

SUPPLEMENTAL MATERIAL

Comparison of Carrier doping in ZnSnO₃ and ZnTiO₃ from first principles

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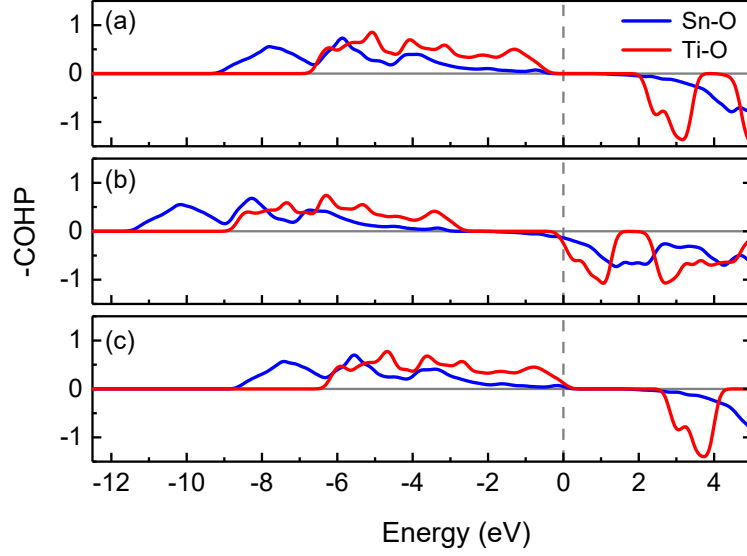


Fig. S1 COHP curves of ferroelectric R3c ZnSnO₃ (blue), R3c ZnTiO₃ (red). (a) is the COHP result of undoped ZnSnO₃ and ZnTiO₃. (b) and (c) are the COHP results of ZnSnO₃ and ZnTiO₃ with doping concentrations of 0.2 e/f.u. and 0.2 h/f.u. respectively.

The crystal orbital hamilton population^{1,2} (COHP) method is used for chemical bond analysis implemented in the LOBSTER code³. For all interactions considered in our COHP analysis, only first nearest neighbor atomic pairs are considered. In ZnSnO₃ materials, for SnO₆ octahedron, the Sn-O pair with the shortest bond length is selected as the representative case of COHP Sn-O interaction. In ZnTiO₃ materials, for TiO₆ octahedron, the Ti-O pair with the shortest bond length is selected as the representative case of COHP Ti-O interaction.

TABLE SI. ICOHP values for different doping concentrations of ZnSnO₃ and ZnTiO₃.

Material	concentrations	ICOHP (eV)
ZnSnO ₃	undoped	-4.870
	0.2 e/f.u.	-4.517
	0.2 h/f.u.	-4.968
ZnTiO ₃	undoped	-4.596
	0.2 e/f.u.	-4.014
	0.2 h/f.u.	-4.610

We calculate the integrated COHP (ICOHP) which indicates the bond strength (the more negative the value, the stronger the bond strength). Table SI lists the ICOHP values for different doping concentrations of ZnSnO₃ and ZnTiO₃. For Sn-O and Ti-O bonds, electron doping reduces the strength of the bond, and hole doping slightly enhances the bond strength.

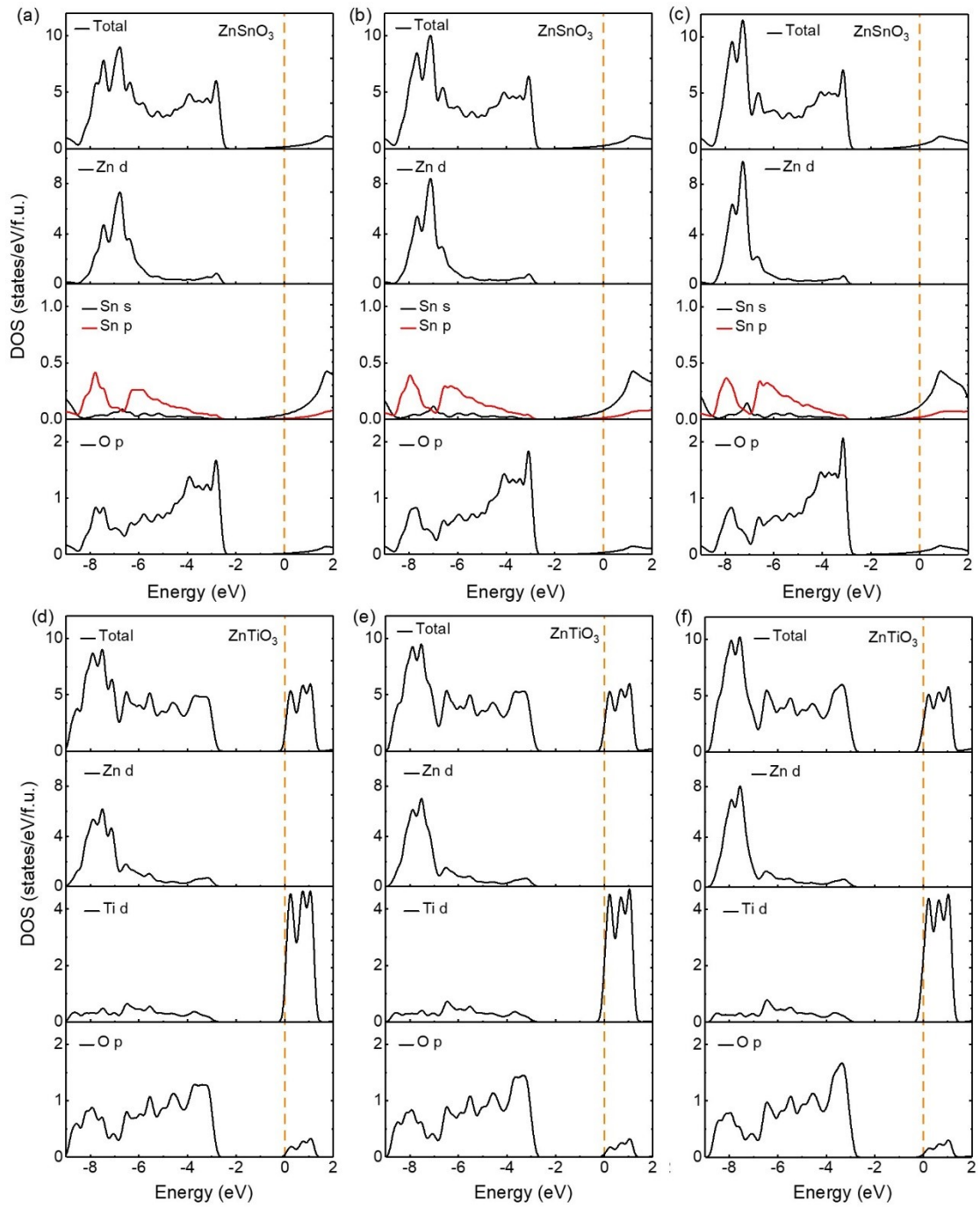


Fig. S2 Total and partial density of states of ZnSnO_3 and ZnTiO_3 . The doping concentration of (a) and (d) is 0.1e/f.u., (b) and (e) is 0.2 e/f.u., (c) and (f) is 0.3 e/f.u. The orange dashed line represents the Fermi level.

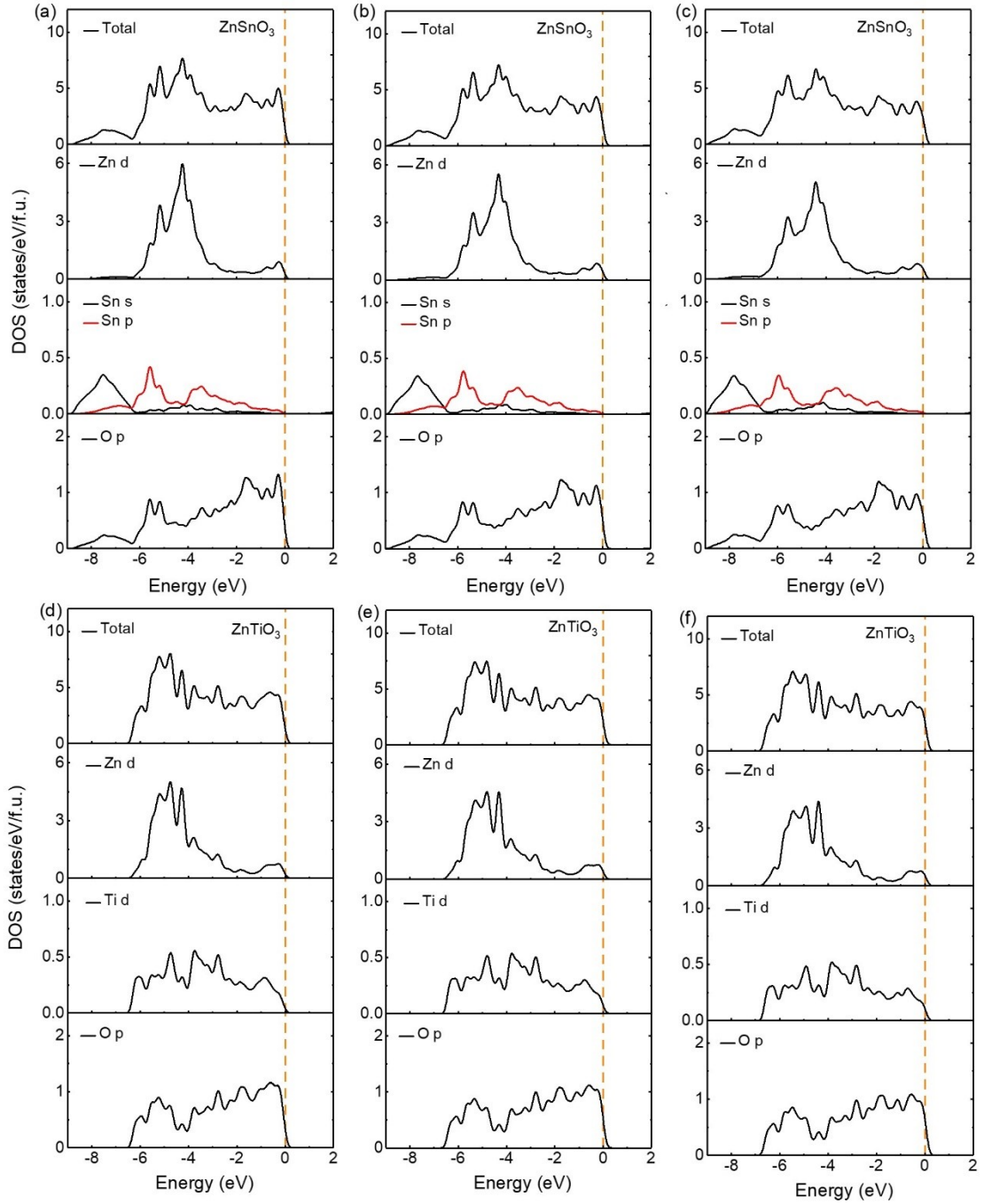


Fig. S3 Total and partial density of states of ZnSnO_3 and ZnTiO_3 . The doping concentration of (a) and (d) is 0.1 h/f.u., (b) and (e) is 0.2 h/f.u., (c) and (f) is 0.3 h/f.u. The orange dashed line represents the Fermi level.

We compare the electronic structure of carrier doping of ZnSnO_3 and ZnTiO_3 . Fig. S2 shows the density of states of ZnSnO_3 and ZnTiO_3 when the doping concentrations are 0.1 e/f.u., 0.2 e/f.u. and 0.3 e/f.u. respectively. For the two materials ZnSnO_3 and ZnTiO_3 , we can see one peak near the bottom of the valance band (VB) as shown by the black curves of the total density of states (DOS). Partial density of states (PDOS) reveal that the peak near the bottom of the VB is contributed by the Zn-d orbital. Near the top of VB is contributed by O-p orbital. Zn-d and O-p orbital hybridization reflects that the bonding between Zn and O in ZnSnO_3 and ZnTiO_3 is mainly ionic and less covalent. This is consistent with the undoped characteristics. For ZnSnO_3 material, near the bottom of the conduction band (CB) is

contributed by Sn-*s* orbital. For ZnTiO₃ material, near the bottom of the CB is mainly contributed by Ti-*d* orbital. As the electron doping concentration increases, the peak contributed by Zn-*d* orbital near the bottom of VB increases, and the energy level range of Zn-*d* orbital decreases. As the electron doping concentration increases, the O-*p* orbital has a clear shift to the top of VB. This reflects the weakening of the covalent bond between Sn and O. Similarly, the covalent bond between Ti and O also weakens. By electron doping, the Fermi level moves into the bottom of the conduction band. For ZnSnO₃, it is mainly occupied by Sn-*s* orbital, and for ZnTiO₃ material, it is mainly occupied by Ti-*d* orbital.

Fig. S3 shows the density of states of ZnSnO₃ and ZnTiO₃ when the doping concentrations are 0.1 h/f.u., 0.2 h/f.u. and 0.3 h/f.u., respectively. Similar to electron doping, in the case of hole doping we can see a peak near the bottom of VB, which is contributed by Zn-*d* orbital. As the hole doping concentration increases, the peak of Zn-*d* orbital contribution near the bottom of VB decreases. For hole doping, in the two materials ZnSnO₃ and ZnTiO₃, the Fermi level locates in the top of the valence band. The top of the valence band is mainly occupied by Zn-*d* and O-*p* orbitals.

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