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**An *ab initio* study of electronic, mechanical, and piezoelectric properties of the trigonal, tetragonal and cubic phases of lead-free perovskite SnBO3 (B = Ti, Zr, Hf)**

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**Abstract**

This study offers a comprehensive ab initio analysis of the structural, electronic, and mechanical properties of the trigonal (R̅3̅), tetragonal (P4mm) and cubic (Pm̅3̅m) phases of SnBO3 (BTi, Zr, Hf) [oxide](https://www.sciencedirect.com/topics/materials-science/oxide-compound) [perovskite](https://www.sciencedirect.com/topics/materials-science/perovskite%22%20%5Co%20%22Learn%20more%20about%20perovskite%20from%20ScienceDirect%27s%20AI-generated%20Topic%20Pages) compounds using various functionals namely GGA-PBE, PBE0, HSE06, and B3LYP. From formation energy calculation, trigonal symmetry has been found to be the most stable phase. In the structure optimization, B3LYP estimates the largest volume under trigonal and tetragonal symmetry. However, for the cubic system of SnBO3, SnTiO3 possess the largest volume when using PBE-GGA, while B3LYP estimates the largest in SnZrO3 and both PBE-GGA and B3LYP estimates the same magnitude in SnHfO3. When Ti atom is replaced with either Zr or Hf, a notable shift in the second oxygen atomic coordinate was observed in the tetragonal phase along the z-direction, which impacts the [lattice parameters](https://www.sciencedirect.com/topics/materials-science/lattice-constant) leading to an expansion along the a-axis but with contraction along the c-axis. Structural changes have been found to correspond with electronic transitions. While the electronic transition in SnTiO3 takes place along �→Γ, the transitions in both SnZrO3 and SnHfO3 occurs along �→Z in k space. In the cubic system, SnTiO3 showed an indirect X→Z transition, whereas SnZrO3 and SnHfO3 demonstrated a direct X→X transition. Density of states calculations have revealed that contribution from the B-site atom in the energy states around the conduction band edge is reduced as Ti atom is substituted with Zr atom and subsequently with Hf atom for all the crystal phases. Mechanical stability was consistent across all the compounds in all the calculations with various exchange-correlation functionals considered. Analysis of the [mechanical parameters](https://www.sciencedirect.com/topics/materials-science/mechanical-property) of the trigonal phase of SnBO3 has deduced that only SnTiO3 using hybrid functionals shows [brittleness](https://www.sciencedirect.com/topics/materials-science/brittleness). While only SnHfO3 consistently exhibited a ductile nature throughout the functionals considered in the tetragonal phase, all compounds in the cubic phase were ductile. Interestingly, while the [bulk modulus](https://www.sciencedirect.com/topics/materials-science/elastic-moduli) increased sequentially from Ti to Zr and then to Hf when B site atom is substituted in tetragonal structures, SnTiO3 emerged as the most robust system in the cubic phase. In the tetragonal system, when Ti atom in SnBO3 is replaced with either Zr or Hf, the [piezoelectric](https://www.sciencedirect.com/topics/materials-science/piezoelectricity) response exhibits massive increase associated with the change in atomic position of the second oxygen atom along the c-axis and the response is also predicted to be highest in SnHfO3.

**Graphical Abstract**



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**Introduction**

ABO3 perovskite oxides stand out as a significant group of compounds, renowned for showcasing diverse properties like ferroelectricity, pyroelectricity, piezoelectricity, and optoelectronics [1], [2], [3], [4]. PbTiO3 (PTO), a lead-based oxide perovskite, in particular, has garnered significant attention due to its pronounced ferroelectric and piezoelectric properties at room temperature [5], [6]. In addition, some ferroelectric materials, including PTO, exhibit noteworthy pyroelectric properties, with PTO being recognized for its high pyroelectric coefficient and low permittivity [7], [8]. These attributes motivate researchers to work on improving PTO's inherent qualities via doping and other techniques, leading to the development of compounds like lead zirconate titanate (PZT) [9], [10]. PZT is renowned for its high sensitivity as sensors and actuators [11] and also due to its impressive operational temperature range of 150–250 °C [12]. Additionally, other variants based on PTO, such as Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT) and PbZrO3–PbTiO3–Pb(Ni1/3, Sb2/3)O3, have also been developed [13], [14]. However, there are rising environmental and health concerns regarding lead usage. As awareness grows, there is a pressing need to explore alternatives to lead-based compounds, thus fueling the search for viable lead-free options.

In the quest to find a substitute for the Pb ion, SnTiO3 (STO) has emerged as a promising contender due to its close resemblance to PTO in terms of lattice parameters and band gap nature in both its tetragonal and cubic forms [15]. Although synthesizing STO is difficult because the Sn atom prefers the 4+ oxidation state over 2+, it has been successfully created in the polytypes (̅�3̅ and ̅�3̅) using soft chemistry via a metathesis reaction involving layered K2Ti2O5 and hydrated SnCl2 at temperatures below 320 °C [16]. Another synthesis approach involves a co-precipitation method using a blend of SnCl2 and TiCl4 in isopropanol, combined with hydrogen peroxide and ammonia solution, followed by heating at 800 °C [17]. The synthesized ̅�3̅configuration of SnTiO3 bear a striking resemblance to the honeycomb-like arrangement found in Ilmenite FeTiO3. Nevertheless, their increased length is attributed to the stereochemical influence of Sn2+ lone pairs. Though to some extend certain developments have been made in the experimental aspects of STO, there are still plenty of scope for further research. To explore its technological application and to fabricate devices based on STO, it is crucial to provide reliable theoretical data. On a search for photocatalyst, possible phases of SnTiO3 were investigated in which the FeTiO3-type was found to have the lowest energy. It was confirmed to possess the most stable state and they also have found two metastable states, namely the PbTiO3-type and the CaTaO2N-type [18]. *Taib, M.F.M.,* et al. [19], in their first principles investigation on various phases of STO have predicted that tetragonal (P4mm) phase is most stable. Lead-free STO in the tetragonal (P4mm) symmetry has also been reported to exhibit a piezoelectric response almost on par with PTO [20]. Further, when subjected to pressures between 0–30 GPa, STO displays consistent mechanical stability, though its primary band gap diminishes as pressure rises [21]. Among the Sn-based ABO3 perovskite compounds, SnZrO3 has been studied in its cubic phase and reported to have direct band gap of 3.09 eV with a stronger hybridization between Sn-5p and O-2p compared to STO. When comparing Zr-5d and O-2p hybridization, it appears weaker than the Ti-4d and O-2p combination [22]. Reported theoretical work on the cubic form of SnZrO3 (SZO) and SnHfO3 (SHO) for renewable energy materials have revealed that high ductility makes them better suited for optical rather than thermoelectric applications [23].

A notable study by Agarwal et al. [24] discussed challenges in synthesizing SnTiO3 and explored the properties of the P4mm phase of STO using both LDA and HSE06 methods. The tetragonal forms of SnZrO3 and SnHfO3, which might offer exciting alternatives, remain unstudied using hybrid functionals. The cubic phase of SnTiO3 has been analyzed with the HSE06 functional, indicating potential enhancements in thermoelectric performance with increasing temperature, possibly optimized by doping [25]. While the cubic phase's structural properties have been examined with the HSE06 exchange-correlation functional, it hasn't been tested with other hybrid functionals. Without experimental validations for many electronic and mechanical properties, reliance on these theoretical predictions remains cautious, along with SnZrO3 and SnHfO3 especially considering potential variances due to B-site ion substitutions.

The Local Density Approximation [26] was one of the earliest exchange-correlation functions and only considered the local electron density. However, Perdew, Burke, and Ernzerhof introduced the Generalized Gradient Approximation (GGA), which calculates energy gradients more widely and is now a predominant exchange-correlation function. Nonetheless, these methods often underestimate the electronic properties of semiconductors and insulators. Meta-GGA offers some improvements by incorporating a kinetic energy term but still struggles with calculations for condensed matter. A major issue with Density Functional Theory (DFT) is the electron self-interaction error. While Hatree-Fock theory addresses this error, it tends to overestimate energies due to a missing correlation term. To tackle this, hybrid functionals were introduced, combining exact exchange with semi-local functional terms. Axel Becke pioneered this approach in 1993[27].

In this work, density functional theory will be implemented using the conventional exchange-correlation functional (PBE-GGA) and compare its outcome with three leading hybrid exchange-correlation functionals: PBE0, HSE06, and B3LYP. This approach seeks to generate predictive insights beneficial for experimentalists. In this context, we will also explore the effects of substituting B-site atoms with elements such as Ti, Zr, and Hf. Our computational exploration will encompass the trigonal (R-3), tetragonal (P4mm) and cubic (Pm3m) phases of SnBO3 (BTi, Zr, Hf), focusing on delineating their structural, electronic, and mechanical characteristics. A specialized analysis will also be dedicated to understanding the non-centrosymmetric piezoelectric attributes of the tetragonal phase.

**Section snippets**

**Computational methods**

Based on Density Functional Theory (DFT) all our calculations are performed on CRYSTAL17 code [28]. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm that came as default remained unchanged and has been used for structure optimization. Sn, Ti, Zr, Hf, and O have been treated with all-electron basis sets, which are optimized for crystal calculations. The Triple-Zeta Valence with Polarization (TZVP) basis set has been used for every atom in the compounds considered [29]. The first Brillouin

**Structural and dynamical properties**

The study of structural properties is critical since a tiny deviation in the structure can drastically change the character and capabilities of a compound, notably in this research as we consider two different crystal structures in addition to altering the B-site atom. The initial structure of the SnBO3 compounds considered in this work is taken from the corresponding crystalline phases of the well-known PbTiO3. The structures presented in this study are generated using VESTA [40]. The

**Conclusion**

We have reported ab initio study of the structural, electronic, and mechanical properties of the trigonal (̅�3̅), tetragonal (P4mm) and cubic (Pm̅3̅m) phases of SnBO3 (BTi, Zr, Hf) oxide perovskite compounds using various functionals namely GGA-PBE, PBE0, HSE06, and B3LYP. We have found that all the compounds in ̅�3̅, P4mm and Pm̅3̅m symmetries exhibit negative formation energy, thus indicating thermal stability of the compounds. When Ti atom is replaced with either Zr or Hf, a notable shift in the

**CRediT authorship contribution statement**

**Lalhumhima:** Conceptualization, Writing – original draft, Software, Investigation, Formal analysis, Visualization, Methodology. **Bernard Lalroliana:** Writing – review & editing, Investigation, Formal analysis. **R. Zosiamliana:** Writing – review & editing, Formal analysis. **Lalmuanchhana:** Writing – review & editing, Formal analysis. **Dibya Prakash Rai:** Writing – review & editing. **Ramesh Chandra Tiwari:** Writing – review & editing. **Lalmuanpuia Vanchhawng:** Writing – review & editing. **Lalrinthara Pachuau:**

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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