional calculations [45,46] were performed in the code VASP [47,48]. For these calculations, equivalent k-point meshes were combined with a well-converged 500 eV plane-wave cutoff for the basis set. For the same choice of density functional, comparable results were obtained with both VASP and FHI-AIMS.

3. Crystal structure

The crystal structure for Sn_2TiO_4 determined by Kumada et al. [31] is isostructural to “red lead” (Pb_3O_4) as shown in Fig. 1. Pb_3O_4 has a crystal structure (space group $P4_2/mbc$, D_{4h}^{13}) containing two distinct cation sites characteristic of the Pb atoms found in both litharge Pb(II)O (8h Wyckoff position, pyramidal arrangement with three nearest-neighbor oxygens) and rutile Pb(IV)O_2 (4d Wyckoff position, distorted oxygen octahedron), respectfully [49]. Despite being considered of the mineral spinel class, its crystal structure is unique and occurs only for a handful of other materials including Sb_2CoO_4, Pb_2SnO_4 and Sb_2ZnO_4 [50]. There are 28 atoms per crystallographic unit cell and a notable hollow in the center of the crystal, understood to be stabilized by van der Waals interactions between the lone pair electrons [51]. The synthesis of Sn_2TiO_4 in the Pb_3O_4 structure is therefore not unexpected given that it simultaneously satisfies the coordination preferences of both the Ti(IV) and Sn(II) ions.

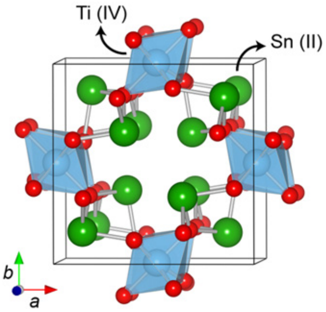

Fig. 1. The crystal structure of Sn_2TiO_4. The Ti distorted octahedral are filled blue; Sn atoms are colored green, and oxygen coloured red.

Taking the reported crystal structure as a starting point, both the internal positions and lattice vectors were optimized to their equilibrium positions for each density functional under the constraint of tetragonal symmetry. The equilibrium structural parameters are collected in Table 1. The calculated lattice constants are within 1% of experiment and the local bonding environments are well reproduced, namely, the mildly distorted Ti octahedra and the highly distorted four coordinate Sn site.

The vibrational spectra of Sn_2TiO_4 single crystals have been recently measured [52], with a small number of sharp peaks observed in the Raman spectrum. While there exists 84 vibrational modes, owing to the 28 atoms in the unit cell, these are significantly reduced by the symmetry selection rules. Analysis of the calculated phonon frequencies, under point group D_{4h}, results in a set of four Raman active peaks from 250 to 300 cm^{-1} (B_{2g}, A_{1g} and E_g), an isolated peak at 475 cm^{-1} (A_{1g}), and the highest intensity peak present at 628 cm^{-1} (A_{1g}). These are in excellent agreement with the reported spectrum [52].

4. Thermodynamic properties

Given the absence of available experimental data, we have calculated the fundamental thermodynamic properties of Sn_2TiO_4, which will be of importance for the design of efficient synthetic routes, as well as the control of phase equilibria. The enthalpy of formation,

$$(\Delta H_f)\ 2Sn(s) + Ti(s) + 2O_2(g) \rightarrow Sn_2TiO_4$$

is found to be −1406.8 kJ/mol, indicative that the isolated stoichiometric compound is stable thermodynamically. The enthalpy of mixing with respect to the parent binary oxides

$$(\Delta H_{mix})\ 2SnO + TiO_2 \rightarrow Sn_2TiO_4$$

is −0.5 kJ/mol, which is consistent with the slow reaction rate for solid-state synthesis that can be substantially promoted by microwave irradiation [32]. Finally, the probability for formation of the ternary material from a mixture of rutile dioxides can be assessed

Table 1
Equilibrium structural paramaters of Sn_2TiO_4 derived from experiment [31] and computation (PBEsol). The percentage deviations are shown in parenthesis.

	Experiment [31]	PBEsol
a (Å)	8.492	8.474 (−0.21%)
c (Å)	5.923	5.914 (−0.15%)
Volume (Å^3)	426.93	424.68
Ti (4d site)	0, 1/2, 1/4	0, 1/2, 1/4
Sn (8h site)	0.145, 0.163, 0	0.146, 0.161, 0
O (8g site)	0.664, 0.164, 1/4	0.663, 0.164, 1/4
O (8h site)	0.098, 0.621, 0	0.097, 0.621, 0
Sn–O (Å)	2 × 2.09	2 × 2.10
	1 × 2.21	1 × 2.21
	1 × 2.76	1 × 2.77
Ti–O (Å)	2 × 1.97	2 × 1.96
	4 × 1.99	4 × 1.98