# First-principles characterization of chemical stability, defect formation energies and *n*-type conductivity in SrZrO$_3$

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## ABSTRACT

Thermodynamics and the electronic structure of intrinsic vacancies in SrZrO$_3$ have been investigated by using density functional theory based a*b-initio* calculations. Our results indicate that the hole-doped state can be achieved in Sr and Zr deficient SrZrO$_3$, while the O vacancy retains the insulating character by introducing a defect level in the band gap. We utilize electronic charge density calculations and atoms-in-molecules concept to elucidate the changes in electronic properties by introducing the vacancy defects. The variation of formation energy as a function of Fermi level shows that fully charged oxygen vacancy in SrZrO$_3$ can lead to a hole-doped state. Moreover, we explore the chemical stability and defect formation energies of charge neutral and fully charged intrinsic vacancies under various synthesis conditions and analyze full and partial Schottky reactions. In addition to intrinsic vacancy defect, the clustering of neutral oxygen vacancies in SrZrO$_3$ is examined in different crystallographic planes which provides useful information for tailoring the electrical conduction of this material. Therefore, we propose that hole-doped, semiconducting and *n*-type character in SrZrO$_3$ further enhance its device application for semiconductor industry which are achievable through intentional incorporation of intrinsic defects and oxygen vacancy clustering.

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## 1. Introduction

The diverse device applications of perovskite oxide (ABO$_3$) compounds with an aristotype cubic symmetry have been stimulating immense amount of research work exploring their semiconducting, ferroelectric, ferromagnetic and superconducting properties [1–4]. A further interest in these materials roots from the possibility of optimizing their properties by exploiting their stoichiometry which can be altered by means of incorporating defects and impurities into the perovskite lattice [3]. From experimental point of view, synthesis of nonstoichiometric ABO$_3$ can result from evaporation losses during annealing or sintering or due to the precipitation of the constituent species. The consequent creation of point defect (i.e. the formation of A, B or oxygen vacancies) introduces extra free charge carriers which modify their physical properties [5]. Since present day materials processing techniques capable of controlling chemical composition and atomic structure at microscopic level have brought about considerable

progress in the understanding and control of complex defect equilibria of point defects in oxide compounds [6], defect engineering has emerged as the most exciting field of materials science that promises tailoring electronic and other properties of materials for their functional applications. For example, defect engineering has been effectively put to use for controlling the stoichiometry and crystal symmetry of perovskites by means of changing the growth conditions such as varying oxygen partial pressure and tensile stress during synthesis [3,7,8]. On the other hand, rapid improvements in the computational facilities and the progress in computer implementation of theoretical condensed matter physics models, particularly density functional theory (DFT), has enabled the exploration of the properties of nonstoichimetric materials with increased accuracy. This is particularly important in view of the fact that unlike the experimental models of point defect which are based on many assumptions, the present day computer simulation of materials allow the study of realistic configurations which provide accurate insight and help tailor physical properties for particular technological requirements [6].

The introduction of dopants and defects in 3*d*, 4*d* and 5*d* perovskite oxides of alkaline-earth metals promise significant

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improvements in their ionic conductivity which are important for technologies required for solid oxide fuel cells as a source of renewable energy [9,10]. In this context, strontium zirconate, SrZrO₃ (SZO), stands out among other 4d perovskite oxides due to its versatile properties. Being a high temperature acceptor-doped protonic conductor with higher conductivity in wet environments as compared to SrCeO₃, SZO has emerged as an important candidate for fuel cells, hydrogen concentration cells and humidity sensors [11–13]. More recent investigations in this direction have further the interest in SZO as its Mn and C and V and P co-doping systems which promise to be efficient visible light photocatalysis materials for splitting water into hydrogen [14]. In addition, SZO is well suited for high temperature electronic and optical applications as substrate material [15] due to its large band gap ($E_g$) ~ 5.96–6 eV [16,17], however, doping with rare earth ions and the presence of complex cluster vacancies can lead to visible photoluminescence that qualifies SZO as a suitable material for displays, X-ray phosphors and medical imaging applications [18,19]. The high relative permittivity, large breakdown strength, and high-temperature electrical properties [20] make SZO an ideal choice for high voltage capacitor applications [21], while the ferroelectric nature of SZO superlattices (SZO/SrTiO₃) [22] and resistive switching properties of transition metal doped SZO films for nonvolatile memory technology [23] gives it the advantage of being important candidate for device fabrication.

Since the transport properties of protonic conductors strongly depend on their chemical composition [24], it is imperative to have a deeper understanding of defect chemistry of the underlying un-doped material. Labrincha et al. [25] studied transport properties of un-doped SZO samples prepared with solid state reaction method showing that SZO behaves as a mixed ionic and p-type conductor in air. They found that the p-type conductivity of un-doped SZO increases for oxygen partial pressure ($Po_2$) greater than 10 Pa [25] which may be attributed to the increasing concentration of cation vacancies under oxidation conditions. Similarly, oxygen vacancies play a crucial role in functional applications of SZO. The resistive switching properties of double-layer SZO memory devices, for example, are caused by the redistribution of oxygen vacancies between the oxygen deficient and oxygen rich SZO layers [23]. This has motivated various researchers to use first-principles DFT calculations for probing the role of oxygen vacancies and their diffusion in SZO for its potential use in future resistive switching random access memory (RRAM) devices [26,27]. Since n-type conduction in un-doped perovskite oxides prevails at low $Po_2$ [28], the increase in the leakage current of un-doped SZO thin-film dielectrics grown under oxygen poor conditions has been assigned to the increased oxygen vacancy concentration [29]. Although experimental studies of acceptor-doped and donor-doped SrTiO₃ suggests that p-type and n-type conductivities can be controlled by incorporating impurity atoms [30,31], in the context of current materials processing techniques which allow controlling the chemical composition during synthesis at atomic-scale it is certainly very interesting to theoretically investigate the impact of the intrinsic vacancy defects and clustering of oxygen vacancies on the electronic structure of SZO. To date many DFT based studies of structural, mechanical and opto-electronic properties of pristine and defective SZO [15,19,32,33] have been performed, a detailed description, however, of intrinsic vacancy defects in SZO under various chemical environments using quantum chemical methods and the possibility of attaining n-type conductivity through clustering of oxygen vacancies has not been carried out so far. Since first-principles calculations of the electronic structure lead to a deeper understanding of the thermodynamics of defects in perovskite oxides, in the present work we report results of DFT calculations on the electronic properties of vacancy defects in SZO. It is expected that the detail investigation of intrinsic vacancies and oxygen vacancy clustering reported herein may provide useful information to experimentalists which can help in understanding the nature of non-stoichiometric SZO.

## 2. Calculation methods and structural details

To explore the chemical stability of intrinsic vacancy defects and the effects of vacancy formation on electronic structure of SZO, we employ all electron full-potential linear-augmented-plane-wave plus local orbitals (FP-LAPW + lo) method which is implemented in the WIEN2k suite of computer programs [34]. For the muffin-tin model of crystal potentials, the crystal space has been partitioned into two sections. For the case of non-overlapping muffin-tins centered at the atomic sites, muffin-tin radii (in bohr) of 2.5, 1.8 and 1.75 are chosen for strontium, zirconium and oxygen atoms, respectively, within which spherical harmonic expansion of wave functions, charge density, and potential are performed. In the case of interstitial region, plane wave basis set are used. For the sake of uniformity in the calculations of total energy for different sizes of supercell structures (SSs) used in the present work, the plane wave cutoff parameter, $K_{max}$, is set to $K_{max} = 7.0/R_{MT-O}$ bohr$^{-1}$ (where $R_{MT-O}$ is the muffin-tin radii of oxygen atom), while the maximum values of angular momentum $l_{max}$ and charge density expansion $G_{max}$ are chosen to be 10 and 18, respectively. For computing the exchange-correlation energies, we utilize generalized gradient approximation (GGA) parametrization scheme proposed by Perdew, Burke and Ernzerhof [35].

The SSs for pristine and vacancy containing SZO have been modeled by first computing the GGA lattice parameter of SZO cubic unit cell (space group # 221) with a $12 \times 12 \times 12$ **k**-mesh and seeding-in the experimental lattice parameter 4.154 Å [36] for DFT optimization. The computed GGA lattice parameters are then used for constructing a 40-atoms $2 \times 2 \times 2$ cubic SS (Sr₈Zr₈O₂₄) for the subsequent calculations for pristine SZO. It is worth-mentioning here that this 40-atoms $2 \times 2 \times 2$ cubic SS is equivalent to $2 \times 1 \times 2$ SS of orthorhombic SZO (space group # 62) with high crystallographic symmetry without leading to any differences in the calculated formation energy values of the two crystallographic modification of ABO₃ perovskites [37,38].

For 40-atoms SS of pristine and defective SZO, we have performed total energy calculations using a $6 \times 6 \times 6$ **k**-mesh which was found appropriate for energy minimization when results of calculated minimum total energies are compared with a larger **k**-mesh. The iteratively convergence of self-consistent calculations for total energy is achieved when the difference of energy between two successive iterations is less than $10^{-4}$ Ry. In case of vacancy containing SS, the atomic positions are fully relaxed to minimize the Hellmann–Feynman forces until they are below 0.001 Ry/a.u. In the present work, calculations involving the effects of spin-orbit coupling (SOC) are ignored as our test calculation for bulk unit cell of SZO reveal that the application of SOC on SZO does not change its electronic properties. Furthermore, the enthalpy of formation calculated with and without the inclusion of SOC was also compared. In accordance with earlier DFT reports [39], our results indicate that the differences in the computed minimum total energies from the introduction of SOC can be partitioned into contributions coming from the atomic species and, therefore, do not affect calculated thermodynamic properties. For controlling the size effects, we have used similar calculational parameters for all SS which assume different symmetry structures compared to pristine SS due to the introduction of isolated vacancies and oxygen vacancy clustering. Furthermore, the **k**-mesh for different SSs are scaled with respect to the **k**-mesh used for SZO bulk unit cell.

In case of non-stoichiometric SZO containing isolated $V_{Sr}^q$, $V_{Zr}^q$