



Article Structural Characteristics, Stability, and Electronic Properties of 001 Surface with Point Defects of Zinc Stannate: A First-Principle Study

Jun Li¹, Meilin Zhu², Rou Feng^{3,*}, Yingjie Yuan¹, Zewei Fu¹, Liangliang Meng³, Yingwu Wang⁴, Ying Zhou⁴, Hui Zhang³ and Hongcun Bai^{3,*}

- ¹ Yunnan Tin Industry Group (Holding) Co., Ltd., R & D Center, Kunming 650200, China
- ² College of Basic Medical Sciences, Ningxia Medical University, Yinchuan 750004, China
- ³ State Key Laboratory of High-Efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China
- ⁴ Yunnan Provincial Academy of Science and Technology, No. 488 Dianchi Road, Kunming 650051, China
- * Correspondence: fengrou0603@163.com (R.F.); hongcunbai@nxu.edu.cn (H.B.)

Abstract: This work presents first-principles calculations on the surface and defect impact upon zinc stannate (ZS) materials with perovskite bulk structures. The structure and electronic properties of both a perfect 001 surface and surfaces with a point defect of ZS were investigated by means of density functional theory calculations. The cohesive energies of a perfect 001 surface and those with O, Sn, or Zn defects were decreased compared with that of bulk ZS. Oxygen defects on the 001 surface of ZS formed more easily than others based on the obtained cohesive energy and defect formation energy. The electronic properties close to the Fermi levels of bulk ZS materials were mainly controlled by the O 2p and Sn 5s orbitals. The formation of vacancy on the 001 surface of ZS changed the band structure and band gap compared with that of the bulk. The modulation mechanism was explored by means of structure transformation, band structure, and density of states analysis.

Keywords: perovskite structure; zinc stannate; surface effect; point defect; DFT

1. Introduction

Environmentally friendly flame-retardant materials with high performance are important and fundamental to green, low-carbon, and sustainable development [1]. At present, polymer materials are gradually being used in various applications such as construction, electronic devices, medicine, and transportation due to their advantages of light weight, easy processing, and low cost. However, most polymer materials are flammable organics [2]. This leads to a gradual increase in the frequency of fires, resulting in serious property damage. At the same time, some organic polymer materials produce a significant amount of pungent smoke during combustion [3], and the accompanying toxic and harmful gases directly endanger people's lives and increase the pressure on fire rescue personnel. Therefore, how to improve the flame-retardant properties of polymer materials is a problem that is currently receiving much attention. Research into flame-retardant polymer materials has gradually become a hotspot [4,5]. Among them, adding flame retardants to reduce the incidence of fire is an important research direction [6].

Whether polymer materials have strong flame-retardant properties mainly depends on the selection of flame retardants. Therefore, the properties of flame retardants are of great significance for the application of polymer materials [7]. The flame retardants currently used in polymer materials can be divided into additive flame retardants and reactive flame retardants according to the relationship between the additives and flameretardant materials [8,9]. Reactive flame retardants are used as monomers to bond with the material during the polymerization process, which usually has little effect on the



Citation: Li, J.; Zhu, M.; Feng, R.; Yuan, Y.; Fu, Z.; Meng, L.; Wang, Y.; Zhou, Y.; Zhang, H.; Bai, H. Structural Characteristics, Stability, and Electronic Properties of 001 Surface with Point Defects of Zinc Stannate: A First-Principle Study. *Inorganics* 2022, *10*, 258. https:// doi.org/10.3390/inorganics10120258

Academic Editor: Enrico Benassi

Received: 26 October 2022 Accepted: 9 December 2022 Published: 13 December 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). properties of the material itself and can achieve flame-retardant effects [10]. The simpler and more widely used are additive flame retardants [11], which are directly mixed with the materials and have convenient and wide-ranging applications. More than 85% of the flame retardants currently used are additive flame retardants. Additive flame retardants currently mainly include phosphorus-based, nitrogen-based, silicon-based, halogen-based, intumescent, inorganic fillers, etc. [12]. However, most flame retardants have certain toxicity [13,14]. For example, halogenated flame retardants will release corrosive gases when burning, which will endanger human life. Compared with traditional phosphorusbased and halogen-based flame retardants, and smoke suppressants, tin-based flame retardants have attracted extensive attention from researchers due to their excellent flameretardant and smoke-suppression properties. Zeng et al. studied the ethanol-gas-sensing characteristics and mechanism of ZnSnO₃ [15]. Among them, zinc stannate (ZS) flameretardant products have non-toxic and non-polluting properties, which are very suitable for today's green environmental protection requirements and are expected to become a new type of high-efficiency flame-retardant smoke suppressor combined with the modern highspeed development of polymer materials [16,17]. Previous experiments have successfully prepared ZS products using co-precipitation synthesis, the hydrothermal method, the aqueous solution method, Pechini, and other methods, and some predecessors have applied ZS-coated metal oxides, microencapsulation, and other composite materials into flameretardant PVC products [18]. Therefore, it is of great significance to study the microstructure and properties of ZS at a deeper level.

It is well known that the properties of materials are closely related to their microstructure. For metal oxide-based materials such as ZS, their stability, lifetime, and functionality strongly depend on their interface and defect behavior. Generally, the excellent flameretardant properties of inorganic flame retardants, such as metal oxides, mainly come from the surface oxide film layer [19]. The oxide film layer acts as a protective barrier to prevent combustion inside the material and the polymer structure itself due to environmental corrosion [20]. Physicochemical processes such as atom/molecular adsorption, crystal form transformation, chemical bond relaxation, and breakage usually preferentially occur at point defects on the surface of metal oxide films [21]. Studies have shown that the generation of surface defects can effectively improve their physical and chemical properties to enhance the interaction between reactants and catalyst surfaces, thereby affecting the adsorption-activation-transformation process of reactants at the interface of the catalyst with water or gas [22,23]. This is very important for the modification of surfaces' electronic properties and reactivity, which in turn affects the performance of metal oxide materials in molecular recognition, information transmission, catalysis, and other applications, making it the focus of research in recent years [24–26]. At the same time, this is also one of the basic topics of surface science today.

Therefore, it is very important to study the defects of the ZS surface to systematically understand and modulate its flame-retardant properties. However, only a few studies have been conducted on the electronic structure of ZS [4,27–29]; Liu et al. studied the structure, elasticity, and electronic properties of ZnSnO₃ under pressure using a first-principle method [29]. The correlation between their microstructure and functional properties has not been established. According to our systematic investigation of the published work, the current work mainly focuses on the theoretical calculations of ZS bulk structure to obtain information such as the energy and band structure [4]. No work has been reported on the effect of point defects on electronic structure and properties for ZS. A thorough understanding and explanation of the influence of these intrinsic defects on the stability, electronic band structure, and density of states (DOS) characteristics of ZS is the theoretical basis for the construction of new flame-retardant materials. In this work, first-principles calculations were performed on the structure and electronic properties of perovskite ZnSnO₃ bulk and its low-index surface (001) with the density functional theory (DFT) method. The stability of three-point defect structures on the 001 surface was studied.

important theoretical guidance for the design, construction, and application of ZS-based composites as flame-retardant materials.

2. Results and Discussion

2.1. Geometry Structure

 $ZnSnO_3$ is an R3c structure with an asymmetric center, which belongs to the typical ABO₃-type perovskite crystal [30]. The calculation accuracy of the bulk crystal will directly affect the subsequent surface analysis, so we first provide the calculated structural parameters of the bulk ZS [30]. The lattice constants of bulk ZS by structure optimizations are shown in Table 1. It can be seen that the lattice constants of bulk ZS by first principles in this study are a = 5.351 Å and c = 14.224 Å. The experimental values are a = 5.344 Å and c = 14.221 Å [4]. The calculated values in this study are in good agreement with the reported experimental value [4], and the error is within 0.01 Å. The previous calculations using the density functional theory PBE and the general potential linearized augmented planewave (LAPW) method yield the results of a = 5.562 Å and c = 14.003 Å [31], with larger errors than those in this work compared with the experimental ones. This shows that the calculation method in this work has high accuracy, and the selection of various parameters in the calculation is also reasonable. The deviation between the lattice parameters obtained in this study and the calculated value [31] is approximately 3.9%, which is caused by the inherent error of GGA calculation, which meets the requirements of calculation accuracy and does not affect the conclusions of this paper [25].

Table 1. Lattice constants of ZnSnO₃ (experimental, calculated, and this work, in Å).

Lattice Constants	a = b	с	References
Exp.	5.344	14.221	[4]
Cal.	5.562	14.003	[31]
This work	5.351	14.224	/

To further investigate the effect of defects on the surface geometry, we analyze the radial distribution function (RDF) of the bulk and surfaces of ZS. RDF of ZnSnO₃ bulk; perfect 001 surface; and surfaces with V_O, V_{Sn}, and V_{Zn} defects are shown in Figure 1 and Figures S1–S5 in Supplementary Materials. From the figures, the peaks located at approximately 2.102 Å are all attributed to O-Sn or shorter O-Zn bonds (2.026 Å) for these five structures. The peaks at approximately 2.413 Å are mainly longer O-Zn bonds (2.356 Å) for these ZS-based systems. While the peaks at approximately 3.024 Å mainly contributed to Sn...Zn interactions, the small peaks after 3.421 Å for the whole five systems mainly contributed to the sub-neighboring O...Sn and O...Zn interactions.

It can be seen that the overall structure and peak position of the total RDF of $ZnSnO_3$ bulk, perfect 001 surface, and the three surface defects are similar, which means that the atomic interactions in all of the slab structures of ZS almost maintain the characteristics of bulk $ZnSnO_3$. Therefore, although the surfaces with or without defects are different from the bulk, they still retain the essential geometrical properties of the bulk materials to a certain extent.

Compared with the total RDF of the perfect 001 surface, it can be found that the O-Zn peak intensity decreases by approximately 2.408 Å for the total RDF of the V_O and V_{Zn} defects, which is mainly caused by the breakage of the O-Zn bond. The V_O and V_{Zn} defect systems appear to have new peaks at approximately 1.754 Å and a small peak at approximately 3.012 Å, which is rather different from that in the perfect 001 surface. This is because the V_O defect and V_{Zn} defect break bonds with the atoms originally connected to them during the formation process. These broken atoms undergo geometric reconstruction on the defective surface to seek an equilibrium state with the generation of new chemical bonds.



Figure 1. Radial distribution functions of ZnSnO₃. (**a**) bulk; (**b**) perfect 001 surface; (**c**) V_O surface; (**d**) V_{Sn} surface; (**e**) V_{Zn} surface.

At the same time, we compare and analyze some structural changes among the bulk, perfect surface, and three defect models. We find two different O-Zn bonds (2.026 Å and 2.356 Å, respectively) and two different O-Sn interactions (2.074 Å and 2.135 Å, respectively) in the zinc stannate bulk and also distribute three common bond angles, which are Sn-O-Zn (117.2°) , O-Zn-O (109.9°) , and O-Sn-O (99.1°) . In the 001 perfect surface model, we can also find the above two O-Zn, O-Sn bonds, and three bond angles, which shows that the surface material and bulk material of the slab model maintain a good consistency. After the structure optimization of the V_O defect model, the O-Zn bonds near the defects changed to 1.901 Å, 2.069 Å, 2.109 Å, and 2.219 Å, respectively, which is also the reason for the new small peaks in the RDF. The O-Sn bond changed to 2.047 Å and 2.178 Å, respectively, and the three bond angles also changed, namely Sn-O-Zn (113.3°), O-Zn-O (119.4°), and O-Sn-O (99.1°) . After the V_{Sn} defect is formed, the geometric structure around it changes relatively little. The O-Zn bond changed to 2.026 Å and 2.261 Å, the O-Sn bond changed to 2.038 Å and 2.197 Å, and the three bond angles changed as Sn-O-Zn (119.6°), O-Zn-O (117.4°), and O-Sn-O (99.1°). After optimization, the O-Zn bonds near the V_{Zn} defects vary to 1.962 Å, 2.083 Å, 2.105 Å, and 2.289 Å, and we find that this variation is in good agreement with the peak energies that appear in the RDF. The O-Sn bond changed to 2.024 Å and 2.163 Å, and the three bond angles also changed to varying degrees, namely Sn-O-Zn (114.4°), O-Zn-O (118.9°), and O-Sn-O (106.8°). These changes occurring around the three defects are consistent with the intermolecular interactions exhibited by RDF. The bond lengths and bond angles of the three defect models with large changes after structural optimization are shown in Figure S6 in the Supplementary Materials.

In order to further understand the geometric structure changes around the defect, we also analyzed the Mulliken charge population of the atoms around the defect. The charges of the surface atoms on the 001 perfect surface of zinc stannate are O_{81} (6.779 e), O_{82} (6.779 e), O_{84} (6.780 e), O_{85} (6.780 e), O_{87} (6.778 e), O_{89} (6.778 e), and Zn_{37} (11.540 e). The charges of the O_{81} and Zn_{37} atoms around the optimized V_O defect are 6.822 e and 11.629 e, which are lost by 0.043 e and 0.089 e, respectively. The absence of O atoms leads to the formation of a cationic center around the defect. The O_{82} , O_{84} , O_{87} , and Zn_{37} atoms around the V_{Sn} defect obtained 0.262 e, 0.259 e, 0.256 e, and 0.176 e, respectively, and the formed charges were 6.517 e, 6.521 e, 6.522 e, and 11.364 e. During the formation of V_{Zn}

defects, the charges of the O_{81} , O_{85} , and O_{89} atoms around them are 6.609 e, 6.608 e, and 6.612 e, and they are, respectively 0.170 e, 0.172 e, and 0.166 e. The absence of Sn and Zn atoms results in the formation of an anionic center around the defect.

2.2. Energy and Stability

The cohesive energy is defined as the energy required to disperse a condensed matter until the atoms are isolated, and it is used to measure the atomic tightness of the materials. The cohesive energy can be calculated by the following formula obtained:

$$E_{coh} = (E_{tot} - E_{atom-x} \times N_x)/N_{tot}$$

where E_{tot} is the total energy of various cells, E_{atom-x} is the isolated atomic energy for an x-type single atom, N_x is the number of x-type atoms in a cell, and N_{tot} is the total atomic number of a cell. In general, cohesive energy is presented as a positive value and can be directly obtained from DFT calculations at the same computational levels with the ADF code. This parameter refers to the energy required for the elimination of the intermolecular force gasification of condensed matter and can measure the force between aggregated matters. The E_{coh} of bulk ZS; perfect 001 surface; and surfaces with V_{Zn}, V_O, and V_{Sn} vacancy defects are shown in Table 2. It can be seen that the E_{coh} of bulk ZnSnO₃ is 5.324 eV/atom. The E_{coh} of the 001 surface of ZS is 5.099 eV/atom. That is, the E_{coh} of the 001 surface of the slab-type ZnSnO₃ is reduced by 0.225 eV/atom compared with that of the bulk. Therefore, the slab structure is less thermodynamically stable than that of the bulk for ZnSnO₃. This is because the slab model is formed by bulk cutting, which causes the lattice to abruptly stop at the surface, leading to a decrease in the average coordination number. After further introducing defects, the E_{coh} of the 001 surfaces with a V_{Zn} , V_O , and V_{Sn} defects are 5.122, 5.143, and 5.069 eV/atom, respectively. Among them, the E_{coh} of the V_{Sn} surface model is smaller than that of the defect-free surface, while the E_{coh} of the model with V_{O} and V_{Sn} increased by 0.023 and 0.044 eV/atom, respectively. It can be seen that, although oxygen and zinc defects exacerbate the distribution of dangling bonds, the formation of these oxygen and zinc defects on the 001 perfect surface of ZS is a favorable process from the perspective of thermodynamic cohesion, especially for oxygen defects.

Table 2. Cohesive energy and defect formation energy of $ZnSnO_3$ bulk; perfect 001 surface; and surfaces with V_{Zn} , V_O , and V_{Sn} defects.

Models	E _{coh} /eV/Atom	E _f /eV
Bulk ZS	5.324	/
001 surface	5.099	/
V _{Zn} surface	5.122	1.175
V _O surface	5.143	-4.318
V _{Sn} surface	5.069	4.928

Another important parameter to measure the stability of defective surfaces is the defect formation energy (E_f) [32], which can be calculated as follows:

$$E_f = E_{def} - E_{per} - \mu_i N_i$$

where E_{def} is the total energy of the system with defects, E_{per} is the total energy of a perfect unit cell, N_i is the number of I atoms increasing or decreasing (negative when *i* decreases, positive when *i* increases), and u_i is the chemical potential of *i* atom. We choose μ_{Zn} , μ_{Sn} , and μ_O as the binding energy per atom of the crystal Zn, crystal Sn, and O_2 molecule, respectively, with the same calculation methods according to previous reports [33].

The calculated E_f of 001 surfaces with V_{Zn} , V_O , and V_{Sn} are shown in Table 2. From a thermodynamic point of view, at higher energy, the reaction of the system will not proceed spontaneously. Therefore, the lower E_f indicates a more stable system [34]. When E_f is

negative, it means that heat is released during the formation of defects. The smaller the value for E_f , the lower the energy required to generate the point defect, and thus the easier it is to form the point defect. On the contrary, when the formation energy is positive, it is an endothermic process, and it is not easy to generate the defect [35,36]. From Table 2, the E_f of the V_{Zn}, V_O, and V_{Sn} surfaces are 1.175, -4.318, and 4.928 eV, respectively. Among them, the E_f of the surface with the V_O defect is negative. That is, from a thermodynamic point of view, the formation of O vacancies on the 001 surface of ZS is favorable and is an exothermic process. However, the E_f of V_{Zn} and V_{Sn} are both positive numerically and belong to the endothermic process, which is relatively thermodynamically unfavorable, especially for V_{Sn} defects. Therefore, compared with the V_{Zn} and V_{Sn} defects on the 001 perfect surface of ZS, the formation of O vacancy defects requires the lowest energy and is thermodynamically easier to form [37], which is consistent with the above study based on cohesive energy.

2.3. Band Structure

The electronic structure of bulk ZS was calculated to understand the mechanism of the electronic properties of the bulk material with a comparison of those perfect and defective surfaces. Figure 2 is the calculated band structure of bulk ZS. It can be seen that the conduction band minimum (CBM) and valence band maximum (VBM) of the ZnSnO₃ bulk are both located at the Γ point of the first Brillouin zone, with energy levels of -5.995 and -6.923 eV, respectively. Therefore, the bulk ZS material forms a direct band gap of 0.928 eV at the Γ point. It should be pointed out that GGA usually underestimates the band gap in most cases [38]. The band gap of zinc stannate bulk calculated by Wang et al. using the density functional theory full-potential linearized augmented plane-wave method (FP-LAPW) is 1.0 eV [4], which is in good agreement with the data in this study. It is found that the band near the CBM is contributed by the s orbital of the Sn atom, while the band near VBM is contributed by the p orbital of the O.



Figure 2. Band Structure of Bulk ZnSnO₃.

Figure 3 shows the band structures of the perfect 001 surface and the surfaces with V_O , V_{Sn} , and V_{Zn} vacancies. It can be seen that the VBM of the perfect surface and surfaces with V_O , V_{Sn} , and V_{Zn} defects are located at -5.132, -5.604, -5.701, and -5.925 eV, and the CBM is located at -4.122, -4.614, -4.693, and -4.911 eV, respectively. Therefore, the 001 perfect and defective surfaces all present as a semiconductor with a direct band gap of approximately 1.010, 0.990, 1.008, and 1.014 eV.



Figure 3. Band structures of 001 perfect surface (**a**), V_O (**b**), V_{Sn} (**c**), V_{Zn} (**d**). The dotted line is the Fermi level.

Compared with that for the bulk ZS, the formation of the 001 surface resulted in an increase of 0.082 eV in the band gap, and the entire band structure had a downward shift. However, the overall characteristics of the band structures for the 001 surface of ZS remain nearly consistent with that for the bulk. CBM of 001 perfect surface moves to -4.122 eV from -5.995 eV in bulk materials, and VBM moves from -6.923 eV to -5.132 eV, with a shift of 1.791 eV. This indicates that cutting surface structures from the bulk could change the energy levels and band gaps for ZS materials. Then, we focus on the defective surfaces. The presence of V_O , V_{Sn} , and V_{Zn} defects causes the entire bands to move toward the valence band (Figure 3b-d) compared with that in the perfect surface. Among them, the band shift of the V_{Zn} defect is the largest (0.793 eV downward). The formation of the three defects also leads to some new energy levels in the band structures near VBM. This is mainly because V_O, V_{Sn}, and V_{Zn} vacancy defects will produce different electronic interactions during the defect formation, resulting in subtle differences between the original bands. Of course, despite some changes, the VBM and CBM of the defective systems are still contributed by the p orbital and s orbital, respectively. It is noticed that the perfect surface and various defective surfaces had different responses to molecular adsorption. This is mainly due to the different geometrical arrangements around the defect caused by the atomic absence. As a result, the properties of the material exhibited by specific surfaces and defects will vary.

2.4. Density of States

The total and partial DOS of ZS bulk; perfect 001 surface; and surfaces with V_O , V_{Sn} , and V_{Zn} defects are shown in Figure 4 and Figure S7 in the Supplementary Materials. It is noted that the DFT calculations here are conducted using the self-consistent field crystal orbital (SCF-CO) method. This method constructs the DFT wave function using the linear combination of atomic orbitals (LCAO) and is widely used to discuss the electronic properties of various periodical systems for materials [39–41]. It was found that the lowest region for the valence band of ZS bulk is mainly occupied by the 2s orbital of O atoms, with combinations of a small amount of 5p orbitals of Sn atoms. A DOS from -15.023 to

-12.512 eV contributed to the 5s electrons of the Sn atoms mixed with 2p electrons of O atoms. From -12.507 to -10.032 eV, it is mainly 3d orbitals of Zn and a small amount of 2p of O together with 5p of Sn. In the regions of -10.045 to -6.317 eV for the valence band, DOS mainly contributed to the 2p state of O, with some 5p state of Sn and 3d state of Zn, which indicates the occurrence of orbital hybridization between them. The bottom of the conduction band from -5.028 to -2.531 eV mainly contributed to 5s orbital of Sn in bulk ZS, and those above -2.534 eV are mainly the 5p electronic state of Sn. Therefore, the electronic properties close to the Fermi levels of ZnSnO₃ bulk are mainly dominated by the 5s of Sn and the 2p of O. This is consistent with the conclusion obtained by Gou et al. in the study of a zinc stannate system [27,42]. The electronic configuration of the Zn and Sn in the zinc stannate is (n -1)d¹⁰ns⁰. It is well known that the electronic structure of the transition metal oxide with d¹⁰ electron configuration in the perovskite ABO₃ is generally determined by the O 2p and the s orbital of transition metal. This is consistent with the conclusion obtained by DOS analysis in this work.



Figure 4. Density of states of ZS. (a) bulk; (b) perfect 001 surface; (c) V_O surface; (d) V_{Sn} surface; (e) V_{Zn} surface.

From the DOS of the perfect 001 surface of ZS in Figure 4, the total DOS of the perfect surface is somewhat different from that of the ZS bulk. The relative position of the 001 perfect surface Fermi level shifted upward by approximately 0.825 eV. The reason for this difference is that the slab model is used for the surface, which leads to some dangling bonds due to the abrupt termination of the atoms. Additionally, the co-existence of Zn, Sn, and O atoms in the surface layer compensates the dangling bonds to a certain extent, reduces the influence of the external environment, and stabilizes the surface [38,43]. This makes the perfect 001 surface of the ZS and the bulk material show a relatively similar overall structure, which is also an important reason for the change in the relative position of the Fermi level and electronic structure. In the regions of -15.035 to 5.042 eV in DOS, the intensity of the DOS peaks of ZnSnO₃ bulk is significantly lower than those of the 001 perfect surfaces. This indicates that the interatomic electron interactions of the surface are stronger than the bulk.

From the DOS of the defective surfaces of ZS in Figure 4, it is found that the formation of V_O , V_{Sn} , and V_{Zn} defects leads to a slight change in DOS distributions, and the overall characteristics are consistent with that for the perfect surface. The formations of three defects shift the Fermi level and the density of states downwards. Among them, the surface

with V_{Zn} shifts the most by 0.812 eV. This shift is also observed for the band structures mentioned above. It is also similar to the conclusions of the lead sulfide system with point defects in previous reports [44]. Due to the absence of atoms, the peak intensities of the defective systems of ZS are lower than that of the perfect surface.

The changes in the DOS and band structure near the VBM of the surface with V_O vacancy defects (Figure 3b) were further analyzed and compared with that of the perfect surface. It is found that there is an obvious splitting peak at the top of the valence band. The partial DOS of Zn near the Fermi level in the system with V_O vacancy is significantly reduced. This is mainly caused by the removal of O atoms, which causes the two Zn atoms that are originally connected to break the bond and reconnect to form a new bond. Compared with that of the perfect surface, the DOS of the surfaces with V_{Sn} vacancy and V_{Zn} vacancy appears at a new peak at the Fermi level. Combined with Figure 3c,d, it is also found that there are new electronic bands formed near the VBM. This is mainly because the absence of Sn and Zn atoms causes the surrounding atoms to form unsaturated bonds. Thereby, this could destroy the potential energy field, leading to the irregularity and distortion of the crystal's periodic arrangement [45].

3. Models and Computational Methods

3.1. Structure and Models

The bulk model of ZS is shown in Figure 5. The properties of the materials are closely related to the structure. Tin and zinc elements usually exist in nature with valences of +4 and +2, and they can form a perovskite ternary composite metal oxide with oxygen atoms belonging to the R3c structure of the trigonal system [37]. The perovskite-type ZnSnO₃ bulk (R3c structure with an asymmetric center) was selected in this study.



Figure 5. Structure of perovskite type ZnSnO₃ bulk. Red, blue and yellow are O, Zn and Sn atoms respectively.

Each layer of Zn, O, and Sn atoms contained in the perovskite ZnSnO₃ bulk material is equivalent. This paper focuses on the study of the 001 surface of the ZnSnO₃ material and the surfaces with point defects. These defective models were obtained by removing one corresponding atom from the perfect 001 surface of ZS (Figure 6). The initial model of a perfect 001 surface structure was obtained by cutting the optimized bulk ZS. In order to reduce the interaction between the adjacent defects, the unit cells of the 001 surface were expanded by 2×2 . The surface lattice parameter a = 10.702 Å after expanding into a 2×2 supercell. In the 2×2 supercell structures without defects, there are 120 atoms in total. It can be seen from Figure 6b that there are 18 layers in this model. The first layer has 4 equivalent Zn atoms, the second layer has 12 equivalent O atoms, and the third layer has 4 equivalent Sn atoms. Jiang et al. calculated different 001 terminal surfaces of znc stannate

in the pnma space group using the DFT method [46]. The zinc stannate 001 surface of the perovskite R3c space group also has two different terminals (as shown in Figure 6b): Zn-O and Sn-O. From the results of the DFT calculations, it was found that the Zn-O terminal surface of R3c-type zinc stannate is more stable than that of that with Sn-O terminations by 0.061 eV/atom per cell. Therefore, the studies on the stability and electron properties of defective zinc stannate surfaces in this work are limited on the models with Zn-O terminals. Therefore, the defective surface model can be obtained through the removal of one Zn, O, and Sn atom [22] in the first three layers of the supercell, respectively, for Zn vacancy (V_{Zn}), O vacancy (V_O), and Sn vacancy (V_{Sn}) (Figure 7). There were 119 atoms in each defective ZS surface.



Figure 6. Structures of perfect 001 surface of ZS. Top view (a) and side view (b).



Figure 7. Structures of O defect (**a**), Sn defect (**b**), Zn defect (**c**) on 001 surface of ZS. The defect locations are marked with red circles.

3.2. Computational Methods

All of the DFT calculations in this paper were performed in the BAND module with the help of the Amsterdam Modeling Suite (AMS) software platform [32]. The interaction between the electrons adopts the PBE as a DFT functional under the generalized gradient approximation (GGA) [3]. The geometry and electronic properties of all models were calculated using the self-consistent field crystal orbital (SCF-CO) method, which defines the wave function as a linear combination of atomic orbitals (LCAO). The dispersion correction method of DFT, DFT+D3, is used to correct the influence of van der Waals forces in the calculation. The Slater-type basis functions and the double- ζ + polarized orbital DZP basis sets are used to describe the periodic system [23]. A very large vacuum distance in the zdirection is used to calculate the surface model, which can reduce the interaction of the periodic system and make results more realistic. The precision of SCF energy convergence is 10^{-5} Hartree/cell. In the process of geometric optimization, the detailed calculation is performed using the normal settings. To achieve more accurate results, a good setting is used to calculate the electronic properties. When calculating the ZnSnO₃ bulk, the k-point sampling grid of the first Brillouin zone is $3 \times 3 \times 3$, and the k-point sampling grid is 5×5 for the surface model. Both the plane wave method and the linear combination of atomic orbitals (LCAO) method are common computational methods in materials calculations. The LCAO method has been accepted and recognized by various publications. Unlike the plane wave method, there is no cut-off energy involved in LCAO. Additionally, an energy convergence of 10^{-5} Hartree/cell is accurate enough for SCF calculations.

11 of 13

4. Conclusions

In summary, first-principles DFT calculations are conducted to investigate 001 perfect and defective surfaces for perovskite ZnSnO₃. The structures and electronic properties of these ZS materials are studied in detail. The main conclusions are as follows:

- (1) The perfect 001 surface and the those with V_O , V_{Sn} , and V_{Zn} defects lead to a decrease in the cohesive energy compared with the bulk ZS. V_O vacancy defects system presents both the largest cohesive energy and the most negative defect formation energy. Therefore, from a thermodynamic point of view, V_O defects on the 001 surface of ZS are easier to form than other defects.
- (2) The formation of the V_O , V_{Sn} , and V_{Zn} vacancies on the 001 surface of ZS slightly changes the band structure and band gap compared with that of the bulk. The existence of these defects makes the relative positions of CBM and VBM move toward the valence band, while the overall band gap does not change greatly compared with that of the perfect surface.
- (3) According to DOS analysis, the electronic properties close to the Fermi levels of bulk ZS materials are mainly controlled by the O 2p and Sn 5s orbitals. The introduced surface and defects could lead to the rearrangement of the geometric structure. These defects and structural changes have affected the electronic properties to a certain extent and are slightly different to those without defects.

From the above results, the point defects could affect the electronic properties of zinc stannate surfaces. These finding are important to understand zinc stannate as a flame retardant on the microstructure. Research on the flame-retardant mechanisms of different defect zinc stannate structures is still on going in our group.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/inorganics10120258/s1, Figure S1: The radial distribution functions of zinc stannate bulk; Figure S2: The radial distribution functions of the 001 perfect surface; Figure S3: The radial distribution functions of the O defect; Figure S4: The radial distribution functions of the Sn defect; Figure S5: The radial distribution functions of the Zn defect; Figure S6: Structures of O defect (a), Sn defect (b), Zn defect (c) on 001 surface of ZS; Figure S7: Total and partial density of states of ZnSnO₃ bulk.

Author Contributions: Conceptualization, R.F. and H.B.; methodology, R.F. and H.B.; validation, M.Z., J.L., R.F. and L.M.; formal analysis, R.F. and L.M.; investigation, H.Z., Y.W. and Y.Z.; resources, J.L., Y.Y. and Z.F.; data curation, J.L., R.F. and L.M.; writing—original draft, J.L. and R.F.; writing—review and editing, R.F. and H.B.; visualization, H.Z.; supervision, H.B.; project administration, J.L. and H.B.; funding acquisition, J.L., Y.Y. and Z.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Yunnan Province Major Science and Technology Special Program (No.202002AB080001-2), Yunnan Province Major Science and Technology Special Program (No.202102AB080002), and Yunnan Province "Ten Thousand Talents Plan" Industrial Technology Leading Talent Program (No. YNWR-CYJS-2017-056).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Kanat, M.; Eren, T. Synthesis of phosphorus containing flame retardants and investigation of their flame retardant behavior in textile applications. *J. Appl. Polym. Sci.* **2019**, *136*, 47935. [CrossRef]
- Lu, S.; Hong, W.; Chen, X. Nanoreinforcements of Two-Dimensional Nanomaterials for Flame Retardant Polymeric Composites: An Overview. Adv. Polym. Technol. 2019, 2019, 4273253. [CrossRef]
- 3. Oliveira, M.C.; Ribeiro, R.; Longo, E.; Bomio, M.; Lazaro, S. Quantum mechanical modeling of Zn-based spinel oxides: Assessing the structural, vibrational, and electronic properties. *Int. J. Quantum Chem.* **2020**, *120*, 26368. [CrossRef]
- 4. Wang, H. First-principles study of structural, electronic, and optical properties of ZnSnO₃. *Solid State Commun.* **2009**, *149*, 1849–1852. [CrossRef]

- 5. He, W.; Song, P.; Yu, B.; Fang, Z.; Wang, H. Flame retardant polymeric nanocomposites through the combination of nanomaterials and conventional flame retardants. *Prog. Mater. Sci.* 2020, 114, 100687. [CrossRef]
- Paul, S.; Basak, S.; Ali, W. Zinc Stannate Nanostructure: Is It a New Class of Material for Multifunctional Cotton Textiles? ACS Omega 2019, 4, 2719. [CrossRef]
- Khan, M.; Dutta, J. Comparison of photocatalytic activity of zinc stannate particles and zinc stannate/zinc oxide composites for the removal of phenol from water, and a study on the effect of pH on photocatalytic efficiency. *Mater. Sci. Semicond. Process.* 2015, 36, 124–133. [CrossRef]
- 8. Jose, M.; Nithya, G.; Robert, R.; Dhas, S. Formation and optical characterization of unique zinc hydroxy stannate nanostructures by a simple hydrothermal method. *J. Mater. Sci. Mater. Electron.* **2018**, *29*, 2628–2637. [CrossRef]
- 9. Aziz, S.; Jung, K.; Chang, S. Stretchable strain sensor based on a nanocomposite of zinc stannate nanocubes and silver nanowires. *Compos. Struct.* **2019**, 224, 111005. [CrossRef]
- 10. Montenegro, J.; Ochoa-Muoz, Y.; Rodríguez-Páez, J.E. Nanoparticles of zinc stannates (ZTO): Synthesis, characterization and electrical behavior in oxygen and acetone vapors. *Ceram. Int.* **2019**, *46*, 2016–2032. [CrossRef]
- 11. Qu, H.; Wu, W.; Xie, J.; Xu, J. Zinc hydroxystannate-coated metal hydroxides as flame retardant and smoke suppression for flexible poly vinyl chloride. *Fire Mater.* **2010**, *33*, 201–210. [CrossRef]
- 12. Zhang, B.; Han, J. Synthesis of microencapsulated zinc stannate and its application in flame-retardant poly(vinyl chloride) membrane material. *Fire Mater.* **2018**, *42*, 109–118. [CrossRef]
- 13. Xu, J.; Zhang, C.; Qu, H.; Tian, C. Zinc hydroxystannate and zinc stannate as flame-retardant agents for flexible poly(vinyl chloride). *J. Appl. Polym. Sci.* **2010**, *98*, 1469–1475. [CrossRef]
- 14. Sun, S.; Liang, S. Morphological zinc stannate: Synthesis, fundamental properties and applications. *J. Mater. Chem. A* 2017, *5*, 20534–20560. [CrossRef]
- 15. Zeng, W.; Liu, T.M.; Lin, L.Y. Ethanol gas sensing property and mechanism of ZnSnO₃ doped with Ti ions. *Mater. Sci. Semicond. Process.* **2012**, *15*, 319–325. [CrossRef]
- 16. Xie, J.; Jiao, Y.; Xu, J.; Sun, H. Synthesis of zinc stannate and zinc stannate coated nano-CaCO₃ by homogeneous precipitation. *J. Chem. Res.* **2011**, *2*, 109–111. [CrossRef]
- 17. Eglitis, R.; Kruchinin, S. Ab initio calculations of ABO₃ perovskite (001), (011) and (111) nano-surfaces, interfaces and defects. *Mod. Phys. Lett. B* 2020, *34*, 2040057. [CrossRef]
- Sang, B.; Li, Z.; Yu, L.; Li, X.; Zhang, Z. Preparation of zinc hydroxystannate-titanate nanotube flame retardant and evaluation its smoke suppression efficiency for flexible polyvinyl chloride matrix. *Mater. Lett.* 2017, 204, 133–137. [CrossRef]
- 19. Pramchu, S.; Laosiritaworn, Y.; Jaroenjittichai, A.P. Electronic properties of surface/bulk iodine defects of CsSnBr₃ perovskite. *Surf. Coat. Technol.* **2016**, *306*, 159–163. [CrossRef]
- Zhukovskii, Y.; Kotomin, E.; Piskunov, S.; Ellis, D. A comparative ab initio study of bulk and surface oxygen vacancies in PbTiO₃, PbZrO₃ and SrTiO₃ perovskites. *Solid State Commun.* 2016, 149, 1359–1362. [CrossRef]
- Long, L.; Cao, D.; Fei, J.; Wang, J.; Zhou, Y.; Jiang, Z.; Jiao, Z.; Shu, H. Effect of surface intrinsic defects on the structural stability and electronic properties of the all-inorganic halide perovskite CsPbI₃(001) film. *Chem. Phys. Lett.* 2019, 734, 136719. [CrossRef]
- 22. Xiao, H.; Zhang, Y.; Weber, W. Impact of point defects on electronic structure in Y₂Ti₂O₇. *RSC Adv.* **2012**, *2*, 7235–7240. [CrossRef]
- Ahangari, M.; Mashhadzadeh, A.; Fathalian, M.; Dadrasi, A.; Rostamiyan, Y.; Mallahi, A. Effect of various defects on mechanical and electronic properties of zinc-oxide graphene-like structure: A DFT study. *Vacuum* 2019, 165, 26–34. [CrossRef]
- 24. Zheng, M.; Li, X.; Wang, M.; Guo, L. Dynamic profiles of tar products during Naomaohu coal pyrolysis revealed by large-scale reactive molecular dynamic simulation. *Fuel* **2019**, 253, 910–920. [CrossRef]
- Boonchun, A.; Dabsamut, K.; Lambrecht, W. First-principles study of point defects in LiGaO₂. J. Appl. Phys. 2019, 126, 155703. [CrossRef]
- Yuan, Y.; Chen, G.; Ye, H.; Jin, W.; Zhu, Y.; Wu, Y. First-principles study on native point defects of cubic cuprite Ag₂O. J. Appl. Phys. 2016, 120, 215707. [CrossRef]
- 27. Gou, H.; Gao, F.; Zhang, J. Structural identification, electronic and optical properties of ZnSnO₃: First principle calculations. *Comput. Mater. Sci.* **2010**, *49*, 552–555. [CrossRef]
- Wang, Y.; Yang, C.; Zhang, Y.; Guo, L.; Wang, Y.; Gao, G.; Fu, F.; Xu, B.; Wang, D. Nanoarchitectonics of CdS/ZnSnO₃ heterostructures for Z-Scheme mediated directional transfer of photo-generated charges with enhanced photocatalytic performance. *Int. J. Hydrogen Energy* 2022, *16*, 47. [CrossRef]
- 29. Liu, Q.J.; Qin, H.; Jiao, Z.; Liu, F.; Liu, Z. First-principles calculations of structural, elastic, and electronic properties of trigonal ZnSnO₃ under pressure. *Mater. Chem. Phys.* **2016**, *180*, 75–81. [CrossRef]
- 30. Ni, J.; Liu, N.; Yang, G.; Zhang, X. First-principle study on electronic structure of BaTiO₃ (001) surfaces. *J. Phys.* 2008, 57, 4434–4440.
- Ong, K.; Fan, X.; Subedi, A.; Sullivan, M.; Singh, D. Transparent conducting properties of SrSnO₃ and ZnSnO₃. APL Mater. 2015, 3, 062505. [CrossRef]
- 32. Deml, A.M.; Stevanović, V.; Muhich, C.L.; Musgrave, C.B.; O'Hayre, R. Oxide enthalpy of formation and band gap energy as accurate descriptors of oxygen vacancy formation energetics. *Energy Environ. Sci.* **2014**, *7*, 1996–2004. [CrossRef]
- 33. Zhu, Y.; Bai, H.; Huang, Y. Crystal orbital studies on the 1D silic-diyne nanoribbons and nanotubes. *J. Phys. Condens. Matter Inst. Phys. J.* **2016**, *28*, 045303. [CrossRef] [PubMed]

- 34. Liao, H.; Li, J.; Wei, T.; Wen, P.; Li, M.; Hu, X. First-principles study of C-N point defects on sidewall surface of [0001]-oriented GaN nanowires. *Appl. Surf. Sci.* 2019, 467, 293–297. [CrossRef]
- Alay-E-Abbas, S.; Nazir, S.; Ali, S. Formation energies and electronic structure of intrinsic vacancy defects and oxygen vacancy clustering in BaZrO₃. *Phys. Chem. Chem. Phys. Pccp* 2016, *18*, 23737. [CrossRef] [PubMed]
- Jiang, C.; Peng, W.; Liu, Z.; Deng, X. First-principles calculations for formation energy and magnetism of defect structures in Heusler alloys Mg-V-Z (Z=Al, Ga, In). *Phys. B* 2020, 600, 412388. [CrossRef]
- He, R.; Wan, Y.; Guo, P.; Jiang, Z.; Zheng, J. First-principles investigation of native point defects in two-dimensional Ti₃C₂. *Comput. Theor. Chem.* 2019, 1150, 26–39. [CrossRef]
- 38. Yuan, H.; Li, J. Effect of annealing temperature on the growth of Zn-Sn-O nanocomposite thin films. *J. Alloys Compd.* **2017**, *714*, 114–119. [CrossRef]
- Zhang, J.; Zhang, H.; Yuan, N.; Meng, L.; Geng, C.; Bai, H. Insights into reactive behaviors and mechanisms of nickel-based oxygen carriers doped by Fe/Co during chemical looping combustion from multiple-scale molecular modeling combined with experiments. *Fuel Process. Technol.* 2022, 229, 107181. [CrossRef]
- 40. Xie, H.; Su, W.; Lu, H.; Mo, Z.; Wang, D.; Sun, H.; Tian, L.; Gao, X.; Li, Z.; Shen, J. Enhanced low-field magnetocaloric effect in Nb and Al co-substituted EuTiO₃ compounds. *Mater. Sci. Technol.* **2022**, *118*, 128. [CrossRef]
- Goesten, M.; Xia, Y.; Aschauer, U.; Amsler, M. Conformational Gap Control in CsTaS₃. J. Am. Chem. Soc. 2022, 144. [CrossRef] [PubMed]
- 42. Zhu, W.; Chen, X.; Zhao, Y.; Lai, T. Theoretical study of stability and electronic structure of the new type of ferroelectric materials XSnO₃(X = Mn, Zn, Fe, Mg). *Int. J. Mod. Phys. B* **2014**, *28*, 1450224. [CrossRef]
- 43. Sun, X.; Liu, Y.; Song, Z.; Li, Y.; Wang, W.; Lin, H.; Wang, L.; Li, Y. Structures, mobility and electronic properties of point defects in arsenene, antimonene and an antimony arsenide alloy. *J. Mater. Chem. C* 2017, *5*, 4159–4166. [CrossRef]
- 44. Mishra, N.; Makov, G. Point defects in lead sulfide: A first-principles study. Comput. Mater. Sci. 2021, 190, 110285. [CrossRef]
- 45. Liu, L.; Diao, Y.; Xia, S. Intrinsic point defects in pristine and Zn-doped GaAs nanowire surfaces: A first-principles investigation. *Appl. Surf. Sci.* **2020**, *514*, 145906. [CrossRef]
- Jiang, L.; Chen, Z.; Cui, Q.; Xu, S.; Tang, F. Experimental and DFT-D3 study of sensitivity and sensing mechanism of ZnSnO₃ nanosheets to C₃H₆O gas. *J. Mater. Sci.* 2022, *57*, 1–21. [CrossRef]