

Zirconium-Based Chalcogenide Perovskites AZrS₃ (A = Ca, Sr, Ba): A Critical Review of Structure, Properties, Stability, and Energy Applications

¹Ibrahim Yusuf, ²Ogunmola Enoch Debayo and ³Ajayi Akintunde Ayideji

¹Department of Science Laboratory Technology,
Gombe State Polytechnic Bajoga P.M.B 0190 Funakaye, Gombe State.

^{2,3}Department of Mathematics and Physical Science Afe Babalola
University Ado-Ekiti. P.M.B 5454 Ado-Ekiti, Ekiti State.

*Corresponding Author's Email: yusufibrahim220@gspb.edu.ng

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ABSTRACT

Zirconium based chalcogenide perovskites, AZrS₃ (A = Ca, Sr, Ba), are lead free semiconductors composed of earth abundant elements and are of interest for photovoltaics and optoelectronics. The evidence base is, however, strongly unbalanced. Experimental work concerns mainly BaZrS₃, which is orthorhombic (*Pnma*) at room temperature, has a measured optical gap of about 1.75–1.8 eV and shows band edge absorption coefficients above 10⁵ cm⁻¹. CaZrS₃ remains largely computational, and SrZrS₃ must be specified by polymorph because it also forms a non-perovskite, needle-like phase. This narrative critical review, based on a documented literature search, appraises experimental and first-principles studies of crystal chemistry, phase behavior, synthesis, electronic and optical properties, stability, defects and device relevance, and labels each benchmark as experimental, computed or simulated. Three evidence limitations are emphasized. First, the cubic (*Pm3m*) phase widely used in calculations is predicted by simulation to form only above about 880 K, whereas high temperature diffraction of BaZrS₃ has so far revealed orthorhombic and tetragonal phases. Second, the reduction of the BaZrS₃ gap from 1.78 to 1.51 eV by 4 at. % Ti alloying is experimental, whereas the reported photovoltaic efficiencies of 28–33% are device simulations, not measured devices. Third, inconsistent functionals and structural models prevent quantitative comparison across the Ca–Sr–Ba series. A minimum computational protocol and a staged assessment framework are proposed to support evidence-based comparison of the series.

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INTRODUCTION

The search for stable, efficient, and environmentally responsible semiconductors is central to next-generation energy and optoelectronic technologies. Photovoltaic absorbers, photodetectors, light emitters, optical sensors, and photocatalytic interfaces all depend on a coupled set of material properties: an application-appropriate band gap, strong absorption in the target spectral region, efficient carrier generation and transport, benign or manageable defects, and structural stability under fabrication and operating conditions. No single descriptor is sufficient. A material that absorbs light strongly may still be unsuitable if it transforms, degrades, or accumulates nonradiative recombination centers during processing and use.

Halide perovskites demonstrated how the flexible ABX₃ framework can deliver exceptional light–matter interaction and tunable electronic structure. Their deployment, however, remains constrained by sensitivity to moisture, oxygen, heat, and intense illumination, and by the toxicity of lead. These limitations have stimulated interest in chalcogenide perovskites, in which S, Se, or Te occupies the anion site. First-principles screening by Y.Y. Sun et al. (2015) identified several A²⁺B⁴⁺X₃ chalcogenides, including BaZrS₃, as candidate photovoltaic absorbers, and early experimental work established that such compounds are stable ionic semiconductors with visible-range band gaps (Perera et al., 2016; Niu et al., 2017). Stronger and more covalent metal–chalcogen bonding generally gives lower volatility

and greater chemical and thermal resilience than metal–halide bonding (Sopiha et al., 2022).

Among chalcogenide perovskites, zirconium sulfides with nominal composition $AZrS_3$ ($A = Ca, Sr, Ba$) are particularly attractive because all constituent elements are earth-abundant and non-toxic. Experimental studies of $BaZrS_3$ and related distorted chalcogenide perovskites have established exceptionally strong band edge absorption (Nishigaki et al., 2020), tunable band edge behavior through alloying (Wei et al., 2020b; Sharma et al., 2021), thin-film growth by several routes (Wei et al., 2020a; Comparotto et al., 2020; Surendran et al., 2021; Turnley et al., 2022), photoluminescence, and photoconductive response in $BaZrS_3$ based materials (Yu et al., 2021; Zhao et al., 2024). Many body calculations further indicate that dielectric screening, quasiparticle corrections, and excitonic and polaronic effects are important for interpreting the optical response of the whole $AZrS_3$ series (Kumar et al., 2021); for $CaZrS_3$ and $SrZrS_3$, however, these predictions have not yet been tested experimentally.

Despite this progress, the knowledge base remains fragmented. Detailed experimental work is concentrated on $BaZrS_3$; property coverage varies widely; and comparisons across Ca , Sr , and Ba compounds are often made with nonequivalent computational approximations. Structural phase is a further complication. Experimentally accessible structures are distorted and orthorhombic, whereas the ideal cubic phase is frequently studied computationally as a high symmetry reference. Cubic calculations can reveal intrinsic chemical trends, but they must not be read as evidence of ambient phase stability without supporting energetic, elastic, and phonon analysis.

Several reviews already cover parts of this field. Sopiha et al. (2022) reviewed chalcogenide perovskites as a class, emphasizing both their promise and the materials challenges of synthesis and phase purity, and Agarwal et al. (2025) reviewed $BaZrS_3$ in detail, from synthesis to application. Because these reviews are organized around the material class as a whole or around $BaZrS_3$ alone, they do not provide (i) a side-by-side comparison of $CaZrS_3$, $SrZrS_3$ and $BaZrS_3$ in which each benchmark is labelled by evidence type (experimental, computed or simulated) and by its phase, temperature and method; (ii) a separation of predicted high temperature and cubic phase behavior from experimentally observed phase transitions; or (iii) a translation of the methodological heterogeneity of the first-principles literature into a concrete minimum protocol for comparative calculations. The present review is designed to address these three points.

The aim of this review is to provide an evidence-graded, phase-specific comparison of $CaZrS_3$, $SrZrS_3$ and $BaZrS_3$ that distinguishes experimentally established properties from computed and simulated predictions, and to derive from this appraisal a minimum computational protocol

and a staged framework for comparing the series. To meet this aim, the review organizes the available knowledge into a unified structure property application framework and addresses five questions: (i) how does the perovskite structure govern the behavior of $AZrS_3$ compounds; (ii) what has been learned from synthesis and phase control studies; (iii) how do electronic, optical, mechanical, and thermodynamic properties vary with composition and phase; (iv) what role do first-principles methods play in interpreting experiment; and (v) which scientific and methodological gaps must be closed before reliable materials ranking and device deployment are possible?

Scope, Literature Search and Evidence Appraisal

This article is a narrative and critical review; it is not a systematic review or meta-analysis and does not claim exhaustive coverage of the literature. It was developed from literature assembled for a first-principles investigation of $CaZrS_3$, $SrZrS_3$, and $BaZrS_3$. The sources include foundational DFT literature; studies of phase stability, polymorphism, and crystal growth; reports on bulk crystals, thin films, alloying, photoluminescence, and photoconductivity; many-body calculations of optoelectronic properties; and device level simulations. The evidence is synthesized thematically rather than statistically, and wherever possible quantitative benchmarks are reported with the conditions under which they were obtained. No new calculations or experiments were performed for this review: all numerical values are taken from the cited sources (or, for Table 1, recalculated from tabulated ionic radii), and the computational protocol (Section 5.4), research priorities (Section 13) and assessment framework (Table 4) are proposals derived from the appraisal.

Literature search. The core literature was identified by searching Web of Science, Scopus and Google Scholar, supplemented by the ACS, RSC, Wiley and APS publisher platforms and the arXiv preprint server, for publications from January 2015 (the first first-principles screening of chalcogenide perovskites for photovoltaics) to October 2025. Search strings combined the compound names (“ $BaZrS_3$ ”, “ $SrZrS_3$ ”, “ $CaZrS_3$ ”, “ $AZrS_3$ ”) with the terms “chalcogenide perovskite”, “phase stability”, “polymorph”, “thin film”, “band gap”, “optical”, “defect”, “first-principles” and “solar cell”. The reference lists of retrieved articles and of earlier reviews (Sopiha et al., 2022; Agarwal et al., 2025) were screened for additional sources. Foundational methodological works (on DFT, pseudopotentials and elastic-stability criteria, for example) were included where needed to explain methods, irrespective of publication date.

Selection criteria. Studies were included if they (i) reported experimental or computational results on $CaZrS_3$, $SrZrS_3$ or $BaZrS_3$, or on closely related alloys such as $Ba(Zr,Ti)S_3$; (ii) were published in peer reviewed journals, or were preprints providing data not otherwise

available; and (iii) stated the structural phase and, for experiments, the sample form (single crystal, powder, film or nanoparticle). Broader chalcogenide perovskite studies were included only where they clarify structure, bonding, method or device design. Conference abstracts without data, and studies that did not specify the phase or method, were excluded.

Evidence appraisal. Each quantitative benchmark was classified by evidence type as experimental (E), computed by first-principles or molecular-dynamics methods (C), or device simulated (S); statements that follow from structural chemistry without direct measurement or calculation for the compound concerned are labelled inferred (I). The phase, sample form, temperature and pressure, and computational level are reported with each benchmark where the source states them (Table 2). Where studies conflict, more weight was given to (a) experimental over computed results for the same property and phase; (b) phase-pure, structurally characterized samples over samples of uncertain phase; (c) higher-level over lower-level calculations, for example GW/BSE or hybrid functionals over semilocal DFT for band gaps; and (d) results reproduced by independent groups. Remaining disagreements are stated explicitly rather than averaged.

The focus is on zirconium sulfide perovskites, with broader chalcogenide perovskite studies drawn on where they clarify structure, bonding, methodology, or device design. Particular attention is given to the cubic phase because it permits controlled comparison across the Ca–Sr–Ba series; however, cubic predictions are discussed alongside orthorhombic, tetragonal, and non-perovskite polymorphs so that idealized models are not separated from experimentally relevant phase behavior. The evidence is organized along the causal sequence *composition* → *structure and phase* → *electronic states* → *optical, mechanical and thermal response* → *application*

This sequence emphasizes that device relevant behavior arises from linked properties rather than isolated values, and it helps locate where inconsistent assumptions, numerical settings, or sample conditions produce apparently conflicting conclusions.

MATERIALS AND METHODS

Crystal Chemistry of AZrS₃ Perovskites

The ABX₃ Framework

The ideal perovskite ABX₃ contains a large A-site cation in a 12 coordinate cuboctahedral cavity and a smaller B-site cation octahedrally coordinated by six anions; the BX₆ octahedra share corners to form a three-dimensional network. In AZrS₃, Ca, Sr, or Ba occupies the A site, Zr⁴⁺ the B site, and S²⁻ the anion sublattice. The Zr–S network largely controls the frontier electronic states, whereas the A-site cation chiefly sets lattice dimensions, octahedral tilting, and phase preference.

The ideal cubic phase has space group *Pm3m* (No. 221; Glazer tilt system *a⁰a⁰a⁰*), with A at the cube corners (1a), Zr at the body center (1b), and S at the face centers (3c). In this limit Zr–S–Zr angles are 180°, octahedral tilting is absent, and the electronic and dielectric responses are isotropic. Lower-symmetry phases arise when ionic size mismatch, bonding preferences, strain, pressure, or temperature drive cooperative octahedral rotations and cation displacements. The most common distortion in A²⁺B⁴⁺S₃ compounds is the GdFeO₃-type orthorhombic structure (*Pnma*, *a⁻b⁺a⁻*), whose unit cell is approximately $\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$ relative to the pseudocubic parameter a_p .

These distortions are electronically consequential. Changes in Zr–S distance and Zr–S–Zr angle alter the overlap between S-3p and Zr-4d orbitals, thereby changing band dispersion, effective masses, band gap magnitude, and optical transition strength. Structure is therefore not merely a crystallographic label; it is the central variable linking composition to optoelectronic function.

Tolerance factor, octahedral factor and structural descriptors

The Goldschmidt tolerance factor gives a first geometric estimate of whether a set of ions can form the perovskite framework:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1)$$

where r_A , r_B , and r_X are effective ionic radii. Values near unity favor the cubic structure, values between roughly 0.8 and 0.9 are associated with tilted orthorhombic structures, and values above unity favor hexagonal polytypes. A complementary descriptor is the octahedral factor,

$$\mu = \frac{r_B}{r_X} \quad (2)$$

which measures whether the B cation is large enough to sustain stable octahedral coordination. Table 1 lists values obtained with Shannon radii (Shannon, 1976) (Ca²⁺, Sr²⁺, Ba²⁺ in 12-fold coordination; Zr⁴⁺ (0.72 Å) and S²⁻ (1.84 Å) in 6-fold coordination). The values were recalculated for this revision from Eqs. (1) and (2), giving $t = 0.878, 0.906$ and 0.953 and $\mu = 0.391$, which round to the tabulated values. The conventional 6-coordinate S²⁻ radius is used; a different anion radius would shift t for all three compounds in the same direction and would not change the trend. The tolerance factor rises from about 0.88 for CaZrS₃ to 0.95 for BaZrS₃, consistent with a decreasing drive toward octahedral tilting as the A cation grows. The octahedral factor (≈ 0.39) lies slightly below the empirical threshold of ≈ 0.41 often quoted for oxide and halide perovskites, even though BaZrS₃ is a well-established perovskite. This discrepancy is a direct illustration of the limits of purely ionic descriptors for sulfides.

Table 1: Geometric Descriptors of AzrS_3 Computed from Shannon Ionic Radii ($R_{\text{Zr}} = 0.72 \text{ \AA}$, $R_{\text{S}} = 1.84 \text{ \AA}$; Shannon, 1976). R_{A} Is for 12-Fold and R_{Zr} and R_{S} for 6-Fold Coordination. T and M Were Computed for This Review from Eqs. (1) And (2); The “Expected Tendency” Column Is Inferred (I) From T and M and from The Polymorphs Reported in Section 3.3)

Compound	r_{A} (Å, CN 12)	Tolerance factor t	Octahedral factor μ	Expected tendency
CaZrS_3	1.34	0.88	0.39	Strong tilting; competing non-perovskite phases possible
SrZrS_3	1.44	0.91	0.39	Distorted perovskite (β) and needle-like (α) polymorphs
BaZrS_3	1.61	0.95	0.39	Distorted $Pnma$ perovskite at ambient; higher-symmetry phases at high T

Tolerance factor analysis organizes expected trends but is not a complete stability criterion. Chalcogenide bonding has appreciable covalent character, and the preferred phase depends on electronic energy, lattice dynamics, temperature, pressure, and synthesis history. Jess et al. (2022) showed that combining ionic-radius arguments with electronegativity differences gives a better separation of distorted perovskite, needle like, and hexagonal phases for ABS_3 and ABSe_3 compounds than the Goldschmidt factor alone, and Turnley et al. (2024) argued that tolerance-factor analysis should be rethought specifically for chalcogenides. Robust assessment therefore requires total energy comparison among competing structures, elastic criteria, and phonon calculations in addition to geometric descriptors.

Cubic, Distorted and Non-perovskite Phases

The cubic phase is valuable as a theoretical reference because it minimizes structural complexity and exposes chemistry-driven trends. Experimentally, however, BaZrS_3 crystallizes in the orthorhombic $Pnma$ structure. Flux-grown single crystals give $a = 7.056(3) \text{ \AA}$, $b = 9.962(4) \text{ \AA}$ and $c = 6.996(3) \text{ \AA}$ (single-crystal X-ray diffraction; Niu et al., 2019), corresponding to a pseudocubic parameter of $\approx 4.97 \text{ \AA}$; the same study grew the $n = 2$ Ruddlesden–Popper phase $\text{Ba}_3\text{Zr}_2\text{S}_7$ ($P4_2/mnm$), highlighting that closely related structure types compete during synthesis.

The temperature and pressure dependence of the BaZrS_3 structure has recently been clarified. Raman and optical measurements found no first-order structural transition under hydrostatic compression to at least 8.9 GPa at room temperature, while the band gap shifted continuously (Gross et al., 2017). Machine-learning molecular dynamics predicts a first-order $Pnma \rightarrow I4/mcm$ transition near 610 K and a continuous $I4/mcm \rightarrow Pm\bar{3}m$ transition near 880 K at zero pressure, with harmonic phonons showing that the cubic phase is dynamically unstable at 0 K (Kayastha et al., 2025). Synchrotron diffraction on samples heated in air identified a $Pnma \rightarrow Cmcm$ change near 400 °C and a tetragonal $I4/mcm$ phase above about 500 °C, with band gap discontinuities at the transitions and reversible recovery of the $Pnma$ phase on cooling from up to 600 °C (Jaiswal et al., 2024). The two

studies agree that BaZrS_3 leaves the $Pnma$ structure on heating, but they differ in sequence and temperature: the simulations predict a direct $Pnma \rightarrow I4/mcm$ transition at $\approx 610 \text{ K}$ ($\approx 337 \text{ °C}$), whereas the measurements show an intermediate $Cmcm$ phase near 400 °C ($\approx 673 \text{ K}$) before the tetragonal phase appears. The cubic $Pm\bar{3}m$ phase therefore remains a simulation-based prediction above $\approx 880 \text{ K}$ ($\approx 607 \text{ °C}$); it was not reported in the high temperature diffraction study, and oxidation in air at higher temperature (Section 8.3) complicates its direct verification. Because typical synthesis temperatures exceed these transition temperatures, as grown samples may pass through them on cooling and could contain residual polymorphs or transformation-induced microstructure.

SrZrS_3 illustrates another kind of complexity: it is known in a needle-like α form (edge-sharing octahedral chains, NH_4CdCl_3 -type) and a distorted perovskite β form, which have distinctly different optical gaps (Niu et al., 2017). Reported properties of “ SrZrS_3 ” must therefore always be tied to the polymorph. CaZrS_3 is far less studied experimentally; its small A cation places it closest to the boundary where perovskite stability competes with alternative structures, although this expectation is inferred from t (Table 1) rather than established by phase stability measurements. Properties established for BaZrS_3 , including its phase transition sequence and optical gap, should therefore not be transferred to CaZrS_3 or SrZrS_3 without direct evidence.

Consequently, calculated cubic properties should be interpreted as reference state descriptors. A cubic structure that is mechanically or dynamically unstable may still reveal useful chemical trends, but it cannot be treated as a deployable phase without a plausible stabilization pathway such as temperature, epitaxial strain, alloying, or nanoscale confinement.

RESULTS AND DISCUSSION

Synthesis, Processing, and Phase Control

Bulk Crystals and Phase Identification

Experimental realization of chalcogenide perovskites is more demanding than geometric models suggest. Sulfur activity, precursor reactivity, high processing temperatures, competing binary and Ruddlesden Popper

phases, oxygen contamination, and kinetic barriers all affect phase formation. Flux growth with BaCl_2 yields high quality BaZrS_3 crystals with X-ray rocking curve widths of about 0.011° (Niu et al., 2019), and iodine catalyzed solid state reactions have produced polycrystalline transition metal perovskite chalcogenides with band gaps spanning the visible range and high luminescence efficiency (Niu et al., 2017). Careful diffraction, Raman spectroscopy, and composition analysis are essential because secondary phases such as ZrO_2 , ZrS_2 , BaS_x , and $\text{Ba}_3\text{Zr}_2\text{S}_7$ can coexist with the target compound.

Bulk and single crystal specimens provide benchmarks for intrinsic structure, Raman modes, optical absorption, thermal behavior, and photoconductivity. Conclusions from bulk crystals cannot always be transferred to thin films, where strain, grain boundaries, interfaces, sulfur deficiency, oxygen incorporation, and substrate-induced texture modify both phase stability and optical response.

Thin-film Deposition

Thin films are a prerequisite for most devices, and several complementary routes have been demonstrated. Wei et al. (2020a) produced BaZrS_3 films with near edge absorption coefficients above 10^5 cm^{-1} . Comparotto et al. (2020) combined sputtering at ambient temperature with rapid thermal processing, and X-ray absorption and diffraction later showed that crystallization from an amorphous Ba–Zr–S network is accompanied by sulfur loss and segregation of oxygen as ZrO_2 (Mukherjee et al., 2023). Pulsed laser deposition produced epitaxial films with a clear in-plane relationship to the substrate, visible photoluminescence, and photodetectors with high on/off ratios (Surendran et al., 2021). Low temperature processing enabled thin film electronic and optoelectronic devices (Yu et al., 2021).

Solution based approaches have broadened the processing window considerably. Turnley et al. (2022) obtained BaZrS_3 at temperatures as low as 500°C by sulfurizing solution deposited precursors, and the method extends to BaTiS_3 and BaHfS_3 . Single phase molecular precursor inks sulfurized at 575°C yield BaZrS_3 and BaHfS_3 films whose photoluminescence intensifies and blue shifts with sulfurization time (Pradhan et al., 2023), and colloidal routes have produced luminescent BaZrS_3 nanoparticles at low temperature (Yang et al., 2022). Lower temperatures are important for compatibility with transparent conducting oxides and for tandem integration. Across these studies film quality depends on far more than nominal composition. Growth mechanism, sulfur incorporation, oxygen contamination, annealing profile, interfacial reactions, and microstructure all affect the band gap and the sharpness of the absorption edge. Reproducible comparison therefore requires reporting of phase fractions, thickness, grain size, texture, stoichiometry (including O content), substrate, and full

thermal history alongside optical or electronic measurements.

Pressure, Strain and Alloying

External and chemical perturbations provide routes to tune both phase and band structure. Hydrostatic pressure reduces the BaZrS_3 band gap continuously without a first order transition up to $\approx 9 \text{ GPa}$ (Gross et al., 2017), whereas temperature drives tilt-ordering transitions to orthorhombic $Cmcm$ and tetragonal $I4/mcm$ phases in experiment (Jaiswal et al., 2024) and, in simulations, to the cubic phase (Kayastha et al., 2025). Kayastha et al. (2025) further predict that tensile strain stabilizes higher symmetry phases, suggesting that coherent epitaxy on suitably chosen substrates could, in principle, provide access to near-cubic structures at lower temperatures; the stability window and relaxation mechanisms remain to be established experimentally.

Alloying is a chemically accessible route. Substituting a small fraction of Zr with Ti, whose $3d$ states lie lower than Zr $4d$ states at the conduction band minimum, reduces the measured band gap of $\text{Ba}(\text{Zr}_{1-x}\text{Ti}_x)\text{S}_3$ from 1.78 to 1.51 eV at $x = 0.04$; higher Ti contents destabilize the distorted perovskite phase (Wei et al., 2020b). In chemical-vapor-deposited films, Ti alloying lowered the gap from about 1.75 to 1.4 eV (Sharma et al., 2021). A machine learning guided study compared A-site Ca and B site Ti substitution and their photoluminescence (Sharma et al., 2023). Anion alloying with Se offers a further route. Alloying can thus extend spectral coverage, but it may also introduce compositional disorder, local strain, phase separation, and defect states; the optical gain must be weighed against structural purity and carrier lifetime.

First-Principles Methods for Chalcogenide Perovskites

This section summarizes how first-principles methods have been applied in the cited literature and why their approximations matter when AZrS_3 data are interpreted. The equations are standard definitions reproduced for clarity; no new calculations were performed by the authors. The minimum protocol in Section 5.4 is a methodological recommendation derived from this appraisal, not a set of results.

Density Functional Theory Framework

DFT is the dominant framework for relating atomic structure to ground-state electronic properties. The Hohenberg–Kohn theorems establish that the ground state density $n(\mathbf{r})$ uniquely determines the external potential and that the correct density minimizes the energy functional (Hohenberg & Kohn, 1964). The Kohn–Sham formulation maps the interacting system onto auxiliary single-particle equations (Kohn & Sham, 1965), written here in Hartree atomic units:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(r)\right]\psi_i(r) = \varepsilon_i\psi_i(r) \quad (3)$$

$$n(r) = \sum_i f_i |\psi_i(r)|^2 \quad (4)$$

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \quad (5)$$

Here ψ_i and ε_i are the Kohn–Sham orbitals and eigenvalues, f_i are the occupation numbers, v_{ext} is the external (ionic) potential and v_{H} is the Hartree potential. The exchange correlation potential v_{xc} contains all many-body effects not captured by the noninteracting kinetic and Hartree terms. Because its exact form is unknown, practical calculations use the local density approximation, generalized gradient approximations such as PBE (Perdew et al., 1996) and PBEsol, meta-GGAs such as SCAN (J. Sun et al., 2015), or screened hybrid functionals such as HSE06 (Heyd et al., 2003). For periodic solids, Kohn–Sham orbitals are expanded in plane waves, reciprocal space is sampled on k-point meshes, and core electrons are treated with pseudopotentials or the projector augmented-wave method (Blöchl, 1994; Kresse & Joubert, 1999). Quantum ESPRESSO provides structural optimization, electronic structure, Density Functional Perturbation Theory (DFPT) phonons, and post-processing within this framework (Giannozzi et al., 2017, 2020). Burke (2012) gives an accessible perspective on the strengths and limitations of these approximations.

From Optimised Structure to Measurable Properties

A standard workflow begins with convergence tests for plane wave cutoff and k-point density, followed by relaxation of atomic positions and cell parameters. Forces are obtained from the derivative of the total energy,

$$\mathbf{F}_I = -\frac{\partial E_{\text{tot}}}{\partial \mathbf{R}_I} \quad (6)$$

where $\mathbf{R}_I$ is the position of nucleus I and E_{tot} is the total energy of the converged electronic ground state. Because plane waves do not depend on atomic positions, the force follows directly from the Hellmann–Feynman theorem without Pulay corrections, and optimization continues until forces, stresses, and energy changes fall below set thresholds (typically 10^{-3} Ry/bohr, 0.5 kbar, and 10^{-5} – 10^{-6} Ry). Band structures and densities of states follow from non-self-consistent calculations on high symmetry paths and dense meshes. The fundamental gap is

$$E_g = E_{\text{CBM}} - E_{\text{VBM}} \quad (7)$$

where CBM and VBM denote the conduction-band minimum and valence-band maximum. Optical properties are organized around the complex dielectric function,

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (8)$$

whose imaginary part is obtained from interband transition matrix elements and whose real part follows by Kramers–Kronig transformation. Refractive index, extinction coefficient, absorption coefficient, reflectivity, optical conductivity, and electron energy loss function are then derived (Dressel & Grüner, 2002; Fox, 2010).

Effective masses are obtained from the curvature of the bands near their extrema,

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E_n(\mathbf{k})}{\partial k_i \partial k_j} \quad (9)$$

where $E_n(\mathbf{k})$ is the energy of band n, i and j denote Cartesian directions, and the derivatives are evaluated at the band extremum. The inverse effective mass is in general a tensor; a single scalar m^* is meaningful only for an isotropic, parabolic band, so for the anisotropic orthorhombic phases direction-resolved or conductivity averaged masses should be reported. Effective masses are inputs to estimates of mobility, exciton binding energy, and device models.

Beyond Semilocal DFT

Semilocal DFT is effective for structures, relative energies, orbital character, and broad composition trends, but it systematically underestimates band gaps; PBE gaps for BaZrS₃ are typically several tenths of an electron Volt below the experimental ≈ 1.75 – 1.8 eV. Hybrid functionals partly correct this by mixing a fraction of exact exchange. The GW approximation computes quasiparticle energies from the electron self-energy, and the Bethe–Salpeter equation (BSE) adds electron–hole interaction to the optical spectrum. Applying hybrid-DFT and GW/BSE to AZrS₃ (A = Ca, Sr, Ba), Kumar et al. (2021) found that the ionic contribution to dielectric screening is negligible and that a charge-separated polaronic state is more stable than the bound exciton, with important implications for carrier separation in devices. These are computed results; they have not yet been tested experimentally for CaZrS₃ and SrZrS₃. The many-body treatment is therefore needed whenever computed absorption onsets are compared quantitatively with experiment.

Spin orbit coupling is small for Zr and S but should be tested when heavier substitutions (Hf, Se) are considered. For finite temperature behavior, the harmonic approximation fails for dynamically unstable reference phases; anharmonic approaches such as machine learning molecular dynamics (Kayastha et al., 2025) or self-consistent phonon methods are required.

Methodological Limitations and Comparability

Comparability is a persistent problem. Results vary with structural phase, exchange–correlation functional, pseudopotential, spin orbit treatment, convergence thresholds, k-point density, optical broadening, scissor corrections, and treatment of excitons. A reported difference between two compounds may therefore reflect chemistry, methodology, or both. Lejaeghere et al. (2016) showed that well-converged modern codes agree closely for elemental equations of state, which suggests that discrepancies in the AZrS₃ literature are more likely to stem from physical approximations and incomplete reporting than from code differences.

A minimum protocol for comparative studies is therefore proposed by the authors on the basis of this appraisal; it is a recommendation for future work and has not been applied to generate results in this review. Calculations should include both the cubic $Pm\bar{3}m$ reference and the experimentally relevant phases ($Pnma$ for $BaZrS_3$; α and β for $SrZrS_3$) so that chemical trends can be separated from distortion effects. A consistent functional hierarchy should be used: PBEsol or SCAN for structures, HSE06 for band gaps, and G_0W_0 /BSE for optical spectra. All compounds should share one pseudopotential family with stated valence configurations, and plane-wave cutoffs, k-meshes, and force, stress, and energy thresholds should be reported. Each phase should be tested against the Born criteria, phonon dispersion, and convex-hull energy before its properties are interpreted. Optical calculations should state the broadening, number of empty bands, and treatment of local field and excitonic effects, and input files and relaxed structures should be deposited in an open repository.

Electronic Structure

Band-edge Chemistry

The electronic behavior of zirconium sulfide perovskites is governed mainly by hybridization between S-3p and Zr-4d states. S-p states dominate the upper valence band, while Zr-d (t_{2g} -derived) states form the lower conduction band. Replacing O with S raises the valence band maximum substantially, which is why $AZrS_3$ compounds have visible range gaps whereas the parent oxides $AZrO_3$ are wide gap insulators (Niu et al., 2017). Changes in Zr–S bond length, Zr–S–Zr angle, crystal field splitting, and octahedral tilting alter orbital overlap and therefore modify band dispersion and gap magnitude: greater tilting narrows the Zr-d bandwidth and generally widens the gap.

The A-site cation influences the frontier states mainly indirectly, through structural control rather than direct orbital contribution near the band edges. Substitution from Ca to Sr to Ba changes the lattice size and tilt tendency, making the series a useful platform for studying how geometry regulates semiconductor behavior within a chemically related family.

Direct and Indirect Transitions

Whether the fundamental gap is direct or indirect affects radiative recombination and near edge absorption. Distorted $BaZrS_3$ is generally reported to have a direct gap at Γ , but transition character depends on phase and approximation. The ideal cubic structure can have band extrema at different k-points from the orthorhombic structure because tilting folds the Brillouin zone and changes symmetry allowed interactions. Statements about direct gap behavior must therefore identify the structural model and, for experiments, the phase composition and measurement method.

The very high band-edge absorption coefficients ($>10^5 \text{ cm}^{-1}$) measured for $BaZrS_3$, distorted perovskite $SrZrS_3$, $BaHfS_3$, and $SrHfS_3$ have been attributed to the large density of states contributed by the flat Zr/Hf-d conduction band together with strong p–d transition matrix elements (Nishigaki et al., 2020). Photoluminescence and photoconductivity confirm that photoexcited carriers participate in radiative and conductive processes in $BaZrS_3$ (Surendran et al., 2021; Zhao et al., 2024). Optical onset, photoluminescence peak, and quasiparticle gap are nonetheless distinct quantities whose differences arise from exciton binding, band tails, defects, disorder, and temperature.

Carrier Transport Implications

Band curvature indicates carrier effective mass: dispersive bands imply light carriers and potentially high mobility, whereas flat bands imply heavy carriers. The relatively flat Zr-d conduction band in $AZrS_3$ tends to give heavier electrons than in conventional III–V semiconductors, while the strong ionicity of the lattice enhances polar optical phonon scattering and polaron formation (Kumar et al., 2021). Real transport also depends on defects, grain boundaries, and interfaces, so electronic structure calculations provide necessary but not sufficient evidence for device quality transport.

Projected density of states and charge density analysis identify the orbitals at the band edges and predict which defects or substitutions will perturb them most. A defect level deep in the gap may act as a nonradiative recombination center, whereas a shallow level near a band edge may dope the material without severe trapping. Systematic defect calculations remain much less developed than ideal crystal band calculations, particularly for $CaZrS_3$ and $SrZrS_3$.

Optical and Spectroscopic Properties

Dielectric Response and Absorption

The complex dielectric function provides the most direct computational link between electronic structure and optical behavior. Peaks in $\epsilon_2(\omega)$ reflect interband transitions weighted by matrix elements, while $\epsilon_1(\omega)$ describes dispersive polarization. The complex refractive index $N = n + ik$ and absorption coefficient follow from

$$N(\omega) = \sqrt{\epsilon(\omega)} \quad (10)$$

$$\alpha(\omega) = \frac{2\omega k(\omega)}{c} \quad (11)$$

and the normal incidence reflectivity from

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (12)$$

Strong absorption is one of the principal advantages of $BaZrS_3$ and related compounds: with $\alpha > 10^5 \text{ cm}^{-1}$ near the gap, a few hundred nanometers of absorber suffice to capture most above gap photons, reducing material use and carrier collection distance (Nishigaki et al., 2020). Refractive index and reflectivity are equally important at

device level because they control optical confinement, surface losses, and interference in multilayer stacks. Experimentally, BaZrS₃ has a direct optical gap of about 1.75–1.8 eV (Wei et al., 2020b; Sharma et al., 2021), which pressure shifts continuously (Gross et al., 2017) and high temperature phase transitions shift discontinuously (Jaiswal et al., 2024).

Excitons, Polarons and Photoluminescence

An absorbed photon creates an electron hole pair that may remain bound as an exciton. Within the hydrogenic (Wannier–Mott) model, the binding energy scales as

$$E_B = \frac{\mu^*}{m_0 \epsilon_{\text{eff}}^2} \times 13.6 \text{ eV} \quad (13)$$

where $\mu^* = m_e^* m_h^* / (m_e^* + m_h^*)$ is the reduced effective mass of the electron hole pair, m_0 is the free-electron mass, ϵ_{eff} is the effective dielectric constant and 13.6 eV is the hydrogen Rydberg energy. ϵ_{eff} lies between the high-frequency (ϵ_∞) and static (ϵ_0) values: ϵ_∞ is appropriate when E_B exceeds the longitudinal optical phonon energy and ϵ_0 when E_B is much smaller, and the hydrogenic model itself applies only to isotropic, parabolic bands. Large high frequency dielectric constants in AZrS₃ favour modest exciton binding, while heavy *d*-band electrons raise μ^* . GW/BSE calculations predict non negligible excitonic effects and polarization dependent response in AZrS₃, together with strong electron phonon coupling that favors charge-separated polarons over bound excitons (Kumar et al., 2021). Independent particle DFT spectra should therefore be viewed as a baseline rather than a complete description of near edge absorption.

Photoluminescence probes radiative recombination and is sensitive to band edge states, alloy disorder, defects, and carrier localization. PL has been observed in epitaxial films (Surendran et al., 2021), solution processed films (Pradhan et al., 2023), and nanoparticles (Yang et al., 2022), and alloying modifies the emission energy (Sharma et al., 2023). Distinguishing intrinsic band-edge emission from defect-assisted luminescence requires combining steady state spectra with temperature dependent and time resolved measurements and, ideally, absolute PL quantum yield determinations.

Raman, Infrared and Ellipsometric Signatures

Raman and infrared spectroscopy fingerprint lattice symmetry, bond vibrations, octahedral distortion, and phase transformations. *Pnma* BaZrS₃ has many Raman active modes, and their pressure and temperature evolution has been used to probe structural stability (Gross et al., 2017; Jaiswal et al., 2024). Raman is also sensitive to Ti alloying: no additional modes appear up to 4 at. % Ti, indicating the absence of phase separation at that level (Wei et al., 2020b). Calculated phonon modes support peak assignment and reveal dynamic instability through imaginary frequencies.

Spectroscopic ellipsometry measures the complex dielectric function and refractive index over a broad spectral range and is therefore a natural bridge between first principles calculations and thin film optical design. Reliable comparison requires explicit treatment of surface roughness, oxide overlayers, substrate response, film thickness, and possible phase mixtures. A shared library of measured and calculated optical constants would substantially improve device modelling for this family.

Mechanical, Thermal and Thermodynamic Stability

As in Section 5, the relations below are standard definitions used in the cited studies and are reproduced to support the discussion; no new elastic, phonon or thermodynamic calculations were performed for this review.

Elastic Behavior

Mechanical stability determines whether a predicted phase can resist small homogeneous deformations. For a cubic crystal the independent elastic constants are C_{11} , C_{12} , and C_{44} , and the Born stability conditions are $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$, $C_{44} > 0$ (14)

The Voigt–Reuss–Hill averages then give the bulk modulus B , the shear modulus G , Young's modulus E , and Poisson's ratio ν ; for a cubic crystal,

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (15a)$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}, \quad G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad (15b)$$

$$G = \frac{G_V + G_R}{2} \quad (15c)$$

$$E = \frac{9BG}{3B + G}, \quad \nu = \frac{3B - 2G}{2(3B + G)} \quad (15d)$$

where G_V and G_R are the Voigt (uniform-strain) and Reuss (uniform-stress) bounds on the shear modulus. For a cubic crystal the Voigt and Reuss bulk moduli coincide, so B in Eq. (15a) needs no averaging. The Pugh ratio B/G (with ≈ 1.75 as the conventional ductile–brittle boundary) and the Zener anisotropy factor

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (16)$$

are also widely reported. These descriptors are relevant to film cracking, delamination, residual stress, and tolerance to thermal cycling. For orthorhombic phases nine independent constants must be computed and the corresponding generalized Born criteria applied.

Mechanical stability does not guarantee thermodynamic or dynamic stability, but failure of a Born criterion shows that the assumed phase is not a local minimum with respect to the corresponding strain. Comparative elastic data computed under a single protocol for the full Ca–Sr–Ba series remain sparse, despite the fact that A site size changes the flexibility and packing of the ZrS₆ framework. Elastic calculations validated by pressure dependent diffraction or acoustic measurements would

clarify whether optical benefits are accompanied by adequate mechanical robustness.

Formation Energy and Phase Stability

A simple formation energy relative to the elements is $\Delta E_f = E_{\text{tot}}(\text{AZrS}_3) - E_{\text{tot}}(\text{A}) - E_{\text{tot}}(\text{Zr}) - 3E_{\text{tot}}(\text{S})$ (17) where $E_{\text{tot}}(\text{AZrS}_3)$ is the total energy per formula unit and $E_{\text{tot}}(\text{A})$, $E_{\text{tot}}(\text{Zr})$ and $E_{\text{tot}}(\text{S})$ are the total energies per atom of the elemental reference phases. Equation (17) gives ΔE_f per formula unit; dividing by the five atoms of the formula unit gives the value per atom. A negative value is necessary but not sufficient for stability. The compound must also be stable against decomposition into competing binary and ternary phases (e.g., $\text{AS} + \text{ZrS}_2$, or Ruddlesden–Popper $\text{A}_{n+1}\text{Zr}_n\text{S}_{3n+1} + \text{ZrS}_2$), which is assessed through the energy above the convex hull, chemical-potential stability regions, and finite-temperature free energies. In a high-throughput DFT analysis, Carr et al. (2025) found BaZrS_3 and BaHfS_3 to be the only compositions in their set calculated to be both perovskite in the ground state and stable against decomposition into competing phases ($\Delta E_d \leq 0$). Because competing phases missing from the underlying database could destabilize a compound further, these decomposition energies are lower bounds, and the result for BaZrS_3 should not be extended to CaZrS_3 or SrZrS_3 . Jess et al. (2022) emphasize the need to distinguish nominal ABX_3 composition from the thermodynamically preferred structure type, which for some compositions is needle-like or hexagonal rather than perovskite.

Dynamic and Finite Temperature Stability

Phonon calculations test stability against small atomic displacements. Imaginary frequencies indicate a tendency toward distortion and often reveal the pathway from a cubic reference to a lower-symmetry structure: for BaZrS_3 , the unstable modes of the cubic phase are octahedral rotation modes at the Brillouin-zone boundary that condense into the observed tilt pattern (Kayastha et al., 2025). Quasi-harmonic calculations estimate free energy, heat capacity, entropy, and thermal expansion, but they cannot describe phases that are only stabilized by anharmonic fluctuations; molecular dynamics approaches are needed there.

Thermal expansion matters practically because mismatch with substrates and contact layers causes cracking during high-temperature sulfurization (Pradhan et al., 2023). Chemical stability is also finite: BaZrS_3 oxidizes to BaSO_4 and ZrO_2 when heated in air at around 700 °C (Jaiswal et al., 2024), so processing atmospheres must be controlled. Future work should combine temperature resolved diffraction, Raman spectroscopy, and anharmonic lattice dynamics calculations to construct a consistent pressure temperature composition phase diagram for the whole series.

Defects and Carrier Dynamics

Real materials contain vacancies, antisites, interstitials, impurities (notably oxygen), surfaces, and grain boundaries, which together determine carrier concentration, trapping, nonradiative recombination, ionic motion, and long-term stability. Sulfur vacancies are a natural concern under sulfur poor processing, and oxygen substitution is difficult to avoid when oxide precursors are sulfurized. The formation energy of a defect D in charge state q is

$$E_f[D^q] = E_{\text{tot}}[D^q] - E_{\text{tot}}[\text{host}] - \sum_i n_i \mu_i + q(E_F + E_{\text{VBM}}) + E_{\text{corr}} \quad (18)$$

where n_i atoms with chemical potential μ_i are added or removed, E_F is the Fermi level measured from the valence band maximum E_{VBM} , and E_{corr} is a finite-size correction. Transition levels between charge states locate the defect in the gap and determine whether it is shallow or deep. Electronic impact depends on charge state and local relaxation and cannot be inferred from stoichiometry alone; hybrid-functional supercell calculations under well-defined chemical potential conditions are required. Thin-film measurements integrate intrinsic band behavior with microstructure. Grain boundaries may act as recombination sites or conductive pathways, secondary phases add parasitic absorption, and disorder produces Urbach tails that obscure the intrinsic gap. Time resolved photoluminescence, transient absorption, impedance spectroscopy, deep level transient spectroscopy, and Kelvin-probe methods, combined with first principles defect calculations, are needed to identify dominant loss mechanisms.

Single crystal studies illustrate how processing defects control device behavior. Zhao et al. (2024) achieved ohmic contacts to BaZrS_3 crystals and observed positive surface photovoltage consistent with p-type conduction, but mechanical polishing used to remove surface oxide introduced dense deformation grain boundaries that produced a trap dominated photoconductive response. Linking such observables to specific defect species is a major opportunity for coordinated theory and experiment.

Energy and Optoelectronic Applications

Photovoltaics

With a measured optical gap of ≈ 1.75 – 1.8 eV, BaZrS_3 is somewhat wider than the single junction optimum (≈ 1.34 eV) but well matched to the top cell of a tandem with silicon. Its strong absorption, tunability by Ti or Se alloying, and environmental stability make BaZrS_3 an attractive absorber; comparable device relevant data for CaZrS_3 and SrZrS_3 are not yet available. BaZrS_3 has received the most attention because thin-film fabrication and optical characterization are comparatively mature. Ti alloying to 4 at. % reduces the measured gap to ≈ 1.51 eV, for which the detailed-balance efficiency limit is $\approx 32\%$ (Wei et al., 2020b); this limit is a theoretical thermodynamic bound, not an achieved efficiency.

Device simulations indicate what might be attainable. Using SCAPS-1D, Vincent Mercy et al. (2024) reported a simulated efficiency of 28.08% for an FTO/ZrS₂/BaZrS₃/SnS/Au stack and 32.58% for a Ba(Zr_{0.96}Ti_{0.04})S₃ absorber with a Pt back contact, attributing the gains to reduced interfacial barriers and extended near-infrared absorption. These are simulated power conversion efficiencies from one dimensional drift diffusion modelling, not experimentally achieved device efficiencies. Such values are conditional on assumed defect densities, mobilities, band offsets, and interface recombination velocities and should be interpreted as targets rather than predictions; no experimental BaZrS₃ solar cell approaching these values has yet been reported. The principal photovoltaic challenges are phase pure synthesis at temperatures compatible with transparent contacts, control of sulfur and oxygen stoichiometry, band alignment with transport layers, suppression of interface recombination, and demonstration of high quality, stable junctions.

Photodetectors and Photoconductors

Strong visible absorption and demonstrated photoconductivity support photodetection. Epitaxial BaZrS₃ films gave fast photodetectors with high on/off ratios (Surendran et al., 2021), low temperature processed films have been integrated into devices (Yu et al., 2021), and optimized contacts on single crystals are improving dark current and response speed (Zhao et al., 2024). Desirable characteristics include high responsivity, low dark current, fast response, spectral selectivity, and operational stability; band-gap engineering through alloying may enable wavelength specific detectors.

Light Emission, Photonics, Thermoelectrics and Spectroscopy Platforms

Bright photoluminescence in polycrystalline transition-metal perovskite chalcogenides (Niu et al., 2017) and in BaZrS₃ films and nanoparticles suggests potential for light emission, particularly after compositional tuning. The high refractive index and dielectric response make these materials relevant to optical coatings, resonant structures, and multilayer photonic stacks. BaZrS₃ has also been explored for thermoelectrics owing to its low lattice thermal conductivity (Kayastha et al., 2025). Finally, Raman, infrared, and ellipsometric signatures serve as sensitive probes of phase, strain, bonding, and defects; this spectroscopy centered uses are valuable even before mature photovoltaic devices exist.

Comparative Assessment of CaZrS3, SrZrS3 and BaZrS3

Table 2 collects the principal quantitative benchmarks discussed in this review, with their evidence type and conditions, and Table 3 summarizes the qualitative evidence and major uncertainties across the series, deliberately separating established evidence from expectations based on structural chemistry. BaZrS₃ has the strongest experimental foundation, whereas CaZrS₃ and SrZrS₃ require more extensive phase-controlled synthesis and property measurement. Theoretical comparison under a common many body protocol is available (Kumar et al., 2021), but experimental validation for the Ca and Sr members remains limited.

Table 2: Principal Quantitative Benchmarks for AzrS₃ with Their Provenance. Type: E, Experimental; C, Computed (First Principles or Molecular Dynamics); S, Device Simulation. Uncertainties Are Given Where the Source Reports Them; “≈” Marks Values Quoted Without a Stated Uncertainty

Quantity	Compound / phase	Value	Type	Conditions as reported	Source
Lattice parameters	BaZrS ₃ , <i>Pnma</i>	$a = 7.056(3)$, $b = 9.962(4)$, $c = 6.996(3)$ Å	E	Flux-grown single crystal; single-crystal X-ray diffraction	Niu et al. (2019)
Optical band gap	BaZrS ₃ , <i>Pnma</i>	≈1.75–1.8 eV (direct)	E	Room-temperature optical measurements	Wei et al. (2020b); Sharma et al. (2021)
Band-edge absorption coefficient	BaZrS ₃ ; distorted-perovskite SrZrS ₃	>10 ⁵ cm ⁻¹	E	Near the band edge	Nishigaki et al. (2020)
Gap tuning by Ti	Ba(Zr _{1-x} Ti _x)S ₃	1.78 → 1.51 eV at x = 0.04	E	No additional Raman modes to x = 0.04; higher x destabilizes the perovskite	Wei et al. (2020b)
Pressure response	BaZrS ₃ , <i>Pnma</i>	No first-order transition to 8.9 GPa;	E	Hydrostatic compression; Raman and optical; room temperature	Gross et al. (2017)

Quantity	Compound / phase	Value	Type	Conditions as reported	Source
High-temperature phases (measured)	BaZrS ₃	continuous gap shift $Pnma \rightarrow Cmc$ ≈ 400 °C; $I4/mcm$ above ≈ 500 °C	E	Synchrotron diffraction, heating in air; reversible from ≤ 600 °C	Jaiswal et al. (2024)
	BaZrS ₃	$Pnma \rightarrow I4/mcm$ ≈ 610 K; $\rightarrow Pm\bar{3}m$ ≈ 880 K	C	Machine-learning molecular dynamics; zero pressure	Kayastha et al. (2025)
	BaZrS ₃	$\rightarrow BaSO_4 + ZrO_2$ at ≈ 700 °C	E	Heating in air	Jaiswal et al. (2024)
Hull stability	BaZrS ₃	$\Delta E_d \leq 0$ (on the hull)	C	High-throughput DFT; lower bound on instability	Carr et al. (2025)
Excitons and polarons	AZrS ₃ (A = Ca, Sr, Ba)	Charge-separated polaron more stable than bound exciton	C	Hybrid DFT and GW/BSE	Kumar et al. (2021)
Solar-cell efficiency	FTO/ZrS ₂ /BaZrS ₃ /SnS/Au	28.08%	S	SCAPS-1D; assumed defect densities, mobilities and band offsets	Vincent Mercy et al. (2024)
Solar-cell efficiency	Ba(Zr _{0.96} Ti _{0.04})S ₃ , Pt back contact	32.58%	S	SCAPS-1D; as above	Vincent Mercy et al. (2024)

Table 3: Qualitative Comparison of Zirconium Sulfide Perovskites. Statements for Less-studied Compositions should be Treated As Research Hypotheses Rather than Settled Rankings. Evidence Labels: [E] Experimentally Established; [C] Computed (first-Principles or Molecular Dynamics); [I] Inferred from Structural Chemistry or by Analogy with BaZrS₃, without Direct Measurement or Calculation for that Compound. Entries Labelled [I] are not Rankings

Criterion	CaZrS ₃	SrZrS ₃	BaZrS ₃
A-site size / t	Smallest (t $\approx$ 0.88); strongest drive toward distortion [I]	Intermediate (t $\approx$ 0.91) [I]	Largest (t $\approx$ 0.95); closest to cubic geometry [I]
Known polymorphs	Distorted perovskite; limited structural data [E, limited]	Needle-like α and distorted-perovskite β [E]	$Pnma$ at RT [E]; Cmc and $I4/mcm$ at high T [E]; $Pm\bar{3}m$ above ≈ 880 K [C, not yet observed]
Experimental maturity	Limited [E]	Limited; strong absorption reported for β phase [E]	Highest: crystals, films, alloys, devices, PL, photoconductivity [E]
Cubic-phase interpretation	Reference only; requires rigorous stability testing [I]	Intermediate-composition benchmark [I]	Linked to high-T phase evolution and strain [C + E]
Electronic/optical evidence	Mainly theoretical [C]	Theoretical plus polymorph-specific experiments [C + E]	Gap ≈ 1.75 – 1.8 eV; $\alpha > 10^5$ cm ⁻¹ ; tunable by alloying [E]
Primary opportunity	Establish phase stability and intrinsic band edges [I]	Exploit polymorph control for gap tuning [I]	Improve film quality, defect control, interfaces [I]
Key uncertainty	Synthesizability and phase preference [I]	Polymorph selection; sparse standardised data [I]	Translating strong optics into efficient, stable devices [I]

The most defensible current conclusion is not that one composition is universally superior, but that each must be assessed using the same linked criteria. Structural plausibility should be established first, followed by

electronic suitability, optical effectiveness, defect tolerance, mechanical robustness, and thermodynamic stability. A composition with an ideal calculated gap but an unstable cubic phase should not outrank a slightly less optimal absorber that can be synthesized reproducibly and integrated into a device.

Critical Research Gaps

Composition Imbalance

The literature is dominated by BaZrS₃. This concentration has accelerated progress for one compound but limits confident generalization across the family. Comparable synthesis, structural characterization, and spectroscopy are needed for CaZrS₃ and both SrZrS₃ polymorphs.

Phase Ambiguity

Reported properties are not always linked unambiguously to a single crystallographic phase. Cubic, tetragonal, orthorhombic, needle like, Ruddlesden–Popper, and oxide secondary phases have different gaps and optical signatures, and high temperature processing may leave residual polymorphs. Diffraction, Raman spectroscopy, composition mapping (including oxygen), and, where appropriate, total scattering methods should precede any assignment of intrinsic properties.

Methodological Heterogeneity

First-principles studies use different functional, pseudopotentials, structures, convergence settings, and optical approximations; experiments vary in substrate, thickness, microstructure, and analysis method (for example, Tauc plot exponents and baseline treatment). Benchmark datasets computed and measured under standardized conditions are needed to separate genuine chemical trends from methodological variation.

Limited defect Resolved Understanding

Ideal crystal calculations dominate the theoretical literature, whereas defects likely control carrier lifetime, conductivity, and recombination in real films. Formation energies, transition levels, migration barriers, and defect complexes, including O related defects, should be computed across relevant chemical potential conditions and compared with defect sensitive experiments.

Incomplete Integration of Stability and Performance

Optical promise is often discussed separately from mechanical, dynamic, and thermodynamic stability. Integrated screening should reject or qualify candidates that fail convex hull, elastic, or phonon criteria. The same principle applies to alloying: a red shifted absorption edge is beneficial only if phase purity, carrier lifetime, and operational stability remain acceptable.

Future Research Directions

Seven research priorities follow from the gaps identified above. They are proposals by the authors rather than established conclusions, and they are grouped below into computational, experimental and device-oriented directions.

The computational priorities are as follows. (i) *Standardized comparative calculations*: CaZrS₃, SrZrS₃ and BaZrS₃ should be calculated with a single pseudopotential family, functional hierarchy, set of convergence thresholds, k-point density and optical broadening, in both the cubic reference and the experimentally relevant phases (Section 5.4). (ii) *Beyond semilocal electronic structure*: within this common framework, hybrid functionals or GW should be used for quasiparticle gaps and the BSE for excitonic spectra, with semilocal DFT retained for structural screening and trend analysis; electron–phonon coupling should be included to assess polaron formation. (iii) *Anharmonic phase mapping*: machine learning molecular dynamics and free energy calculations, combined with epitaxial strain studies and temperature resolved experiments, are needed to determine when tetragonal or near cubic structures can be stabilized and whether they retain favorable optoelectronic properties.

Two experimental priorities complement these calculations. (iv) *Defect aware synthesis*: sulfur chemical potential, oxygen content, annealing atmosphere, grain structure and impurities should be related to calculated defect energetics and measured carrier dynamics, so that processing conditions can be chosen on physical grounds. (v) *Experiment-facing optical databases*: for phase pure samples, thickness dependent absorption, ellipsometric dielectric functions, photoluminescence quantum yields, carrier lifetimes and their uncertainties should be reported in a form that can be compared directly with calculations. Finally, two device-oriented priorities are needed. (vi) *Interface engineering*: band offsets, interfacial reactions and recombination velocities should be measured for candidate electron and hole transport layers rather than optimizing the absorber in isolation. (vii) *Operational stability protocols*: films and devices should be tested under controlled heat, illumination, electrical bias, humidity and atmosphere while their structural and chemical evolution is monitored, so that stability claims rest on the same footing as efficiency claims.

A proposed decision framework is presented in Table 4. It has not been validated against comparative performance data, but it can organize future computational and experimental studies and help prevent premature ranking based on a single favorable property.

Table 4: Proposed Integrated Framework for Evaluating AzrS₃ Compounds. The Framework Is A Recommendation Derived From This Review; It Is Not Based On, And Should Not Be Read As, Validated Comparative Performance Data

Assessment level	Core descriptors	Validation route
Structure and phase	Lattice parameters, t and μ , relative energies of polymorphs, phonons, hull energy	XRD, Raman/IR, pressure- and temperature-dependent measurements
Electronic response	Band gap, direct/indirect character, DOS, effective masses, defect levels	Absorption onset, photoemission, transport, photoconductivity
Optical response	ϵ_1 , ϵ_2 , n , k , α , reflectivity, exciton/polaron binding	UV-Vis, ellipsometry, PL, time-resolved spectroscopy
Mechanical and thermal	Elastic constants, moduli, B/G , thermal expansion, free energy	Stress/strain measurements, thermal cycling, temperature-resolved diffraction
Device relevance	Band alignment, lifetime, mobility, interface recombination, stability	Complete devices tested under standardized operating conditions

CONCLUSION

This review has appraised experimental and computational evidence on the zirconium sulfide perovskites CaZrS₃, SrZrS₃ and BaZrS₃, labelling each benchmark by evidence type and conditions. Three conclusions are established by the current evidence. First, BaZrS₃ is a reproducible orthorhombic (*Pnma*) semiconductor at room temperature with a measured optical gap of about 1.75–1.8 eV, band-edge absorption above 10^5 cm^{-1} , photoluminescence and photoconductivity, and it has been grown as single crystals and as sputtered, epitaxial and solution-processed films. Second, its gap can be lowered experimentally to about 1.51 eV by 4 at. % Ti alloying, and it shows no first-order transition to at least 8.9 GPa at room temperature. Third, on heating it transforms to *Cmcm* and then *I4/mcm* phases, whereas the cubic phase used in many calculations is, at present, a simulation-based high-temperature prediction.

Other statements remain predictions or hypotheses. The photovoltaic efficiencies of 28–33% reported for BaZrS₃-based stacks are SCAPS 1D simulations that depend on assumed defect and interface parameters, and no experimental device approaching them has been reported. For CaZrS₃ and SrZrS₃, phase behavior, optical constants, defects and device performance remain largely uncharacterized; SrZrS₃ must always be specified by polymorph, and findings for BaZrS₃ cannot be transferred to either compound without direct evidence. Composition rankings across the series are therefore not yet justified. The research priorities that follow from this appraisal standardized calculations under the minimum protocol of Section 5.4, anharmonic phase mapping, defect aware synthesis, experiment-facing optical data, interface engineering and operational stability testing are proposals rather than conclusions. The contribution of this review is evidence graded, phase specific comparison of the AzrS₃ series, together with a protocol and a framework for future comparison. Its main limitation is the evidence base itself: most data concern BaZrS₃, and the literature

search, although documented, was narrative rather than systematic.

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