# First principles studies of SnO at different structures

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## ABSTRACT

**Purpose:** Structural and mechanical properties of the Sn (tin) based oxides SnO and $SnO_2$ are investigated. The aim of this study to determine in which structural phase SnO is found and to calculate its elastic constants at different pressures.

**Design/methodology/approach:** Calculations have been made for three different structures of SnO by density functional theory (DFT). The behavior of structural parameters (lattice constants, internal parameters) and bulk modulus under different pressures, and elastic constants are calculated by using ab initio calculations. Generalized Gradient Approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) parameterization is used.

**Findings:** All of six elastic constants of litharge SnO and three elastic constants of rocksalt structure of SnO are calculated for the first time in this study. Among three structures of SnO, namely, rocksalt, cesium chloride and tetragonal litharge, the most energetically favorable one is the litharge structure at ambient conditions. The calculation of enthalpies with respect to pressure shows that any phase transition from litharge to rocksalt structure does not occur by applying the pressures of up to 5 GPa to the systems. Equilibrium volume, energy and bulk modulus of rutile $SnO_2$ are also calculated. Our results are compared with other available experimental data and theoretical results.

**Research limitations/implications:** Computer calculation speeds and its information storage area are limitations, it will be possible to reach experimental results as near as in condition that they are improved.

**Practical implications:** It is very difficult to measure elastic constants especially under high pressure experimentally. However, they are calculated by first principles calculations.

**Originality/value:** Behavior of elastic constants and structural parameters under high pressures are determined for the first time in this study. Simulations can lead experimentalist to find new applications of these technologically important materials.

**Keywords:** Density functional theory; Structural properties; Elastic constants; Ab initio calculations

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## PROPERTIES

## 1. Introduction

The tin oxides SnO and $SnO_2$ are of considerable technological interest, especially the dioxide is used in heat reflecting foils, transparent electrodes in liquid crystal displays (LCDs), chemical gas sensors and Sn-oxide/Si solar cells [1,2].

The monoxide is used as anode materials in lithium rechargeable batteries, as coating materials or as catalysts [3].

The physical properties of $SnO_2$ (stannic oxide) are both studied experimentally and theoretically. However, there exists a lack of information about SnO (stannous oxide) or there has been some controversies between them. This motivates us to study the semiconductor SnO at ambient conditions as well as under high pressure. Moreover, $SnO_2$ is produced by using SnO. A number of first-principles studies based on DFT [1, 4-8] and experimental studies [9-14] studying the physical properties of SnO and $SnO_2$ have been performed up to now. The structural and electronic properties of SnO in the structures of tetragonal, rocksalt, herzenbergite and CsCl have been studied by Aron and Graeme [4, 6]. Li et al. has claimed that a phase transition to orthorhombic phase takes place under the pressure of 1.1 GPa [7]. SnO in metastable tetragonal structure at ambient conditions decomposes to $SnO_2$ and Sn above a certain temperature of 600 $^0$K [14] while any phase transition has not been observed at room temperature and under applying the pressure of up to 51 GPa [9]. Electronic properties of both SnO and $SnO_2$ bulk and low-index surface stabilities by using an empirical van der Waals interaction correction have been studied [5]. The structural properties under high pressures have been performed by Giefers et al. [9] and Wang et al. [10]. Li et al. [7] have predicted only four of six elastic constants of tetragonal SnO. The all of the elastic constants for tetragonal and rocksalt structures of SnO have not been calculated in the literature. In this study, our main aim has been to calculate structural and mechanical properties of SnO in the structures of litharge, B1 and B2, and rutile $SnO_2$ at zero pressure.

## 2. Computational method

Total energy calculations have been carried out by using the Vienna *ab initio* simulation package (VASP) [15-17] containing projector augmented wave pseudo potential (PAW) method [18]. The electronic exchange and correlation functions are evaluated within DFT by using Generalized Gradient Approximation (GGA) with the parameterization of Perdew-Burke-Ernzerhof (PBE) [19].
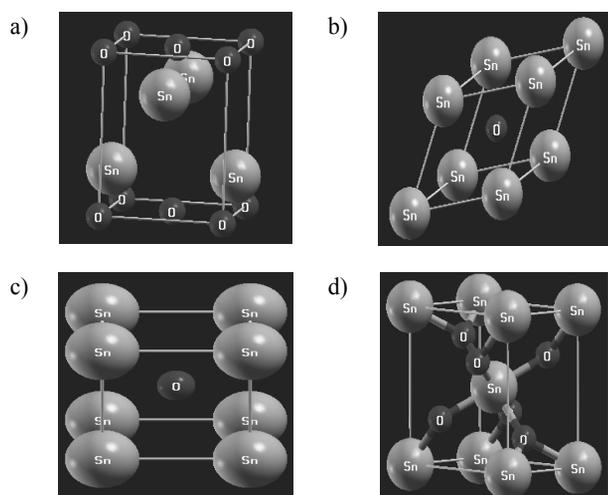
a)

b)

c)

d)



Fig. 1. Crystal structures of a) Litharge-SnO, b) B1-SnO, c) B2-SnO, d) Rutile-$SnO_2$

While total energies are converged at 500 eV kinetic cut-off energy for all structures studied in this work, meshes of k-points for Brillouin zone integrations are converged at 10x10x8 for litharge SnO, 8x8x8 for B1 and B2 SnO structures and 8x8x10 for rutile $SnO_2$ structure using the Monkhorst-Pack method [20].

SnO is known to crystallize in tetragonal litharge-type (tP4, P4/nmm, SG No. 129, Z=2). In this structure oxygen atoms occupy Wyckoff 2c sites at (0,0,0) and (1/2,1/2,0) and Sn atoms occupy Wyckoff 2a sites at (0,1/2,u) and (1/2,0,-u) under ambient conditions [1,11]. On the other hand $SnO_2$ in tetragonal rutile-type (tP6, P4$_2$/mnm, SG No. 136, Z=2) is described as oxygen atoms at ± (v,v,0,1/2 + v,1/2 - v,0.5) and Sn atoms at (0,0,0) and (1/2,1/2,1/2) [5, 21]. Where u and v are the dimensionless internal parameters representing the distance between Sn plane and its nearest neighbor O plane for each structure respectively. SnO cubic structures: NaCl (B1) structure (cF8, Fm3m, SG No. 225) Sn atom at (0,0,0) and oxygen atom at (1/2,1/2,1/2). CsCl (B2) structure (cP2, Pm3m, SG No. 221) Sn atom at (0,0,0) and oxygen atom at (1/2,1/2,1/2). Figure 1 shows corresponding structures of litharge, B1 and B2 structures of SnO and rutile $SnO_2$. Corresponding energies and primitive cell volumes are calculated.

The total energies and pressures calculated as a function of primitive cell volume per molecule are used to determine the structural properties and mechanical response functions (bulk modulus and its pressure derivative) by fitting the data to a third-order Birch-Murnaghan equation of states (EOSs). The third-order Birch-Murnaghan EOS giving the total energy and pressure as a function of volume are as the following [22]:

$$E(V) = E_0 + \frac{9V_0 B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]^3 B' + \left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]^2\left[6 - 4\left(\frac{V_0}{V}\right)^{2/3}\right]\right\} \quad (1)$$

and

$$P(V) = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right] x\left\{1 + \frac{3}{4}\left(B' - 4\right)\left[\left(\left(\frac{V_0}{V}\right)^{2/3} - 1\right)\right]\right\} \quad (2)$$

respectively. In these expressions, $E_0$ is the total energy, $V_0$ is the equilibrium volume, $B_0$ is the bulk modulus at 0 GPa pressure, and $B'$ is the first derivative of the bulk modulus with respect to pressure. Bulk modulus at different pressures is calculated by using the following equation:

$$B(V) = \left(\frac{B_0}{2}\right)\left\{7\left(\frac{V_0}{V}\right)^{7/3} - 5\left(\frac{V_0}{V}\right)^{5/3} - \left(\frac{3}{4}\right)\left(B_0' - 4\right)\left[5\left(\frac{V_0}{V}\right)^{5/3} - 7\left(\frac{V_0}{V}\right)^{7/3}\right]\right. \quad (3)$$
$$\left.\left(\left(\frac{V_0}{V}\right)^{2/3} - 1\right) + \left(\frac{3}{2}\right)\left(B_0' - 4\right) x\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right]\left(\frac{V_0}{V}\right)^{2/3}\right\}$$

### 2.1. Elastic constants

The second order elastic constants are calculated from the first contribution to the strain energy after the application of the strain. The elastic constants of B1 and litharge structure of SnO are calculated in this study. After optimizing energy-volume and pressure-volume data by fitting of them to the Birch-Murnaghan EOS given in Eqs of 1 and 2, the equilibrium volume, bulk

modulus ($B_0$) and its preesure derivative ( $B^{'}$) are determined for SnO. Three elastic constants, $C_{11}$, $C_{12}$ and $C_{44}$ of cubic structures are calculated by following the method given in the reference of [23]. Volume conserving tetragonal shear strain is applied to calculate the tetragonal shear elastic constant of $C_s = (C_{11}-C_{12})/2$. The form of the tetragonal strain tensor and corresponding total energy of the system under this strain are given as;

$$\varepsilon = \begin{pmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta^2/(1-\delta^2) \end{pmatrix} \quad \text{and} \quad E(\delta) = E_0 + 2C_s V_0 \delta^2 + 0(\delta^4) \quad (4)$$

respectively. Here, $E_0$ and $V_0$ are the energy and volume of the unstrained system respectively, $C_s$ is the shear elastic constant and $\delta$ is the deformation parameter. $\delta$ is changed from $\delta$ = -0.03 to $\delta$ = +0.03. The total energy versus $\delta$ data are fitted to the third order polynomial function. Hence, the elastic constants are obtained from the second order coefficients of this fit.

Pure shear elastic constant $C_{44}$ is determined by applying the following monoclinic strain tensor and using the corresponding total energy;

$$\varepsilon = \begin{pmatrix} 0 & \delta/2 & 0 \\ \delta/2 & 0 & 0 \\ 0 & 0 & \delta^2/(4-\delta^2) \end{pmatrix} \text{and} \quad E(\delta) = E_0 + \frac{1}{2}C_{44}V_0\delta^2 + 0(\delta^4) \quad (5)$$

respectively. Bulk modulus of a cubic crystal is defined as

$$B = (C_{11} + C_{12})/3B \quad (6)$$

It has been predicted from Birch-Murnaghan EOS parameters. The elastic constants of bulk modulus and two shear moduli of $C_s$ and $C_{44}$ for cubic structure of SnO are computed by solving energy equations given in Eqs. 4-6.

We need to five different strain tensors and bulk modulus defined by Eq. 12 to calculate six independent elastic constants for SnO in the structure of litharge. We have used the strain tensors and corresponding energy densities given in the Ref. of [24] to get elastic constants of tetragonal structure;

$$\varepsilon = \begin{pmatrix} \delta/(1-\delta^2) & 0 & 0 \\ 0 & 0 & \delta \\ 0 & \delta & 0 \end{pmatrix} \text{and} \quad E(\delta) = E_0 + 2C_{44}V_0\delta^2 + 0(\delta^4) \quad (7)$$

$$\varepsilon = \begin{pmatrix} 0 & \delta & 0 \\ \delta & 0 & 0 \\ 0 & 0 & \delta^2/(1-\delta^2) \end{pmatrix} \text{and} \quad E(\delta) = E_0 + 2C_{66}V_0\delta^2 + 0(\delta^4) \quad (8)$$

$$\varepsilon = \begin{pmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta^2/(1-\delta^2) \end{pmatrix} \text{and} \quad E(\delta) = E_0 + (C_{11}-C_{12})V_0\delta^2 + 0(\delta^4) \quad (9)$$

$$\varepsilon = \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta^2/(1-\delta^2) & 0 \\ 0 & 0 & -\delta \end{pmatrix} \text{and} \quad E(\delta) = E_0 + \frac{(C_{11}-C_{13}-C_{33})}{2}V_0\delta^2 + 0(\delta^4) \quad (10)$$

$$\varepsilon = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \delta \end{pmatrix} \quad \text{and} \quad E(\delta) = E_0 + \frac{C_{33}}{2}V_0\delta^2 + 0(\delta^4) \quad (11)$$

These strains are volume conserving except for $\varepsilon_6$. Bulk modulus of the tetragonal structure can be expressed in terms of elastic constants;

$$B = \frac{1}{9}(2C_{11} + 2C_{12} + 4C_{13} + C_{33}) \quad (12)$$

Six independent elastic constants of litharge SnO are calculated by solving the Eqs. 7-12 for zero pressure.

## 3. Results and discussion

The structural properties of litharge, rocksalt (B1) and CsCl (B2) SnO and rutile $SnO_2$ structures are calculated by using first principles calculations. The volumes are changed around the equilibrium volumes to get the minimized energy of the systems. The data of total energy versus volume and those of pressure versus volume are fitted to Birch-Murnaghan EOS to obtain equilibrium lattice constants, bulk modulus and its pressure derivative for each structures. Fig. 2 shows the plots of total energy as a function of volume, pressure as a function of volume and u-variation of convergence for litharge SnO.

The values of structural properties calculated for the structures interested in this study are compared with other available theoretical and experimental results, and are also listed in Table 1.

The ratio of $c/a$ and internal parameter u of litharge SnO are changed by the application of external pressure. The $c/a$ ratio decreases as the external pressure increases as shown in Fig. 3a as experimental data do [10]. On the other hand, the internal parameter u of litharge SnO increases with the increasing of external pressure as shown in Fig. 3b.

Moreover, the experimental data support this trend [10]. Our results are compatible with the experimental results. We are also interested in the phase transition from litharge phase to B1 rocksalt phase of SnO. Fig. 3c shows the variation of enthalpy as a function of applied pressure for two phases. Phase transition does not take place from litharge to B1 structure, as shown in Fig. 3c.

Elastic constants as a mechanical property, of rocksalt and litharge SnO are calculated under zero external pressure, and given in Table 2 with the available data [7].

Our six elastic constants for litharge structure are compared with the other calculation predicting only four of them [10] in Table 2. To our knowledge, the elastic constants for B1 structure are calculated for the first time in this study.
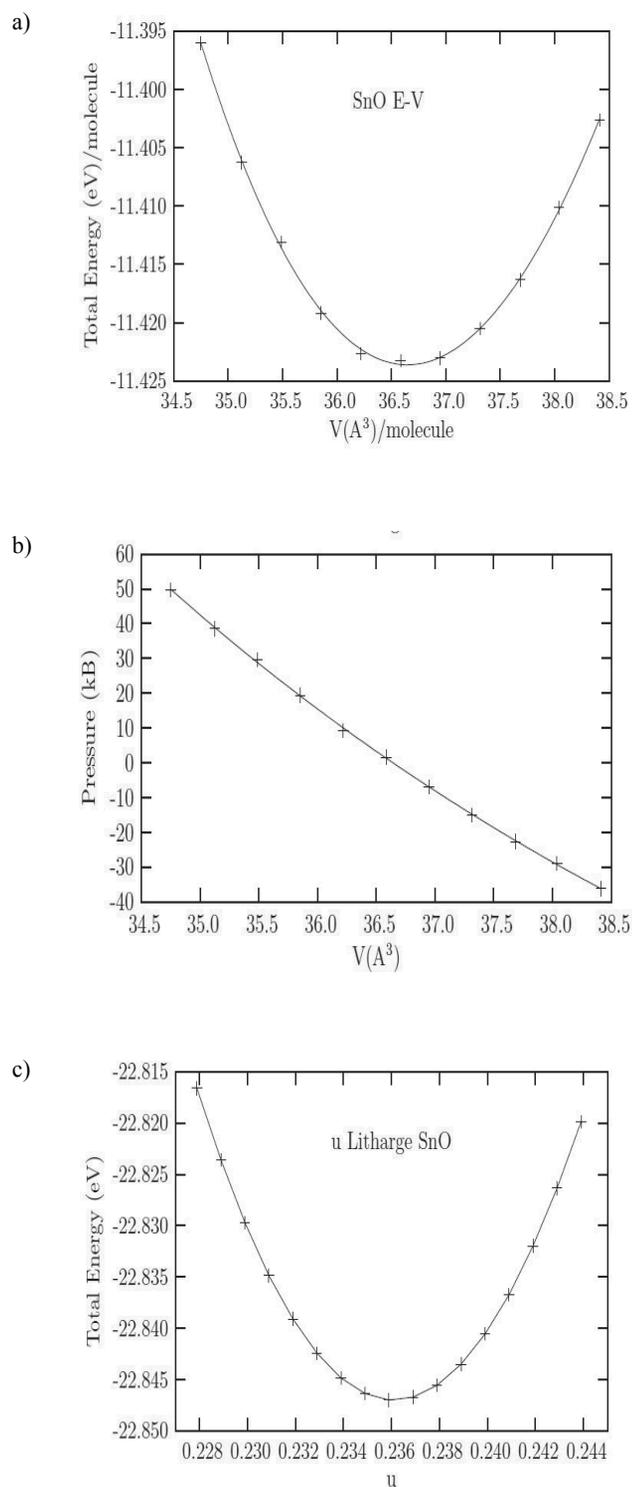
a)



b)



c)



a)



b)



c)



Fig. 2. a) Total energy as a function of volume for SnO Litharge, b) Pressure as a function of volume for SnO Litharge structure, c) Total energy as a function of u for SnO Litharge Structure
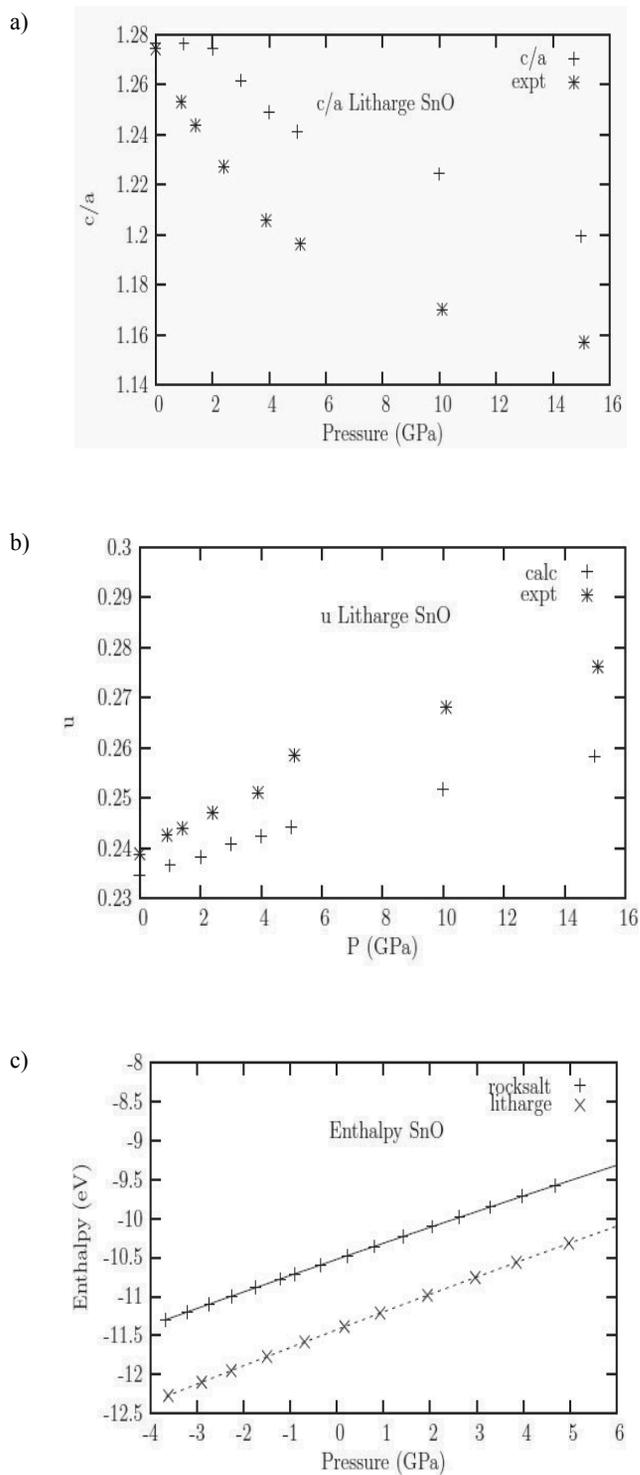
Fig. 3. a) *c/a* versus pressure along with the experimental data from Ref.[10] for litharge SnO, b) u versus pressure along with the experimental data from Ref.[10] for litharge SnO, c) Enthalpies of rocksalt and litharge SnO versus pressure

Table 1.
Lattice constant $a(\text{Å})$, tetragonality ratio $c/a$, internal parameter u, equilibrium energy $E_0(eV)$, volume $V_0(\text{Å}^3)$ and bulk modulus $B_0(GPa)$ for SnO in the structures of litharge, rocksalt, CsCl and for $SnO_2$ in the phase of rutile

| Litharge SnO | $a$ (Å) | $c/a$ | u | $E_0(eV)$ | $V_0$ (Å³) | $B_0(GPa)$ |
|---|---|---|---|---|---|---|
| This study | 3.854 | 1.2735 | 0.2369 | -11.42 | 36.64 | 86.8 |
| Experiment[a] | 3.799 | 1.2674 | 0.2374 | - | 34.77 | 38.0 |
| Experiment[b] | 3.800 | 1.2726 | - | - | 34.90 | 35.0 |
| Calculation[c] | 3.850 | 1.3058 | 0.2300 | -11.54 | 37.32 | - |
| Calculation[d] | 3.850 | 1.2782 | 0.2341 | - | 36.36 | 31.0 |
| | | | | | | |
| Rocksalt (B1) SnO | | | | | | |
| This study | 5.098 | | | -10.52 | 33.12 | 122 |
| Calculation[e] | 5.116 | | | -10.52 | 33.48 | - |
| | | | | | | |
| CsCl (B2) SnO | | | | | | |
| This study | 3.12 | | | -9.885 | 30.37 | 106 |
| Calculation[c] | 3.12 | | | -9.980 | 30.37 | - |
| | | | | | | |
| Rutile $SnO_2$ | | | | | | |
| This study | 4.827 | 0.673 | 0.307 | -18.779 | 37.863 | 177.1 |
| Experiment[f] | 4.737 | 0.673 | 0.306 | - | - | - |
| Experiment[g] | 4.738 | 0.673 | - | - | - | - |
| Calculation[h] | 4.826 | 0.672 | 0.307 | -18.937 | 37.706 | 179.3 |
| Calculation[i] | 4.740 | 0.660 | 0.307 | - | - | 218.0 |

[a]From Ref.[10]    [d]From Ref.[7]    [g]From Ref.[13]
[b]From Ref.[9]    [e]From Ref.[6]    [h]From Ref.[5]
[c]From Ref.[4]    [f]From Ref.[21]    [i]From Ref.[25]

Table 2.
Elastic constants of rocksalt and litharge SnO under zero external pressure

| | $C_{11}$ (GPa) | $C_{12}$ (GPa) | $C_{13}$ (GPa) | $C_{33}$ (GPa) | $C_{44}$ (GPa) | $C_{66}$ (GPA) |
|---|---|---|---|---|---|---|
| This study litharge | 147.8 | 83.9 | 53.4 | 102.2 | 43.9 | 75.6 |
| This Study B1 | 145.6 | 66.7 | | | 36.5 | |
| Calculation[d] | 50.0 | 38.0 | - | - | 20.0 | 80.0 |

[d]From Ref. [7]

# 4. Conclusions

First-principles calculations have been performed to examine the structure of SnO. The structural parameters calculated for SnO and $SnO_2$ are consistent with the other theoretical and experimental data. $c/a$ ratio and internal parameter u as a function of pressure are also in good agreement with experiments. Among three structures of SnO, namely, rocksalt, cesium chloride and tetragonal litharge, the most energetically favorable one is the litharge structure at ambient conditions. The graph of enthalpy versus pressure shows that any phase transition from litharge to rocksalt structure does not occur by applying the pressures of up to 5 GPa to the systems. Structural parameters of $SnO_2$ are also in good agreement with the available experimental and theoretical data. Three elastic constants of rocksalt structure and six elastic constants of tetragonal SnO are calculated for the first time in this study.

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