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Computational Study of Structural and Electronic Properties of Undoped SnO_2 for Renewable Energy

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Abstract. Throughout this research, we report on ab-initio study of structural and electronic properties of undoped SnO_2 in rutile phases using the full-potential linearized-augmented-plane waves method (DFT/FP-LAPW) within the local density (LDA) and TB-mBJ (Tran–Blaha modified Becke–Johnson) correction of gap energy and total density of states. The calculated equilibrium lattice parameters are used for plotting the density of states (DOS) and band structure diagrams. The computational results, which we have found, are compared to author's experimental and theoretical measurements.

Keywords. SnO_2, DFT/FP-LAPW, TB-mBJ, LDA; Renewable energy.

INTRODUCTION

Tin oxide (SnO_2) is transparent conductive oxides, it is n-type semiconductor with a large band gap (E_g = 3.5 eV), is a material with important technological applications. It used widely as a component in microelectronic **(**Fabrício Sensato et al., 2002) and thermoelectric applications **(**Borges et al., 2015) like gas sensors, solar cell **(**Agashe et al., 2008) and catalyst **(**Kolmakov et al., 2003). It was one of the first oxides studied and the most frequently used in high sensibility gas sensors by electrical conductivity variations **(**Göpel and Schierbaum, 1995). SnO_2 is generally noted as a nonstoichiometric oxide, because of deficiently of oxygen. The sensibility to oxygen comes from to the variable valency of Sn. The presence of oxygen that is in the forms of radical ion in different charged states leads to reduce a part of Sn^{4+} to Sn^{2+}. Because of its critical importance in device fabrication and performance, the SnO_2 attract great attention of many researchers in recent years and there are variety works have been reported concerning doped and undoped SnO_2 using theoretical or experimental study.

In this article, we investigate the structural and electronic properties of the rutile phase of SnO_2. First, we calculate the structural properties, after that we calculate the electronic (band energy) properties. Then, we discuss the obtained results.

The ab initio calculations described here are performed with the Wien2k code under Linux based on density functional theory (DFT_FP-LAPW). We use local density approximation LDA and the modified TB-mBJ (Tran–Blaha modified Becke–Johnson) (Schleife et al., 2011; Koller et al., 2011) who is more efficient to predict the electronic properties than LDA. Throughout this research, LDA approximation with TB-mBj correction is used for undoped SnO_2 material. Up to our knowledge, only GGA approximation with TB-mBj correction is used (Hammi et al., 2016), LDA method has not been used before and no paper is previously reported.

COMPUTATIONAL DETAILS

In this study, we have used the density functional theory (DFT) with the method of full-potential linearized augmented plane-wave (FP-LAPW). This method is implemented in WIEN2K package (Blaha et al., 2001; Madsen et al., 2001). We have been used to study all properties (structural, electronic and optic) by local density approximation LDA, it's based on the parameterization given by Moruzzi et al. (1978), the LDA approximation is the most widely used approximation, in density functional theory because she gives the goods results. We have also used the modified TB-mBJ (Tran–Blaha modified Becke–Johnson) exchange potential for LDA (Becke and Johnson, 2006), which greatly improves band gap calculation; it has been integrated with the Wien2K package.

Tin oxide SnO_2 crystallizes in rutile form with space group $P_{42/mnm}$, the Wyckoff of Tin (Sn) atoms at position (0, 0, 0) and (½, ½, ½) and four Oxygen (O) atoms at position ± (u, u, 0; ½+u, ½-u, ½) in each primitive cell. In this work the optimized lattice parameters for SnO_2 unit cell are (a = b = 4.74, c=3.19) and (α = β = γ = 90°) with ideal u= 0.306, the radi of the muffin tin atomic spheres R_{MT} of Sn and O atoms have been 1.95 and 1.68 Bohr, respectively. $R_{MT} \times K_{MAX}$ (cutoff parameter) have been set to 7.0 where R_{MT} de notes the smallest muffin tin radius of atoms and K_{MAX} is the maximum value of the reciprocal lattice vectors used in the plane wave expansion, the Brillouin-zone integration for geometry optimizations and electronic property calculations was performed by using a 3000 k-point.

RESULTS AND DISCUSSION

Structural properties:

The rutile-type SnO_2 belongs to space group $P_{42/mnm}$ (Fig.1). It is characterized by two lattice parameters **a**, **c** and the internal parameter **u**. it's unit cell contains two tin atoms are set at (0, 0, 0; ½, ½, ½) and four oxygen atoms in the following positions ± (u, u, 0; u + ½, ½-u, ½). We notice that the oxygen atomic positions depend on the internal parameter **u**. To find the atomic positions of equilibrium, the parameters can be optimized by calculating the forces on the nuclei and using the damped Newton scheme (Kohler et al., 1996). The total energies were then calculated as a function of volume (Fig. 2 (a)) and the obtained data fitted to the Murnaghan equation of state **(**Murnaghan, 1944):

$$E(V) = \frac{B_0 V}{B_0'}\left[\frac{\left(\frac{V_0}{V}\right)^{B_0'}}{B_0'-1}+1\right] + E_0 - \frac{V_0 B_0}{B_0'-1} \qquad (1)$$

Where:

$$B_0 = V\frac{d^2E}{dV^2} \qquad (2)$$

In figure 2 (b) The c/a ratio has also been optimized at a constant volume. Our results showed that the most stable structure of rutile-type SnO_2 occurs when the axial ratio c/a = 0.679 and u

= 0.306. The structural parameters, bulk properties obtained by using LDA are listed in table 1.

We notice that the obtained results are more compatible with the other calculations and experimental value. Our results are compared with other theoretical calculations and experimental results.

The value of lattice constant a is 1% lower than lattice constant an of experiments value but lattice constant c is 1-2% greater than lattice constant c of experiments value, we found that the most stable structure of rutile-type SnO_2 occurs at c/a=0.6797 in our calculus. About bulk modulus B_0 and pressure derivativeB_0', our value are 2-4% lower than experiments values.

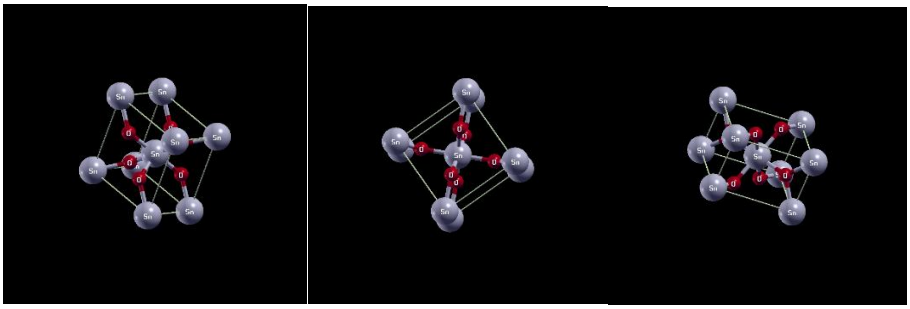
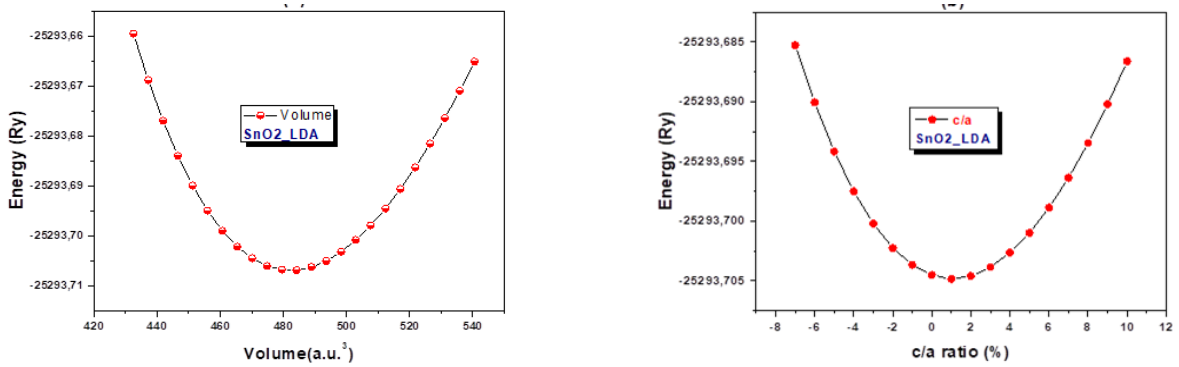


Fig. 1. The optimized structure of pure rutile-SnO_2.



(a) volume (b) ratio c/a for primitive cell of pure rutile-SnO_2

Fig. 2. Calculated total energies as a function, respectively calculated within the DFT-LDA.

Table 1. DFT calculations of equilibrium structural parameters of a (Å), c (Å), internal parameter u, ratio c/a, bulk modulus at zero pressure B_0 (GPa), its pressure derivative B_0' and volume V_0 (Bohr).

	Present work DFT-LDA	**Other theo.**	**Exp.**
a	4.71985	4.830 - 4.776 - 4.826 - 4.715 (Erdem et al., 2014 ; Hassan et al., 2013 ; Duan, 2008 ; Gracia et al., 2007)	4.737 (Haines and Léger, 1997)
c	3.2081	3.236 - 3.212 - 3.237- 3.194 (Erdem et al., 2014 ; Hassan et al., 2013 ; Duan, 2008 ; Gracia et al., 2007)	3.186 (Haines and Léger, 1997)
c/a	0.6797	-	-
u	0.306	0.306 - 0.307 (Erdem et al., 2014 ; Hassan et al., 2013 ; Duan, 2008 ; Gracia et al., 2007)	0.307 (Haines and Léger, 1997)
B_0	218.96	173 – 192 - 179 - 228 (Erdem et al., 2014; Hassan et al., 2013; Duan, 2008; Gracia et al.,	205 (Haines and Léger, 1997)

		2007)	
B’	4.9047	5.4 - 4.8 – 5 – 4 (Erdem et al., 2014; Hassan et al., 2013; Duan, 2008; Gracia et al., 2007)	7 (Haines and Léger, 1997)
V_0	482.2803	-	-

Electronic properties

Figure 3 shows the calculated band structure and the projected density of states (DOS) for rutile-phase of SnO_2 as obtained by including the modified Becke-Johnson exchange potential (LDA-TB-mBJ) along the A-M-X-Γ-R-Z-A path in the first Brillouin zone, the Fermi level is referred to be zero. We notice that rutile SnO_2 has direct band gap at Γ point, the value of calculated band gap obtained by the difference between the valence band maximum and the minimum of conduction band. At figure 4 we drew the total density of state (TDOS) and the partial density of state (PDOS) at equilibrium, we notice that the conduction band consists essentially of Sn 5s and Sn 5p orbits while O 2s states have a low contribution. The upper valence bands are mainly construct from Sn 5p and O 2p states.

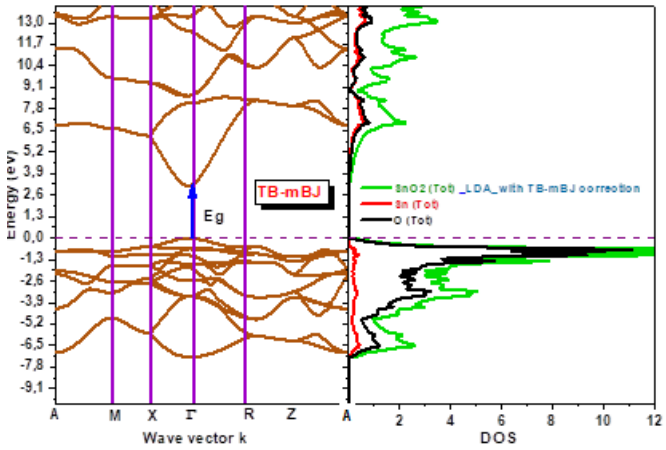


Fig. 3. Band structure and density of states for pure rutile-SnO_2 calculated using Tb-mBJ correction.

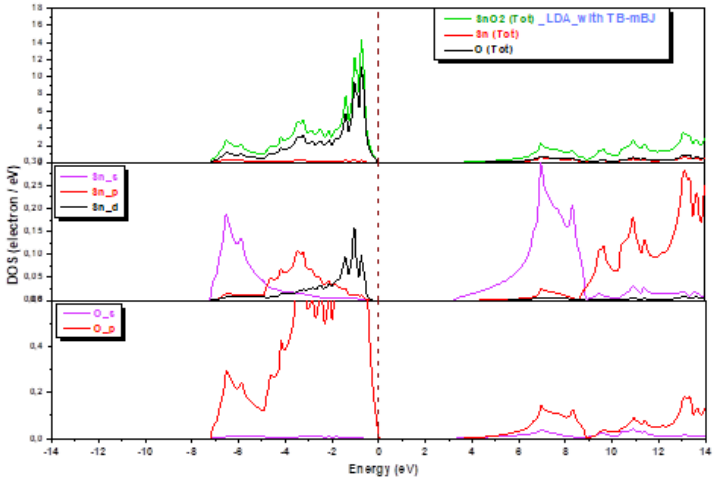


Fig. 4. Total and partial density of states for pure rutile-SnO_2 calculated using Tb-mBJ correction.

In table 2 we presented our calculated value of band gap within the LDA, and TB-mBJ correction compared with some experimental and theoretical values.

We notice that LDA underestimate energy gap value comparing to TB-mBJ result and to the experimental, other theoretical values.

Table 2. The band gap calculated of the rutile-form of SnO_2 within LDA, TB-mBJ correction and compared with the experimental and theoretical values.

	Ours			
	LDA	**TB-mBJ**	**Other theo.**	**Exp.**
Band gap energy Eg (eV)	1.077	3.142	0.832 - 2.760 - 1.38 - 3.50 (Hassan et al., 2013; Li et al., 2010; Gracia et al., 2007)	2.9 – 3.7 (Ferreira da Silva et al., 2004; Baco et al., 2012)

CONCLUSION

We have performed first-principles calculations to investigate the structural and electronic properties of SnO_2 in the rutile-phase by the density functional theory based on full-potential linearized-augmented-plane wave's method (DFT/FP-LAPW) within the local density (LDA) approximation and TB-mBJ correction. The obtained values of the structural parameters such as lattice constants, bulk modulus and its pressure derivatives are in good agreement with experimental and other theoretical value.

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