Bandgap Engineering of $SrZrS_3$ via Substitutional Doping for Photovoltaic Applications

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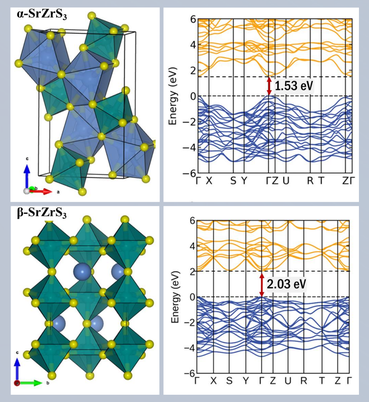
INTRODUCTION

$SrZrS_3$ has been identified as a promising material for high-efficiency, low-cost, and stable photovoltaic (PV) cells owing to its outstanding optoelectronic properties, low synthesis costs, non-toxicity, and high chemical and moisture stability. It exists in two phases: α- and β-phases, both of which exhibit attractive optical and electronic properties, including direct bandgaps, high optical absorptivity, low refractive indices, and low reflectivity. However, their bandgaps are outside the range for PV cells. In this study, we introduced different dopant to the Zr sites of both phases to reduce their bandgaps.



Crystal structure and band structures of α- and β-$SrZrS_3$

Bandgap ranges for PV cells:

Single-junction PVs: 1.1—1.4 eV [1]

Tandem PVs: 1.7—1.9 eV [2]

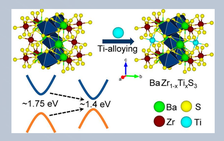
Electronic and optical properties of $SrZrS_3$ in comparison with those of Si

Properties	α-$SrZrS_3$	β-$SrZrS_3$	Si [4]
Dielect. const.	9.36	5.75	11.7
Abs. coef. (cm^{-1})	>10^5	>10^5	10^4
Reflectivity (%)	26	34	42.8
Ref. index	2.8–3.5	3.5–4.0	3.4
Bandgap (eV)	**1.53**	**2.03**	**1.12**

OBJECTIVES

This study aims to engineer the bandgap of $SrZrS_3$ through substitutional doping. The specific objectives are as follows:

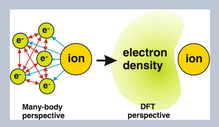
- To identify dopants that effectively reduce the bandgaps α- and β-$SrZrS_3$
- To investigate the effect of dopants and doping concentration on the electronic and optical properties of the material
- To determine the thermodynamic stability of the pristine and doped systems



Bandgap tuning of $BaZrS_3$ via Ti-doping [2]

METHODOLOGY

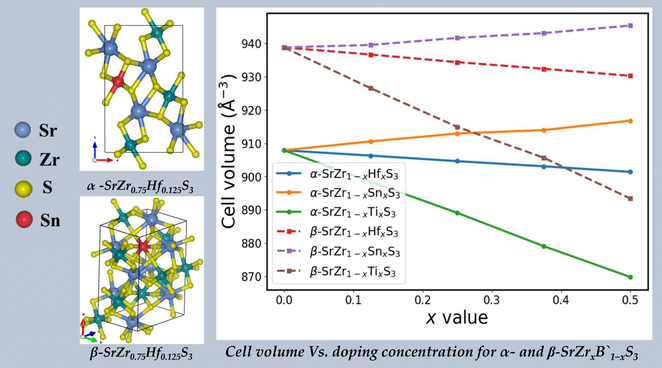
- All simulations are based on density functional theory (DFT) calculations and were performed using the VASP Package.
- DFT-D3 scheme was employed to account for dispersion forces.
- PBE & HSE06 functionals used for structural optimization and electronic properties calculations, respectively.
- All DOS and band structures were plotted using SUMO
- We considered three dopants (Hf, Sn, and Ti) at the Zr site of $SrZrS_3$



RESULTS

Structural Properties of Doped $SrZrS_3$

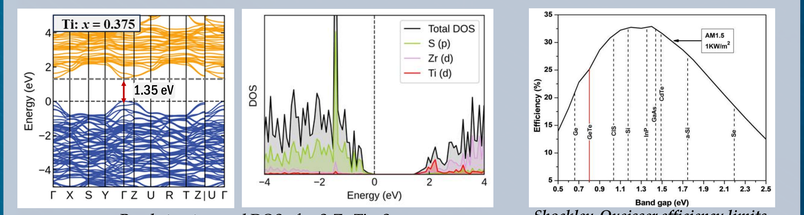
- The lattice parameters and volumes of the Hf- and Ti-doped systems decreased with increasing doping concentration, whereas those of the Sn-doped system increased
- The change in volume is proportional to the difference in the ionic radii of Zr and dopant ($r_{Zr} > r_{Hf} > r_{Sn} > r_{Ti}$)



Cell volume Vs. doping concentration for α- and β-$SrZr_xB`_{1-x}S_3$

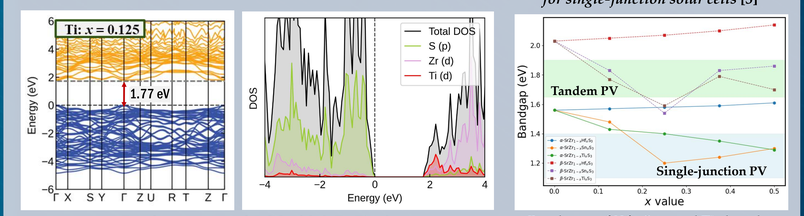
Electronic Properties

- Ti- and Sn-doping lowered the bandgaps of both α- and β-$SrZrS_3$, whereas Hf-doping increased the bandgaps
- The bandgaps of Ti- and Sn-doped α-$SrZrS_3$ are suitable for single-junction PV cells, and those of Ti- and Sn-doped β-$SrZrS_3$ are suitable for tandem PV cells
- Except for Ti-doped β-$SrZrS_3$, all systems exhibited direct bandgaps.



Band structure and DOS of α-$SrZr_xTi_{1-x}S_3$

Shockley-Queisser efficiency limits for single-junction solar cells [3]

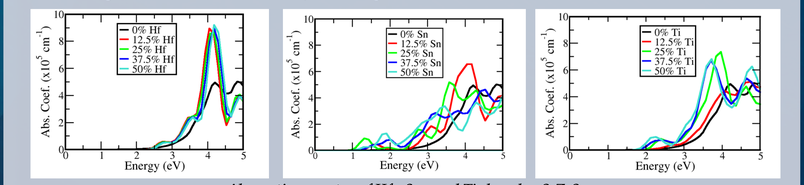


Band structure and DOS of β-$SrZr_xTi_{1-x}S_3$

Bandgaps of Hf-, Sn-, and Ti-doped α- and β-$SrZrS_3$

Optical Properties

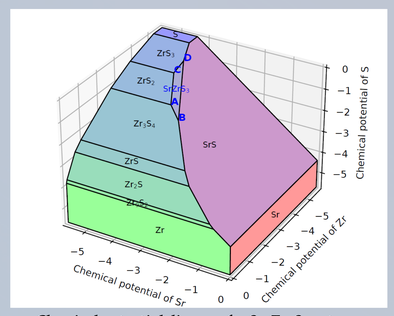
- All dopants increased the absorption coefficient of α-$SrZrS_3$ but lowered that of β-$SrZrS_3$
- All dopants also increased the dielectric constant, reflectivity, and refractive index of α-$SrZrS_3$ and lowered those of β-$SrZrS_3$



Absorption spectra of Hf-, Sn-, and Ti-doped α-$SrZrS_3$

Thermodynamic Stability

- $SrZrS_3$ is stable in the narrow chemical potential region ABCD
- The main competing phases include Zr_3S_4, SrS, ZrS_2, and and ZrS_3



Chemical potential diagram for Sr–Zr–S system

Stability conditions

$$\mu_{Sr} + \mu_{Zr} + 3\mu_S = \Delta H_{f(SrZrS3)}$$

$$a\mu_A + b\mu_B < \Delta H_{f(AaBb)}$$

(for any binary phase A_aB_b)

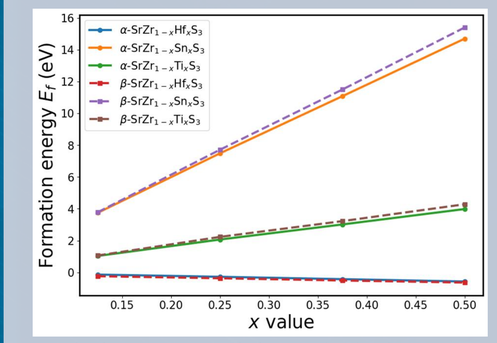
$$\mu_{Sr} < 0$$

$$\mu_{Zr} < 0$$

$$\mu_S < 0$$

Defect Formation Energy

- Hf-doping can be achieved via an exothermic process, whereas Ti- and Sn-doping can only be synthesized via endothermic procedures



Defect formation energies of Hf-, Sn-, and Ti-doped $SrZrS_3$ into binary phases and ternary phases

$$E_f = E_{tot}[X^q] - E_{tot}[pure] - \sum_i n_i\mu_i + q[E_F + E_v + \Delta V]$$

CONCLUSION

- Hf- and Ti-doping shrink both α- and β-SrZrS3, whereas Sn-doping expands them
- Hf-doping increases the bandgaps of both α- and β-SrZrS3, whereas Sn- and Ti-doping lower them
- The three dopants improve the absorption coefficient of α-$SrZrS_3$ but also increased its reflectivity, and refractivity
- Hf-doping is more thermodynamically feasible than Ti- and Sn-doping

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