บทความวิจัย

การศึกษาโครงสร้างและสมบัติทางอิเล็กทรอนิกส์ของซิงค์สแตนเนต ด้วยวิธีการคำนวณเชิงควอนตัมแบบ First Principle

First Principle Calculations of Structures and Electronic Properties of $SnZn_2O_4$

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บทคัดย่อ

ได้ศึกษาโครงสร้างและสมบัติทางอิเล็กทรอนิกส์ของซิงค์สแตนเนตโดยวิธีการคำนวณแบบ density functional ด้วยการประมาณแบบ local density (LDA) โดยใช้พลังงานศักย์แบบ ultrasoft pseudopotentials แทนอันตรกิริยาระหว่างเวเลนซ์อิเล็กตรอนและแกนนิวเคลียสไอออน พบว่าโครงสร้างแถบความกว้างของพลังงานที่คำนวณได้จากการประมาณแบบ LDA ของซิงค์สแตนเนตมีสมบัติเป็นสารกึ่งตัวนำที่มีช่องว่างของแถบพลังงานแคบโดยเป็นแบบ direct มีค่า 0.83 eV สำหรับโครงสร้างแบบสปิเนลปกติ และ 1.09 eV สำหรับโครงสร้างแบบสปิเนลผกผัน เมื่อเปรียบเทียบกับผลทดลองซึ่งมีช่องว่างแถบพลังงาน 3.6 eV อย่างไรก็ตามจากการคำนวณพบว่าได้ผลสอดคล้องกับผลที่คำนวณได้จากงานวิจัยอื่น ซึ่งมีค่าช่องว่างแถบพลังงาน 0.5 eV และ 1.07 eV สำหรับโครงสร้างแบบสปิเนลปกติ และ สำหรับโครงสร้างแบบสปิเนลผกผัน ตามลำดับ

คำสำคัญ : การคำนวณเชิงทฤษฎีแบบควอนตัม ซิงค์สแตนเนต สปิเนลปกติ สปิเนลผกผัน ตัวนำออกไซด์โปร่งใส

Abstracts

The structure and electronic properties of $SnZn_2O_4$ have been investigated using the density functional theory under local density approximation (LDA). The ultrasoft pseudopotentials were used to represent interactions between valence electrons and ion cores. Therefore an underestimated approximation of LDA, there results that $SnZn_2O_4$ exhibits narrow band gap like semiconductors with energy of 0.83 eV for normal spinel and 1.09 eV for inverse spinel when compare with experimental results of 3.6 eV. The calculation results are, however, in agreement with other calculations reported values of 0.5 eV and 1.07 eV for normal and inverse structures, respectively. In addition, the band structure and density of states are obtained, which indicates that $SnZn_2O_4$ has a direct band gap.

Keywords : First Principle Calculations, Zinc Stannate, Normal Spinel, Inverse Spinel, Transparent Conductive Oxide

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INTRODUCTION

Transparent semiconducting oxides (TCOs), such as ZnO, SnO, In_2O_3, CdO, $SnCd_2O_4$ (CTO) and $SnZn_2O_4$ (ZTO), demonstrate great applications in various areas including smart windows, flat-panel displays, thin-film photovoltaic, transparent electrodes for solar cell and polymer-based electronics due to their unique electrical and optical properties. Two of the best TCO materials, indium-tin-oxides and cadmium-tin-oxides, contain either expensive or toxic elements and may not be desirable for future large-area applications. For Zinc stannate, $SnZn_2O_4$ (ZTO), is n-typed semiconducting material with wide band gap of 3.6 eV [1] an inexpensive optically transparent, electrically conducting, and nontoxic oxide, $SnZn_2O_4$ is known to have high chemical sensitivity, high electrical conductivity, high electron mobility, and low visible absorption. $SnZn_2O_4$ is ternary compound that has a general chemical formula $(A)[B_2]O_4$, where parentheses, (…) represents the tetrahedral sites […] represents the octahedral sites, and usually exist in either the cubic spinel structure. Many experimental and theoretical studies have been carried out to understanding the structural, electrical, and optical properties of this ternary compounds. For example, it is known that $CdIn_2O_4$ is possibly more stable in the normal spinel structure, whereas $SnZn_2O_4$ and $SnCd_2O_4$ are more stable in the inverse spinel structure. The inverse spinel can particularly be described by the formula $(B)[AB]O_4$. Using first-principle band structure and total energy methods, we have studied the structural, electronic properties of $SnZn_2O_4$. In particular, we have investigated the relationship that of the different crystal structures, i.e. in between normal and inverse spinel structures and the electronic dispersion relation including density of state in this ternary compound. The finding will help us in future studies and design of high-performance TCOs.

CRYSTAL STRUCTURES

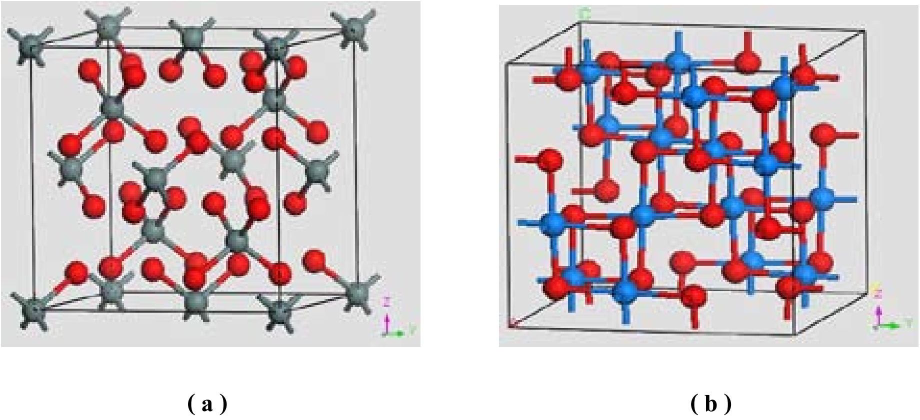
The normal spinel structures are present by AB_2O_4 with space group; Fd3m (O_h^7), in which one-eighth of the tetrahedral void in a face-center-cubic (fcc) close-packed oxygen sublattices are occupied by A atoms [see Fig.1(a)] and one-half of the octahedral voids are occupied by B atoms [see Fig.1(b)]. There exist also an "inverse" spinel structure, where the tetrahedral voids are occupied by B atoms and the octahedral voids are occupied randomly by an equal number of A and B atoms, where A is Sn^{4+} ions and B is Zn^{2+} ions. The normal spinel crystal structure is determined by two parameters: the lattice constant a and the anion displacement u. The bond length between the A atom at the center of a AO_4 tetrahedron and its four nearest-neighbor oxygen atoms is given by

$$R_{tetra} = \sqrt{3}(u - 0.25)a\ , \tag{1}$$

whereas the bond length between the B atom at the corner of octahedron and their six nearest oxygen atoms is

$$R_{octa} = \sqrt{(u - 0.625)^2 + 2(u - 0.375)^2}\ a\ . \tag{2}$$

For the inverse spinel structure, our modeled results are in good agreement with other models, where using a small special quasi random structure (SQS), which has same lattice vectors as normal spinel [2].



(a) (b)

Fig.1 Ball and stick representation of normal $SnZn_2O_4$ spinel structure, (a) showing the position of the O atoms (red balls) bonded to the Sn atoms (grey balls) at the tetrahedral sites, (b) showing the position of the O atoms (red balls) bonded to the Zn atoms (blue balls) at the octahedral sites.

The effective u parameter in the inverse spinel structure is obtained using the averaged tetrahedral and octahedral bond lengths and the formula given above.

MEDTHOD OF CALCULATIONS

Zinc stannate belong to the group of "4-2" cubic oxide spinel, with space group of Fd3m (O^7_h) or number 227. The structural parameters was used in this calculation are taken from Segev and Wei [2] as a starting point for geometry relaxation. In particular, the lattice constant in ours calculation is a = 8.657 Å and the oxygen parameter *u* = 0.361. The cubic unit cell contain one molecule with the atom positions are Zn(0.652, 0.652, 0.652), Sn(0, 0, 0), O(0.361, 0.361, 0.361) [3]. All calculations were performed in density functional theory (DFT) framework. The exchange-correlation potential is described in term of local density approximation (LDA), with the Ceperley-Alder and Perdew–Zunger functional. The core level atoms are represented by ultrasoft pseudopotential. Note that a plane-wave basis set energy cutoff was set 380 eV, whereas the Monkhorst-Pack scheme k-point grid sampling was set to 12X12X12 for the Brillouin zone of both normal and inverses spinel structures. The electronic configuration of Sn($5s^2 5p^2$), Zn($3d^{10} 4s^2$), and O($2s^2 2p^4$) are treated as valence state. The structural parameters of $SnZn_2O_4$ were determined using Broyden-Fletcher-Goldfarb-Shenno (BFGS) minimization technique, with the threshold for converged structure: energy per atom less than 0.5×10^{-5}eV, residual force less than 0.01 eV/Å, stress below 0.02 GPa and displacement of atoms during the structural relaxation less than 0.0005 Å.

RESULTS AND DISCUSSION

The optimized lattices constant are shown in Table I, in comparison with the results of experiment and other available calculations for SnZn2O4. As seen from the Table I, our present results are rather reliable with other calculation results and experiment data.

TABLE I : Demonstration of calculated and experimental results of structural parameters: a and u for normal (N) and inverse (I) spinel.

Sources of data	Exp.[a]	N (cal.[b])	N (cal.[c])	N (cal.[d])	I (cal.[b])	I (cal.[c])	I (cal.[d])
a, b, c (Å)	8.66	8.52	8.63	8.55	8.69	8.66	8.58
u	0.390	0.382	0.383	0.383	0.389	0.383	0.383

[a] ref. [5]

[b] our work

[c] ref. [2]

[d] ref. [4]

The tetrahedral (R_{tetra}) and octahedral (R_{octa}) bond lengths between the cation and oxygen atoms (i.e. Zn-O and Sn-O), shown in Table II, exhibited in agreement with the other calculations [4]. We noted that the bond length increases as the cation valence decreases or as atomic number increases. We found that the octahedral bond length (Rocta) is systematically larger by about 0.1 Å than tetrahedral bond length (Rtetra), due to the larger space available at the octahedral site.

Calculated band structure of normal spinel and inverse spinel $SnZn_2O_4$ are shown in Fig. 2(a) and 2(b), respectively. Coordinates of the special points of the Brillouin zone are as follows (in terms of unit vectors of the reciprocal lattice): L(0.5, 0.5, 0.5), G(0,0,0), X(0.5, 0, 0.5). The energy band gaps, E_g, are 0.826 eV for normal spinel and 1.089 eV for inverse spinel, whereas the corresponding experimental values are 3.6 eV. However, it is well known that LDA calculations provide underestimated energy gap in comparison with experimental values. As seen from Figures 2, such compound has direct band gap at G point, which is in agreement with other calculations [2,4].

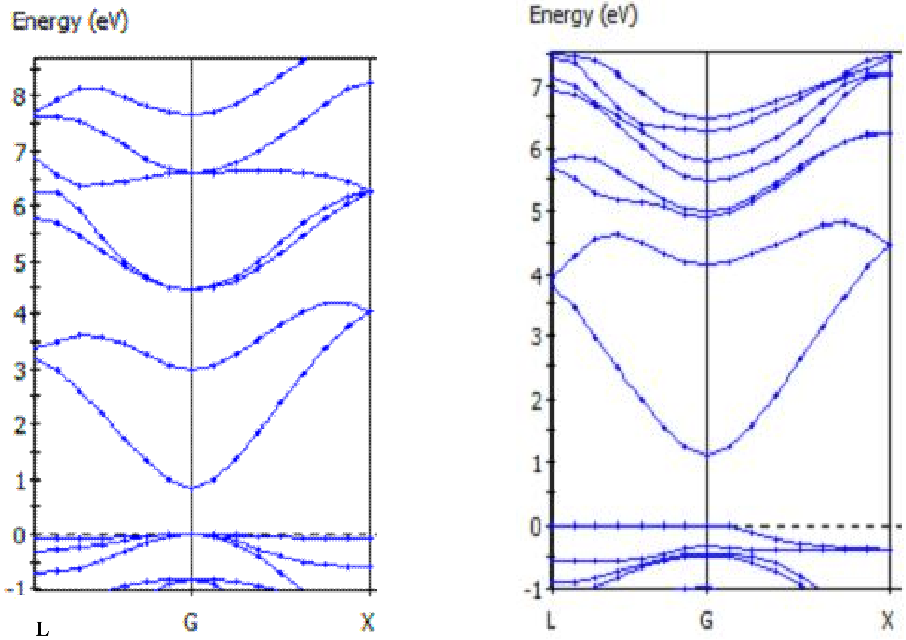
TABLE II : Demonstration the tetrahedral (Rtetra) and the octahedral (Rocta) bond length between the cations and their oxygen atoms nearest neighbors, for normal and inverse spinel $SnZn_2O_4$.

Bonding type	R_{tetra}[a]	R_{octa}[a]	R_{tetra}[b]	R_{octa}[b]
Zn –O	(I)1.947	(N)2.067 (I)2.060	1.975	2.082
Sn –O	(N)1.953	(I)2.063	1.970	2.067

[a] our work

[b] ref. [4,5]

Composition of the calculated energy bands can be resolved with the help of partial density of states (PDOS) and total density of states (DOS) diagrams, as shown in Fig. 3(a) and Fig. 3(b), for normal and inverse spinel structure of SnZn$_2$O$_4$, respectively. We found that the top of valence band consists predominantly of cation d and O *p* states, which hybridized strongly, whereas the bottom of conduction band arises mostly from the mixture of oxygen and cation s states. These diagrams allow concluding that the conduction band edge in normal spinel structure of SnZn$_2$O$_4$ is about 10.9 eV wide and is formed by the Sn-sp states that are hybridized with the *Zn-sp* and O-*p* states. The valence band is wide – about 9.7 eV – and consists of two sub-bands, clearly seen in the band structure as well: the upper one (between -9.6 and 0 eV) is a mixture of Sn-*sp*, Zn-*d* and O-*p* states. The lower one narrows (between -9.7 and -9.6 eV) and due to the Sn-sp states with admixture from Zn-d and O-*p* states. Another band between -15.9 and -19.6 eV is show to be of predominantly O-*s* states with minor contribution of Sn-sp and Zn-*s,p,d* states.

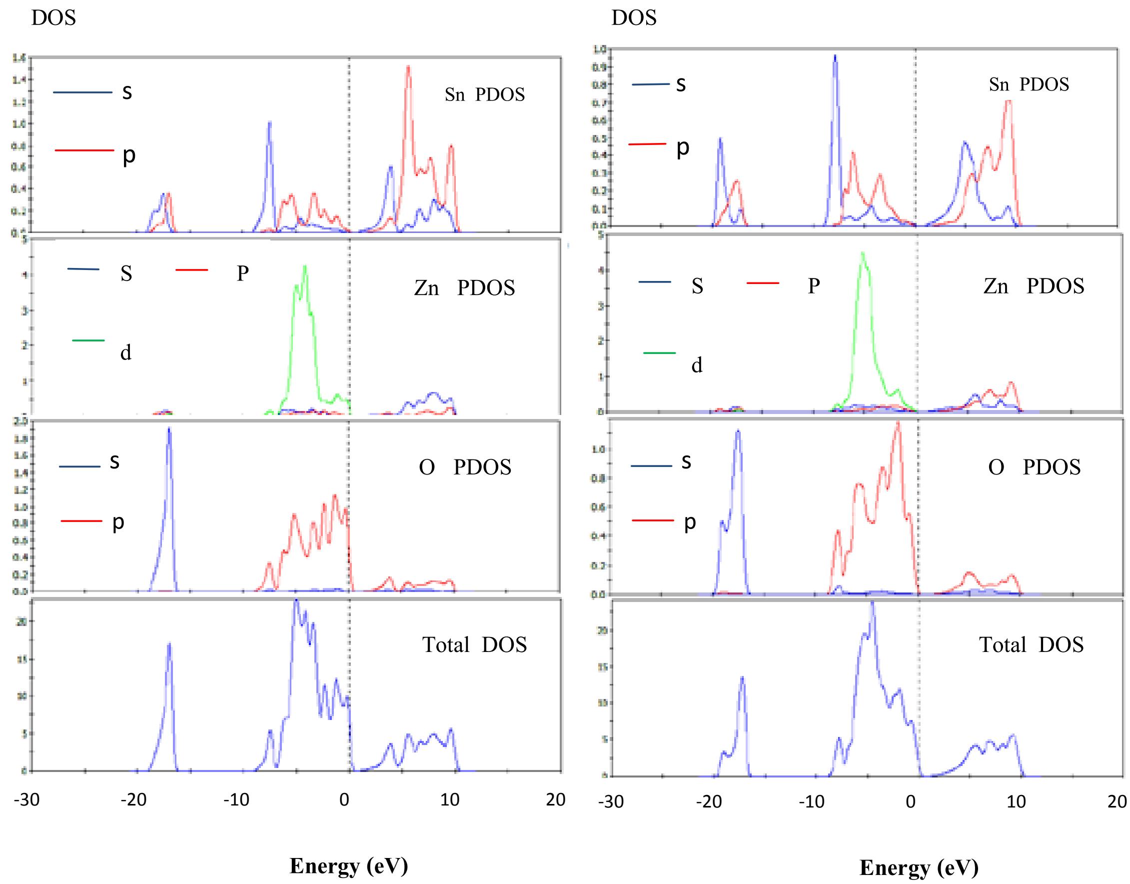


(a)

(b)

Fig. 2 Band structure of (a) normal and (b) inverse spinel of SnZn2O4.

The conduction band in inverse spinel structure of SnZn$_2$O$_4$ is considerably almost the same (about 10.92 eV) the normal spinel structure. There is composed of the Sn-*sp* states, which are hybridized with the Zn-*sp* and O-*p* states. The valence band is somewhat narrower in inverse spinel (about 9.3 eV in comparison with 9.7 eV in normal spinel). It is found that the upper valence bands (between -9.3 and 0 eV), is a mixture of Sn-*sp*, Zn-*d* and O-*p* states. The lower valence bands situated in the range -20.4 to -16.1 eV is show to be of predominantly O-s states with minor contribution of Sn-*sp* and Zn-*s,p,d* states.



(a)

(b)

Fig. 3 Partial and total density of states for (a) normal spinel and (b) inverse spinel structure of $SnZn_2O_4$.

CONCLUSIONS

The first-principle density functional calculations of structural and electronic properties of normal and inverse spinel structures of $SnZn_2O_4$ have been performed using the local density approximation (LDA). The results indicated that the inverse spinel of $SnZn_2O_4$ structure is more stable than normal one. The electronic band structure is characterized as direct band gap for both structures. The conduction band is considerably wider in inverse spinel structure, whereas the valence band is spread over a wider energy interval in normal spinel structures. We found that the top of valence band consists predominantly of cation *d* and O *p* states, with hybridized strongly, whereas the bottom of conduction bands arises mostly from mixture of oxygen and cation *s* states. The finding will help us in future study and design of high-performance transparent conducting oxides.

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