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Supplementary Information: Alloying ZnS in the Wurtzite Phase to Create High-Performing Transparent Conducting Materials

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Alloyed zinc sulfide (ZnS) has shown promise as a relatively inexpensive and earth-abundant transparent conducting material (TCM). Though Cu-doped ZnS has been identified as a high-performing p-type TCM, the corresponding n-doped ZnS has, to date, been challenging to synthesize in a controlled manner, as the dopant atoms compete with hole-inducing zinc vacancies near the conduction band minimum as the most thermodynamically stable lattice defects. We thus aim to identify the most promising n-type ZnS-based TCM, with the optimal combination of physical stability, transparency, and electrical conductivity. In this study, we employ hybrid density functional theory calculations and a new carrier transport model, aMoBT (*ab initio* model for mobility and Seebeck coefficient using the Boltzmann transport equation), to analyze the defect physics of different cation- and anion-doped ZnS, in both the cubic and hexagonal phases. We obtain the formation energies of ZnS doped with B, Al, Ga, In, F, Cl, Br and I, and calculate the electron mobility of these compounds at various dopant compositions, temperatures, and carrier concentrations. Our results show that, among all doped ZnS candidates, Al-doped ZnS (AZS) exhibits the highest dopant solubility, smallest reduction in the electronic band gap, and highest electrical conductivity of $3830 \text{ S} \cdot \text{cm}^{-1}$ at the optimal 6.25% concentration of Al and carrier concentration of $n = 1.0 \times 10^{21} \text{ cm}^{-3}$ at 300 K. Furthermore, our *ab initio* thermodynamics calculations show that all alloyed ZnS compounds, including AZS, are more favorable in the hexagonal (wurtzite) phase rather than the cubic (sphalerite) phase. This is particularly significant since the majority of the previous attempts to synthesize AZS focused on the cubic phase, with much lower measured conductivities and stabilities. Therefore, we propose that Al-doped ZnS, crystallized in the wurtzite phase, is a particularly promising n-type TCM candidate for photovoltaic and optoelectronic applications.

1 Comparing Al:ZnS with Al:ZnO

In addition to ZnS, we also calculated the formation energy of intrinsic defects and substitutional Al (Al_{Zn}) for ZnO in FIG. 1. It can be seen that incorporation of Al in ZnO lattice is much more energetically favorable than zinc vacancy formation, compared to ZnS. Another reason is the phase change (i.e., cubic to hexagonal) in ZnS upon doping, as discussed in the main text, while efforts in AZS synthesis have largely focused on producing the cubic phase^{1–6}. Note AZO does not have this complexity in its morphology. Therefore, Al is incorporated into ZnO with much shorter and stronger, ionic bonds, compared to ZnS. This has been illustrated in Figure 2.

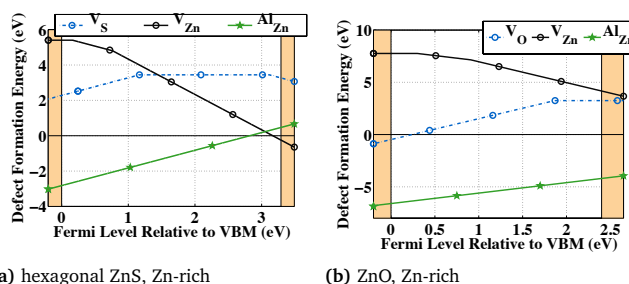


Fig. 1 Formation energy of defects for ZnS versus ZnO

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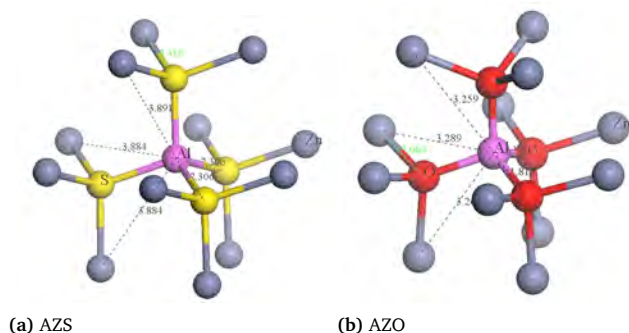


Fig. 2 Illustration of physical differences in bonding between ZnS versus ZnO

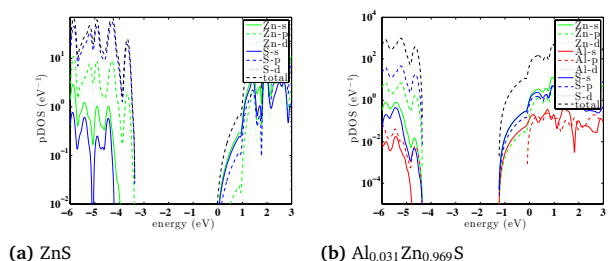


Fig. 3 Partial density of states (pDOS) of undoped and aluminum-doped ZnS. Note that the ordinate axis is logarithmic for clearer presentation of the pDOS of the orbitals on each atom.

2 Effect of Al on the density of states of ZnS

The effect of dopants on effective mass can be attributed to the hybridization of the dopant *s*-orbital with the Zn-*s* and S-*s* or-

bitals. This can be seen in Figure 3, where the partial density of states of undoped ZnS and $\text{Al}_x\text{Zn}_{1-x}\text{S}$ are shown. The partial density of states, and, therefore, the effective mass, are affected in the conduction band edge via Al-*s* orbitals, which leads to an increase in the effective mass. Note that transition metal oxides, such as ZnO, have lower electron effective masses (around 0.2) compared to non-transition metal oxides, such as Al_2O_3 , whose effective mass is around 0.4⁷. Similar increases in the effective mass are observed for halogens substituting for sulfur in these materials.

References

- 1 C. J. Traverse, M. Young, S. Wagner, P. Zhang, P. Askeland, M. C. Barr and R. R. Lunt, *Journal of Applied Physics*, 2014, **115**,.
- 2 B. Long, S. Cheng, H. Zhou, J. Liao, H. Zhang, H. Jia and H. Li, *ECS Solid State Letters*, 2014, **3**, P140–P143.
- 3 A. Jrad, T. Nasr and N. Turki-Kamoun, *Journal of Materials Science: Materials in Electronics*, 2015, **26**, 8854–8862.
- 4 J. Liao, S. Cheng, H. Zhou and B. Long, *Micro & Nano Letters*, 2013, **8**, 211–214(3).
- 5 P. Prathap, N. Revathi, Y. Subbaiah, K. R. Reddy and R. Miles, *Solid State Sciences*, 2009, **11**, 224 – 232.
- 6 K. Nagamani, N. Revathi, P. Prathap, Y. Lingappa and K. R. Reddy, *Current Applied Physics*, 2012, **12**, 380 – 384.
- 7 T. Perevalov, A. Shaposhnikov, V. Gritsenko, H. Wong, J. Han and C. Kim, *JETP Letters*, 2007, **85**, 165–168.