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DFT Based Electronic Structure Studies of $SrZrO_3$ Perovskite

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Abstract:

The present work focuses on the theoretical investigation of the structural, electronic, and optical properties of the perovskite oxide $SrZrO_3$ using Density Functional Theory (DFT) within the framework of the SIESTA computational package. $SrZrO_3$ is an important wide band gap perovskite material known for its excellent dielectric stability, thermal resistance, and ultraviolet optical response, making it highly suitable for advanced optoelectronic and dielectric applications. In this study, first-principles calculations were performed using the Generalized Gradient Approximation (GGA-PBE) along with norm-conserving pseudopotentials and localized numerical atomic orbitals. The electronic band structure and density of states calculations indicated that $SrZrO_3$ behaves like a wide band gap semiconductor or insulating oxide material. The valence band is mainly dominated by oxygen O-2p orbitals, whereas the conduction band mostly consists of zirconium Zr-4d states, indicating significant orbital hybridization and mixed ionic-covalent bonding characteristics. The calculated band structure confirmed the nonexistence of electronic states near to the Fermi level, explaining the smaller intrinsic electrical conductivity and greater dielectric nature of the material.

Keywords — **Put your keywords here, keywords are separated by comma.**

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I. INTRODUCTION

Strontium Zirconate ($SrZrO_3$) is known to be a wide band-gap perovskite oxide and has attracted the attention of the researchers as a phosphor host material due to its ability to accommodate a various rare earth materials as luminescent activator ions. It is also reported to be thermally and chemically stable. This perovskite structure of $SrZrO_3$ provides suitable lattice sites needed for rare-earth doping. This enables efficient energy transfer and strong photoluminescence emissions across the visible region. [1] investigated Tb3+-doped $SrZrO_3$ phosphors and reported efficient host dopant energy transfer with intense green emission, highlighting the effect of the local environment of Tb3+ ions on its optical behavior. Similarly, [2] reported that Eu3+ and Tm3+ doping can effectively tune the emission characteristics of $SrZrO_3$ nanocrystals, indicating their potential use in white-light-emitting (WLED) devices. Pr^{3+}-activated $SrZrO_3$ phosphors have also exhibited strong blue-green photoluminescence emissions and enhanced luminescence emission after high-temperature calcination process, indicating the importance of defect control in search of optimized optical performance [3].

Recently, Singh and Seshadri (2023) [4] synthesized Ho^{3+}-doped $SrZrO_3$ phosphors via the sol–gel techniques and observed intense green emission centered at 545 nm under blue excitation, with concentration quenching occurring after the optimum dopant concentration due to dipole–dipole interactions. Furthermore, studies on intrinsic defects in $SrZrO_3$ have suggested that oxygen vacancies and related defect centers play a very important role in the mechanism of persistent luminescence in such kind of rare-earth-doped systems [5]. These investigations collectively establish $SrZrO_3$ as a versatile and efficient phosphor host for applications in solid-state lighting, displays, optical sensing, and persistent luminescence technologies.

II. BASIC DFT THEORY

A. *Kohn–Sham Formalism*

The Hohenberg–Kohn theorems established the existence of density functionals, they did not provide a practical method for calculations. Kohn and Sham introduced a practical computational framework in 1965 [6].

They replaced the interacting many-electron system with an equivalent system of non-interacting electrons moving in an effective potential.

The Kohn–Sham equation is:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(r)\right]\psi_i(r) = \epsilon_i\psi_i(r)$$

where:

- $V_{eff}(r)$ is the effective potential,
- $\psi_i(r)$ are the Kohn-Sham orbitals,
- ϵ_i are eigenvalues.

The effective potential consists of external ionic potential, Hartree electrostatic potential, and exchange-correlation potential [7].

B. *Exchange–Correlation Functional*

The exchange-correlation functional is the most important approximation in DFT because it includes exchange interactions, electron correlation effects, and quantum mechanical many-body contributions [8].

Since the exact exchange-correlation functional is unknown, approximations are necessary.

1) *Local Density Approximation (LDA)*

LDA assumes that electron density behaves locally like a homogeneous electron gas (Kohn & Sham, 1965).

Advantages of LDA include:

- Simple implementation
- Good structural predictions
- Computational efficiency

However, LDA generally underestimates semiconductor band gaps and becomes less accurate for systems with strongly varying electron density [9].

2) *Generalized Gradient Approximation (GGA)*

GGA improves upon LDA by including electron density gradients [9]. The exchange-correlation energy therefore depends on both electron density and density gradients.

The PBE functional developed by Perdew, Burke, and Ernzerhof is one of the most widely used GGA approximations [9].

Advantages of GGA-PBE include:

- Better lattice parameters
- Improved bonding description
- Better structural optimization
- More realistic electronic properties

The present $SrZrO_3$ study employs GGA-PBE because it provides reliable predictions for oxide materials [10].

3) *Hybrid Functionals*

Hybrid functionals combine DFT exchange with Hartree–Fock exchange [11].

Advantages include:

- Improved band gap prediction
- Better electronic structure accuracy

However, hybrid functionals require significantly higher computational cost and memory [7].

C. *Electron Density*

The electron density is calculated from Kohn–Sham orbitals as follows [6]:

$$n(r) = \sum_i |\psi_i(r)|^2$$

Electron density determines:

- Total energy
- Charge distribution
- Bonding behavior
- Electrostatic potential

- Optical transitions

In oxide perovskites such as $SrZrO_3$, electron density analysis provides information about ionic bonding, covalent hybridization, charge transfer, and orbital overlap [12].

D. Self-Consistent Field (SCF) Procedure

The Kohn–Sham equations must be solved iteratively because the effective potential depends on electron density, which itself depends on the orbitals. The iterative procedure is called the Self-Consistent Field (SCF) cycle [13].

A. Steps in SCF Calculation

Step 1: Initial Density Guess

An initial electron density is assumed.

Step 2: Effective Potential Calculation

The effective potential is calculated using the trial density.

Step 3: Solution of Kohn–Sham Equations

Kohn–Sham equations are solved to obtain orbitals and eigenvalues.

Step 4: New Electron Density

A new electron density is generated from orbitals.

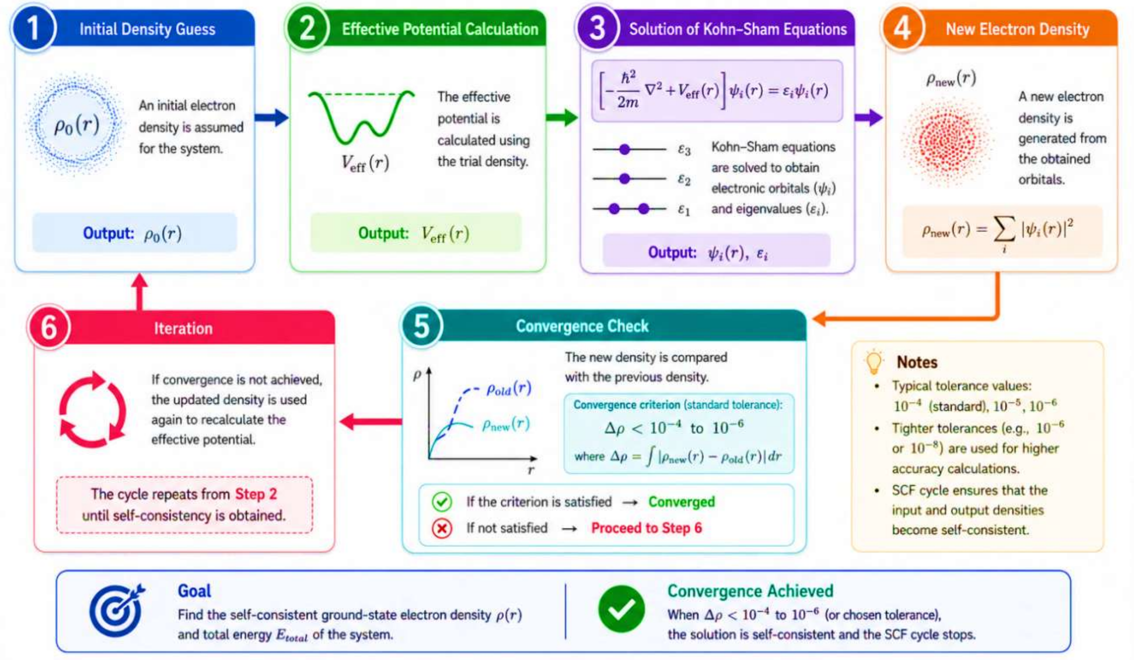
Step 5: Convergence Check

The new density is compared with previous density.

Step 6: Iteration

The procedure repeats until convergence is achieved.

Summary of steps is provided in Figure **01**



An initial electron density is assumed for the system.

Output: $\rho_0(r)$

The effective potential is calculated using the trial density.

Output: $V_{\text{eff}}(r)$

Kohn–Sham equations are solved to obtain electronic orbitals (ψ_i) and eigenvalues (ε_i).

Output: $\psi_i(r),\ \varepsilon_i$

A new electron density is generated from the obtained orbitals.

$\rho_{\text{new}}(r) = \sum_i |\psi_i(r)|^2$

The new density is compared with the previous density.

Convergence criterion (standard tolerance):

$\Delta\rho < 10^{-4}$ to 10^{-6}

where $\Delta\rho = \int |\rho_{\text{new}}(r) - \rho_{\text{old}}(r)|\,dr$

✓ If the criterion is satisfied → Converged

☒ If not satisfied → Proceed to Step 6

If convergence is not achieved, the updated density is used again to recalculate the effective potential.

The cycle repeats from Step 2 until self-consistency is obtained.

Notes
- Typical tolerance values: 10^{-4} (standard), 10^{-5}, 10^{-6}
- Tighter tolerances (e.g., 10^{-6} or 10^{-8}) are used for higher accuracy calculations.
- SCF cycle ensures that the input and output densities become self-consistent.

Goal: Find the self-consistent ground-state electron density $\rho(r)$ and total energy E_{total} of the system.

Convergence Achieved: When $\Delta\rho < 10^{-4}$ to 10^{-6} (or chosen tolerance), the solution is self-consistent and the SCF cycle stops.

Figure **01** Iteration procedure used in DFT

2.4.2 Convergence Criteria

SCF convergence is usually achieved when energy difference and density variation become sufficiently small [13].

Typical convergence criteria are: 10^{-4} eV to 10^{-6} eV

Proper convergence is essential for obtaining accurate structural, electronic, and optical properties.

2.5 Pseudopotential Approximation

Core electrons generally do not participate directly in chemical bonding. Therefore, DFT calculations replace core electrons with effective ionic potentials called pseudopotentials [14].

Advantages of pseudopotentials include:

- Reduced computational cost
- Faster calculations
- Lower basis-set requirements
- Efficient treatment of heavy atoms

SIESTA employs norm-conserving pseudopotentials that preserve valence wavefunction behavior and improve transferability for solids [14].

III. RESULTS AND DISCUSSIONS

A. Comparative total and projected density of states (DOS)

SIESTA based density functional theory calculations were done in order to find the total and projected density of state (DOS) spectrum of the material taken. The comparative total and projected density of states (DOS) spectrum of $SrZrO_3$ shown in Figure 02 provides significant insight into the electronic structure, and other characteristics of the material. The total and projects DOS spectra clearly indicates that $SrZrO_3$ behaves like a wide band gap semiconductor or insulating oxide as a clear energy gap is observed around the Fermi level where the density of electronic states becomes almost zero.

This confirmed the absence of metallic conductivity [15]. It can be noticed that the valence band region is primarily dominated by oxygen-derived O-2p orbitals, whereas the conduction band mainly dominated by Zr-4d electronic states. The finds are consistent with previously reported theoretical investigations of Zirconate perovskites [12, 15]. The strong contribution of Zr-4d in the conduction band region suggests that electronic excitations and optical transitions predominantly involve zirconium d-orbitals. The DOS spectrum also provided the information about the partial overlap between oxygen and zirconium states, which suggests significant O-2p and Zr-4d orbital hybridization. This indicates mixed ionic-covalent bonding within the crystal structure [12]. This kind of orbital hybridization exhibits its contribution to the structural stability, dielectric response, and optical properties of $SrZrO_3$. The broader distribution of states in the valence band further suggests strong orbital interactions and electron de-localization, which enhance lattice stability [16]. The comparatively smaller contribution from Sr-4d and Sr-5s orbitals near the Fermi level indicates that strontium atoms mainly act as structural stabilizers rather than active acting in electronic conduction. The wide electronic band gap observed in the Density of State (DOS) spectrum explains the strong ultraviolet optical absorption behavior of $SrZrO_3$ because high-energy photons are required to excite electrons from oxygen-dominated valence states into zirconium-derived conduction states [17].

Consequently, the material exhibits excellent dielectric behavior, low intrinsic conductivity, high thermal stability, and significant ultraviolet optical activity, making it highly suitable for applications in dielectric resonators, UV photodetectors, optical coatings, fuel cells, sensors, and photocatalytic systems.

Functional Theory approach gives deep information about the electronic behavior and semiconducting nature of the material considered (Figure 03). The band structure plot clearly suggests the presence of a significant energy gap between the valence band maximum (VBM) and conduction band minimum (CBM), suggesting $SrZrO_3$ behaves as a wide band gap semiconductor or insulating perovskite oxide [15]. Nonexistence of band overlap near the Fermi level is an indication that free charge carriers are not available under equilibrium conditions, hence explaining the low intrinsic electrical conductivity of the perovskite considered.

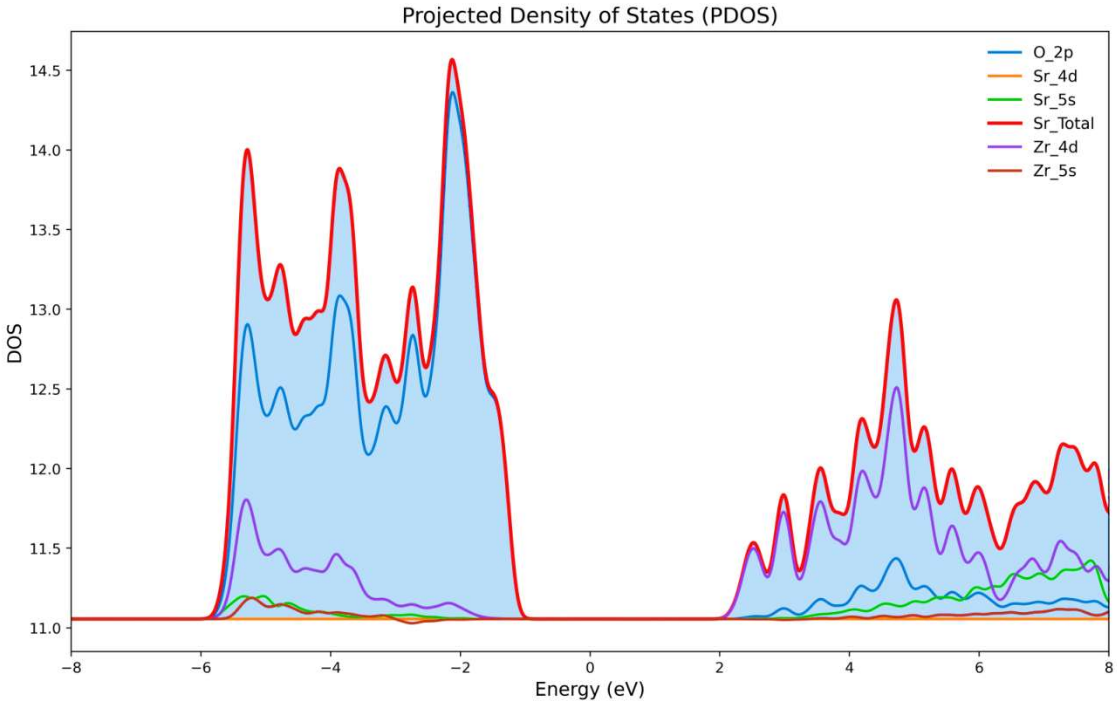


Figure **02** Comparative total and projected DOS of $SrZrO_3$

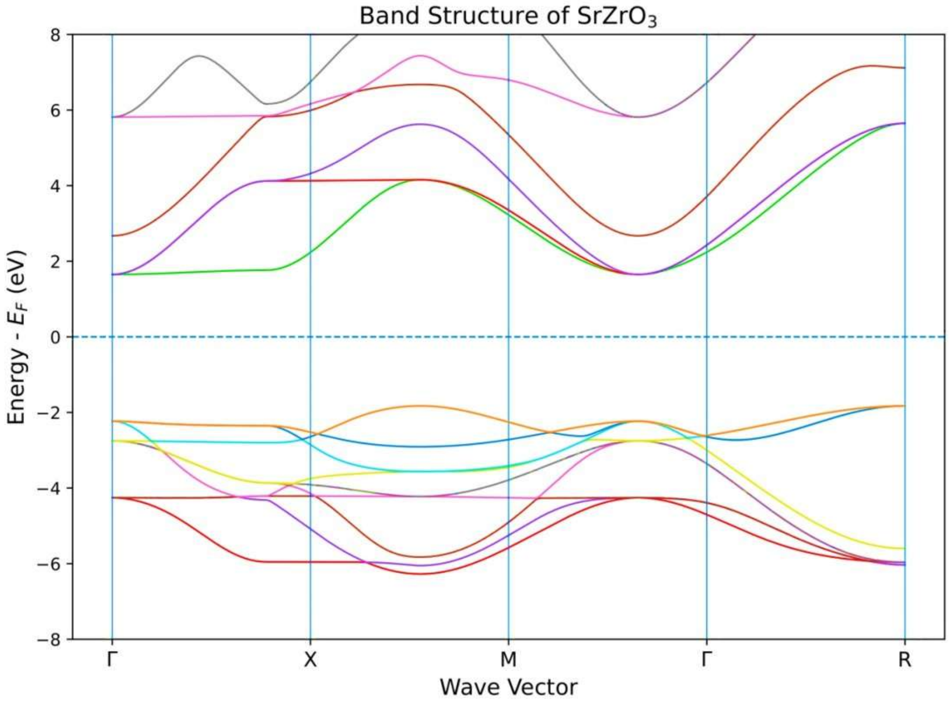


Figure **03** Band Structure of $SrZrO_3$

B. Simulated band structure of SrZrO3

The calculated electronic band structure of $SrZrO_3$ obtained using the SIESTA-based Density The valence band region mainly originates from oxygen-derived O-2p orbitals, while the conduction band is predominantly governed by zirconium Zr-4d states, which is characteristic of transition-metal oxide perovskites [12]. The relatively flat occurrence of several conduction bands is an indicative of localized electronic states and reduced carrier mobility, whereas the broader valence bands is an indicative of stronger orbital overlap. The wide band gap observed in the band structure implies that high-energy photons are required for electronic excitation from the valence band to the conduction band, hence elaborating the strong ultraviolet absorption behavior and dielectric stability of $SrZrO_3$ [17]. Furthermore, the electronic structure confirms that optical transitions mainly occur between O-2p valence states and Zr-4d conduction states, which strongly influence the dielectric response, optical conductivity, and absorption spectra of the material [18]. The calculated band structure therefore establishes $SrZrO_3$ as a promising material for dielectric devices, ultraviolet photodetectors, optical coatings, photocatalytic systems, and high-temperature electronic applications because of its stable wide band gap electronic configuration and strong insulating behavior [17].

IV. CONCLUSION

The density of states and electronic band structure calculations confirmed that $SrZrO_3$ is a wide band gap semiconductor or insulating perovskite oxide. The valence band was found to be mainly dominated by oxygen O-2p orbitals, while the conduction band primarily originated from zirconium Zr-4d states. The absence of electronic states near the Fermi level explains the low intrinsic electrical conductivity and strong dielectric stability of the material. The calculated electronic structure also demonstrated significant O-2p and Zr-4d orbital hybridization, indicating mixed ionic-covalent bonding within the crystal lattice. Therefore, the present study confirms that $SrZrO_3$ is a promising material for advanced optoelectronic devices. The work also demonstrates the effectiveness of the SIESTA-based DFT approach for investigating complex oxide perovskite materials.

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