Understanding the thermodynamic pathways of SnO-to-SnO$_x$ phase transition

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A B S T R A C T

SnO decomposes into SnO$_2$ and Sn above a certain temperature either directly or through intermediate phases. This phase transition, although has been known for a century, is not well understood yet. Further, to date, a consensus on the correct stoichiometry and crystal structures of intermediate SnO$_x$ phases formed during that phase transition is absent. Our work attempts to elucidate SnO-to-SnO$_x$ phase transition at thermodynamic growth conditions for the first time. The results presented here show that oxygen-poor and tin-rich growth conditions promote SnO-to-SnO$_x$ phase transition to happen. At these growth conditions, indirect phase transition is the most probable, and in such transition, the formation of any (Sn$_2$O$_3$ or Sn$_3$O$_4$) intermediate phases is equally probable depending on initial growth conditions. All these findings are consistent with experimental results. Further, it was demonstrated that empirical van der Waals (vdW) correction of SnO is required to reproduce the pathways of this phase transition correctly. At the end, the opto-electronic properties of Sn$_2$O$_3$ have been investigated.

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Due to versatile electro-optical and electro-chemical properties, tin-oxides (SnO$_x$, $1 \leqslant x \leqslant 2$) promise a wide range of applications in different technological aspects such as transparent electrode, solar cell, efficient catalyst, anode material in lithium rechargeable batteries, and gas sensor element [1–5]. Despite of presence of different SnO$_x$ phases, only SnO and SnO$_2$ are known to be stable and well-studied; α-SnO is a p-type semiconductor while SnO$_2$ displays n-type activity [6]. The SnO$_x$ ($1 < x < 2$) phases are formed as intermediate tin-oxides while SnO decomposes above a certain temperature (>300 °C [6,7]) into SnO$_2$ and Sn. Various chemical formulae for these intermediate phases have been proposed. Some studies [8,9] proposed Sn$_3$O$_4$ as the stoichiometry of the intermediate SnO$_x$ phase, while Sn$_2$O$_3$ chemical formula was proposed by others [7,10]. Though Sn$_5$O$_6$ chemical formula has also been mentioned as another probable intermediate SnO$_x$ phase [11], not much information is available of it. Several studies verified Sn$_3$O$_4$ [6,12–15] and Sn$_2$O$_3$ [16] as the correct intermediate SnO$_x$ phase. At this point, a valid question arises: why is a general consensus absent on measured stoichiometry of intermediate SnO$_x$ phases? The answer of this question calls for a methodical investigation of SnO $\rightarrow$ SnO$_2$ phase transition. However, although many studies have reported the SnO decomposition followed by the formation of various SnO$_x$ phases while annealing at oxygen environment,

the SnO to SnO$_x$ phase transformation process is still not well understood. Further, to the best of our knowledge, no theoretical study has been done thus far in this regard. These motivated us to pursue the present work which primarily intends to investigate the chemical mechanisms of SnO to SnO$_x$ phase transformation with respect to different oxygen growth conditions by means of *ab initio* calculation.

Additionally, the opto-electronic properties of Sn$_2$O$_3$ will be investigated. Since Sn and O are earth-abundant and non-toxic materials, Sn–O derived technologies promise to be cost- effective and eco-friendly. Further, Sn$_2$O$_3$ has been reported as mixed-valence states metal oxide in the previous studies [17,18]. Another intermediate tin-oxide (Sn$_3$O$_4$) has shown to have attractive photo-catalytic properties owing to its mixed-oxidation states [19]. Metal oxides of this novel feature are also exhibit other unique properties, such as magnetism [20] and superconductivity [21]. Despite this fact, Sn$_2$O$_3$ finds itself in limited applications such as detecting NO gas [22] and enhancing, as dopant, opto-electronic properties of ZnO [23]; however, it could be a potential candidate for many other applications. The proliferation of the versatile use of it is possible if its physical properties, such as band gap, optical absorption ability, and stability, as well as the suitable growth conditions are known. At present, very limited information is available in these regards. This prompts us to study opto-electronic properties of it in conjunction with the investigation of SnO $\rightarrow$ SnO$_2$ phase transition which should shed light on its preferable growth conditions.

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The theoretical investigation, regardless of properties, of any material requires knowing its crystal structure as a prerequisite. Although their existence has been reported for more many years [8], unfortunately, to date, the crystal structures of SnO_x intermediate phases are not unambiguously determined. Recently, probable monoclinic crystal structures of intermediate SnO_x phases have been predicted [17,24]. The crystal structure of Sn_3O_4 was later verified by precession electron diffraction [25]. This predicted structure produces a DFT-HSE (exact exchange, $\alpha = 25\%$) band gap (2.5 eV [19]) comparable to experimental counterpart (2.4 eV [19]). However, the crystal structures of Sn_3O_4 synthesized in nanobelt [26] and microflower [27] forms were found to have triclinic symmetry and different band gaps (2.9–2.97 eV); these findings are consistent with the first reported [9] structural description of Sn_3O_4. Due to the absence of atomic configurational information in the literatures [9,26,27], predicted structure [17] could not be compared. In contrast, crystal structure of Sn_2O_3 is least studied and predicted structures were not verified experimentally. Moreover, predicted structures, although show good agreement with each other, are different from the first proposed triclinic structure by Murken and Trömel [7]. A good agreement between theoretical and experimental XRDs of Sn_2O_3 has been claimed [17], however, crystal systems, lattice parameters, and number of formula unit in the cell differ significantly in two cases. Despite this fact, Sn atom in the predicted structure exhibits a mixed-valence state which is consistent with experimental result [18]. Under such circumstances, the crystal structures of those phases need to be precisely determined or at least verified at first. Since the crystal structure of Sn_3O_4 was once verified [25], we rather restrict ourselves in predicting the crystal structure of Sn_2O_3 only.

For the first task, a number of possible candidate structures ("Motif Structures") were chosen for global optimization within the context of density functional theory (DFT). These structures were generated from different existing structures in mineral database by means of following strategy [28,29]: this algorithm includes replacement of existing cations (A) and anions (B) in A_2B_3 stoichiometric compounds by Sn and O, respectively as well as manipulation (e.g. removal or addition of cations/anions) of different stoichiometric compounds (A_mB_n) to reach the stoichiometry A_2B_3 followed by former procedure to form Sn_2O_3. The evolution of different motif (possible) structures of Sn_2O_3 (more than 250) from existing structures is shown in Fig. 1. In addition, StructurePredictor [30,31] software generated structures were considered for global optimization as well. Based on the lowest energy calculated by DFT, the ground state structure was predicted. It is noted that different flavors of crystal structure prediction softwares are available, such as CALYPSO based on particle swarm optimization (PSO) [32]. This was, for example, recently applied to study new two-dimensional monolayers [33]. We have rather used our 'hands-on' method to extend our previous successes [28,29] on a specific stoichiometric oxide to a general case. The formation of unit cell of motif structures was accomplished in two steps. In the first step, those stoichiometric existing structures were chosen for which Sn_2O_3 unit cells can be obtained without addition or removal of extra atoms to unit cells. Such existing structures are Sn_2X_3 (X = S and F), A_2O_3, and ABO_3 (A, B = IIIA, IVA, and VA elements). IIIA and VA elements were chosen because of their most chemical resemblance to IVA elements as nearest neighbors in the periodic table; IVA elements were selected as they belong to same group as does Sn. Moreover, some proximity of crystal structures of Sn_2O_3 (while lattice vector 'c' is doubled) with monoclinic Pb_2O_3 counterpart [34] has been reported in Ref. [7]. Since crystal structure of Sn_2O_3 [7] was determined as two formula unit in cell, and found to have some similarity with Pb_2O_3 [34] structure, Pb_2O_3 (Z = 2) structures were modified with experimentally determined lattice parameters as well. In the second step, Sn_2O_3 unit cells were constructed using Sn based existing structures which have stoichiometry $A_2Sn_2O_3$ (A belongs to same definition as before), SnO_2, and SnO; removal of all A atoms in $A_2Sn_2O_3$ and removal/addition of suitable numbers of O atoms in SnO_2/SnO generate unit cells with atomic ratio Sn:O = 2:3. Since Sn_2O_3 is formed [7,16] as intermediate tin-oxide while SnO disintegrates into SnO_2, we have considered those primary phases derived Sn_2O_3 motif structures for optimizations as well. The unit cells of SnO_2 and SnO phases were doubled, tripled, and quadrupled to consider more degrees of freedom in removing and adding O atoms. It is noted that all possible polymorphs rather than only ground state structures of aforementioned existing compounds were considered in forming the unit cell of Sn_2O_3; 'Materials Project' (mp) website [30,31] was used in search for those possible polymorphs. The
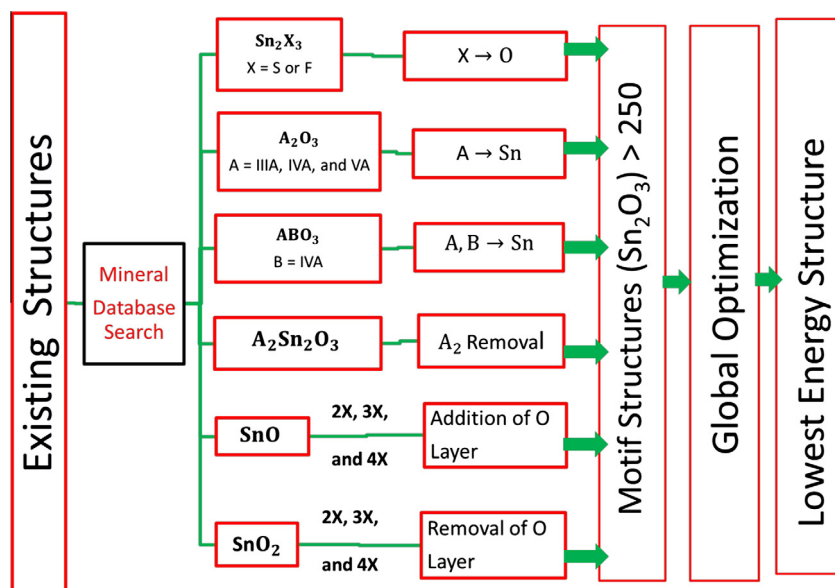

Fig. 1. Evolution of different 'Motif Structures' of Sn_2O_3. 'nx' ($n = 2$, 3, and 4) indicates that original structures, which had $Z = 1 (Z = $ No. of formula unit) in the cell, were doubled, tripled, and quadrupled to form motif structures; structures having $Z = 2$ in the cell were doubled only.