First principle calculations of structural, electronic, optical and thermoelectric properties of tin (II) oxide

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Abstract
This work aims to study structural, electronic, optical, and thermoelectric properties of Tin(II) Oxide (SnO) by first-principles calculations by using the software VASP within the Perdew-Burke Enzerhof (PBE), HSE03 and HSE06 functionals. Bandstructure, total density of states (TDOS), orbital and site projected density of states (PDOS), dielectric functions of SnO have been calculated. We found that the bandgap of 0.77 eV calculated within HSE06 is in excellent agreement with experimentally established findings. TDOS agrees well with experimentally established x-ray photoelectron spectroscopic (XPS) measurements. By analysis of PDOS contributions of Sn-5s and O-2p at the valence band has been established. Boltzmann semi-classical transport theory is further used to obtain a figure of merit, which has a maximum positive value of 0.14 at around 390 K, and this indicates the possibility of application of SnO as a thermoelectric material.

1. Introduction
Tin oxide is a well known material in two major forms: tin(iv) oxide (SnO₂) and tin(II) oxide (SnO). SnO₂ has technologically important applications in gas sensors, lithium-ion rechargeable batteries, photoelectronic devices, transparent semiconducting oxides, photovoltaic cells, thin-film transistors, flat-panel displays [1–3], etc. Considering the various applications, most researchers have focused their attention on SnO₂ simply because of its n-type electrical conductivity, coupled with its wide bandgap of 3.6 eV [2, 4, 5]. Although some studies on SnO are available, they are not systematic. SnO undergoes disproportionation at a specific temperature and pressure [2, 6]. Potential applications of SnO in thermoelectric generators and solar cells has increased the research attention to the material. It should be noted here that the availability of the well-known chalcogenide-based thermoelectric materials such as, e.g., PbX, BiX, SnX, and Sb₂X₃ (X = S, Se, Te)) limited and some of them are toxic [1]. SnO is more abundant, non-toxic and environmentally friendly materials [3]. There is little information on thermoelectric properties of bulk SnO. The aim of this paper is study of electronic, optical, structural and thermoelectric properties of SnO.

2. Computational methods
The computational work has been performed by Vienna ab-initio simulation package (VASP) [7] within the projected augmented wave (PAW) and Quantum Espresso [8]. Tetragonal litharge crystal structure of SnO of space group P4/nmm, space group number 129 [1, 2, 9] has been studied, which has been reported to be the thermodynamically stable phase at ambient conditions [9]. This work treated Sn(5s² 4d¹⁰ 5p²) and O(2s² 2p³) as valence electrons to study the electronic and structural properties of SnO. The exchange-correlation functional used in this work are Perdew-Burke Enzerhof(PBE) [10] together with modified Hartree–Fock exchange Hybrid
Functionals HSE03 and HSE06. $5 \times 5 \times 4$ Monkhorst–Pack $\bf{k}$-points were used for self-consistence calculations while $18 \times 18 \times 16$ $\bf{k}$-points grid was employed for non-self consistency and Bolztrap calculations to sample the Brillouin zone. The tetrahedron method for the integration of the Brillouin zone was also employed. The optimized value of 500 eV energy cutoff is used as the plane wave cutoff energy. Full optimization of the lattice has been performed until the difference in energy and forces between two successive iterations is less than $10^{-6}$ eV and $10^{-3}$ eV, respectively. Thermoelectric properties were obtained by efficient Boltzman semi-classical transport theory as implemented in Bolztrap code \cite{11}. Boltzmann transport properties are governed by the following equations: the figure of merit of the system is described by the equation as

$$ZT = \frac{S^2 \sigma T}{K}$$

where $S$ is the Seebeck coefficient, $\sigma$ is the electrical Conductivity, $T$ Absolute temperature, and $K$ is the total thermal Conductivity. The electrical conductivity is obtained by the equation

$$\sigma_{\alpha\beta}(T; \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\epsilon) \left[ -\frac{\delta f_\mu(T; \mu)}{\delta \epsilon} \right] d\epsilon$$

(2)

$$\sigma_{\alpha\beta}(\epsilon) = \frac{e^2}{N} \sum T_{ik} \delta(\epsilon - \epsilon_{ik})$$

(3)

Seebeck coefficient

$$S_{\alpha\beta}(T; \mu) = \frac{1}{e T \Omega \sigma_{\alpha\beta}(T; \mu)} \int \sigma_{\alpha\beta}(\epsilon)(\epsilon - \mu) \left[ -\frac{\delta f_\mu(T; \mu)}{\delta \epsilon} \right] d\epsilon$$

(4)

Thermal conductivity given as

$$K_{\alpha\beta}^0(T; \mu) = \frac{1}{e^2 T} \int \sigma_{\alpha\beta}(\epsilon)(\epsilon - \mu)^2 \left[ -\frac{\delta f_\mu(T; \mu)}{\delta \epsilon} \right] d\epsilon$$

(5)

with $e$ as the electronic charge, $\Omega$ is the volume of unit cell, $N$ being the number of K-point sample, $\mu$ as chemical potential, $\alpha$ and $\beta$ are the tensor indices. The code is based on the well known Fourier interpolation to obtain bands analytical expression. Our relaxation time is taken to be constant according to the consideration that electron contribution to the transport are in narrow range of energy, as this was earlier examined and confirmed to be good approximation \cite{11}.

3. Results and discussion

3.1. Structural properties

Figure 1 displays crystal structure of the thermodynamically stable phase of SnO. It crystallizes into a distorted tetragonal structure with the space group $P4/nmm$ No, 129 and two molecular units per unit cell. Table 1 shows the equilibrium lattice constants of the lattice as relaxed by Quantum Espresso and VASP with PBE, HSE03, and HSE06 functionals. The results obtained from these optimizations show that the lattice parameters calculated
within PBE are overestimated while those obtained from HSE03 and HSE06 show better agreement with experimentally established parameters.

3.2. Electronic properties

Figure 2 shows total density of states (TDOS) as compared with the XPS valence band spectra measurements of [13]. Our TDOS reproduced fairly well with the XPS spectra [13] with the little difference in the highest peak which might be ascribed to the pseudopotentials used in our calculations. The lowest energy band between $-20$ to $-15$ eV results from hybridization of Sn(5p) with O(2s). The low energy region between $-10$ to $-6$ eV is mainly contributed by Sn(5s) and O(2p). The topmost valence band between $-5$ to $0$ eV consists of hybridized Sn(5p) and O(2p) with little contribution of Sn(5p). The band is delocalized, which shows strong dispersion in the valence band with low effective masses for holes [14]. This is one of the indicators that SnO might favor p-type electrical properties. The conduction band is dominated by Sn(5p) and O(2p) [2, 9, 15]. As expected, the band gaps calculated by hybrid functionals HSE03 and HSE06 are larger than that estimated within PBE. Figure 3 displays the results for orbital and site projected density of states (PDOS) obtained from calculations within HSE06 and shows the gap that agrees well with the experimental results [1, 2, 12]. The results show contributions of both Sn and O electrons on the energy bands (figure 3). PDOS further indicates the contributions of the orbitals resulting in various peaks in TDOS.

The electronic band structure presented in figure 4 revealed an indirect bandgap of 0.34 eV and 2.66 eV for the direct bandgap obtained within the PBE calculations whereas 0.77 eV is established for the indirect bandgap within HSE06 with optical bandgap of 2.76 eV. The conduction band minimum is located at the M-point (0.4, 0.4, 0.0) whereas the topmost valence band is at the Γ-point (0.0, 0.0, 0.0). The bandgap obtained from PBE (figure 4) is underestimated whereas that obtained within the hybrid functional is in good agreement with experimental values of 0.7 eV and 2.8 eV for indirect and direct band gaps respectively [2, 16–18].

Table 1. Lattice parameters for tetragonal phase of SnO.

|     | $a$ (Å) | $c$ (Å) | $c/a$ |
|-----|---------|---------|-------|
| PWScf| 4.02    | 4.28    | 1.06  |
| PBE  | 3.87    | 5.01    | 1.29  |
| HSE03| 3.83    | 4.98    | 1.30  |
| HSE06| 3.77    | 4.93    | 1.31  |
| PBE[1]| 3.86   | 5.04    |       |
| PBE[6]| 3.86   | 5.04    | 1.31  |
| PBE[12]| 3.89  | 4.98    | 1.28  |
| HSE03[1]| 3.80  | 4.94    |       |
| HSE06[1]| 3.80  | 4.96    |       |
| Expt[1]| 3.81  | 4.84    | 1.27  |

Figure 2. TDOS for SnO (solid line) as compared to experimentally measured XPS spectra (dash line) of [13].
3.3. Optical properties

The study of the optical properties is of great importance for optoelectronic device applications. The optical parameters can be computed from the complex dielectric function as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The other optical constants can be calculated from the equation. The imaginary part of the dielectric function in VASP is numerically obtained by direct evaluation of the matrix elements between the occupied and unoccupied electronic states. The Kramers-Kronig relations are used to derive the real part $\varepsilon_1(\omega)$ of the dielectric function. All other optical constants are obtained from the knowledge $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.

Figure 5 shows the real and imaginary parts of the macroscopic dielectric function that have been used to calculate refractive index and extinction coefficient as compared to experimental results of [19]. The material becomes polarized when it is exposed to an electric field due to the electric dipoles. $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are plotted as a function of the energy in the energy range 0–4 eV and compared with experimental results (figure [19]). Static dielectric constant $\varepsilon_1(\omega)(0)$ in figure 5 at zero energy is 6.9, indicating the dielectric constant of SnO which fairly agrees with the experimentally established value of 7.8 of [2] and 7.25 of [16]. Location of the peak at 3.0 eV is also in good agreement with that discussed in [2]. Refractive index (n) is another important technical parameter describing beam propagation in the medium; static refractive value at n(0) is obtained around 2.7 which agreed favourably with earlier reports of [2, 16, 19]. The peak positions and pattern for refractive index and extinction coefficient are similar to the work reported in [20]. The analysis of the absorption coefficient (figure 5) shows good absorbance of the UV part of the sunlight.

![Figure 3. PDOS for SnO calculated within HSE06.](image1)

![Figure 4. Band structure for SnO calculated within PBE functional.](image2)
The electron energy loss function $L(\omega)$ shown in figure 6 is the energy loss of an electron passing through the material with high velocity. The material becomes transparent when the frequency of the incident photon is greater than the plasma frequency. The photoconductivity of the material is peaked at $4\,\text{eV}$. Dependence of electrical conductivity on energy repeats that for the absorption coefficient is shown in figure 5.

The summary of some optical constants as obtained with PBE, HSE03 and HSE06 functionals are presented in table 2. Below and compared with other existing theoretical and experimental values where available.
3.4. Thermoelectric properties

The ability of a material to produce useful electrical power is quantized by its power factor $PF = S^2 \sigma$. Here $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity. Materials with high power factor can generate energy in space constraint applications. From figure 7, the power factor increased steadily at lower temperatures and followed with an almost linear increase as both temperature and carrier concentrations increases. The large power factor was obtained in the case of low resistivity and the positive value of power factor is an indication of a thermoelectric behaviour of SnO. The Seebeck coefficient in figure 8, increases sharply from negative to positive up to 100 K, reduces rapidly after 300 K and become monotonic after 600 K, this illustrates the bipolar effect, which takes place when many bands contribute to carrier transport and is mostly strong in electron and hole bands, the conduction (hole) radically reduces the Seebeck coefficient because the holes carry the opposite charge from electrons. Also, the n–p transition noticed in the temperature-dependent Seebeck coefficient was due to the presence of electrons and holes as dominant charge carriers which indicate the existence of n-type and p-type thermoelectric elements [21, 22].

Also, thermal conductivity in figure 8 is greater at higher temperatures, which is an indication that more electrons are thermally excited to the conduction band. The dimensionless figure of merit plot gave a maximum value of 0.14 at around 390 K which is an indication that if this system is alloyed with appropriate material, it can be a highly efficient thermoelectric material [3].

4. Conclusion

In conclusion, we have studied electronic, structural, optical and thermoelectric properties of SnO by first-principles calculations. We report that the band gap is underestimated in the calculations within PBE and is estimated in high accuracy by hybrid functional calculations that agreed well with the experimentally established results. Electronic structure calculations are consistent with the experimentally measured x-ray photoelectron measurements. Also, our study show that SnO has potential for thermoelectric applications. Our results show strong potential of SnO for applications as a thermoelectric material.
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