Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Resonance Levels in GeTe Thermoelectrics: Zinc as a New Multifaceted Dopant

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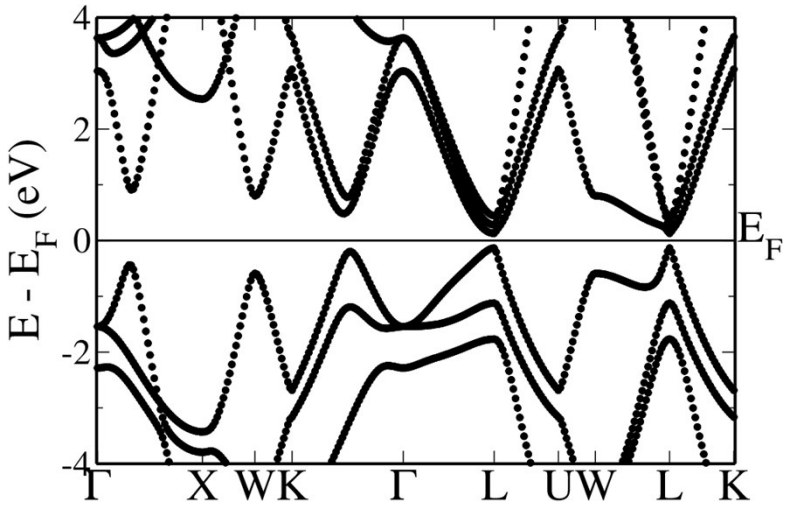

Figure S1. Electronic structure of GeTe primitive cell. The energy levels are shifted with respect to the Fermi level which is set to zero. The light hole valence and conduction band occur at L point while the heavy hole valence and conduction band occur at K+δ" in K→Γ direction in the Brillouin zone.

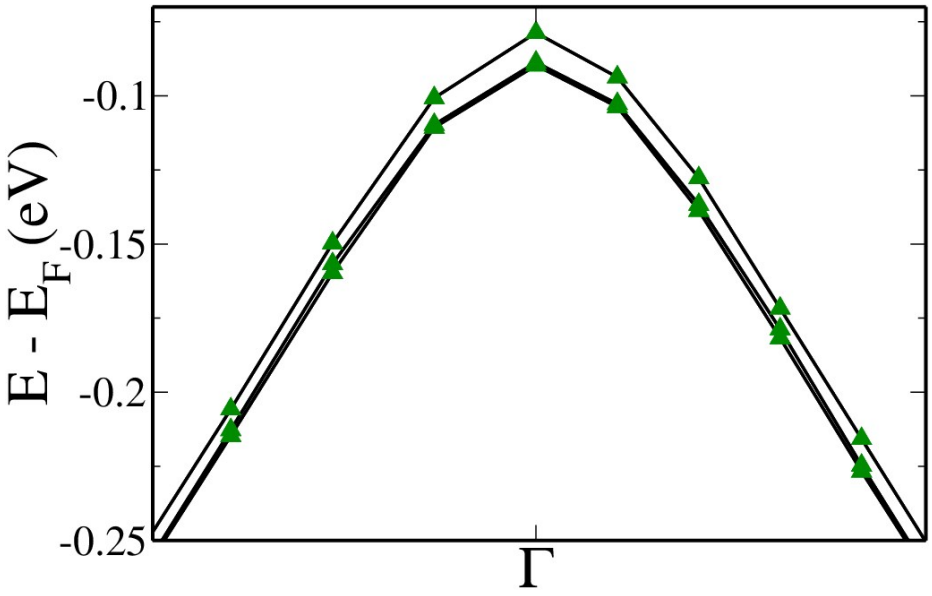

Figure S2. Electronic structure of $Ge_{15}ZnTe_{16}$: magnified view showing loss of degeneracy in the valence bands leading to 4 sets of doubly degenerate valence bands with 3 sets remaining below the Fermi level and one set splitting off as resonance level (not shown in the figure).

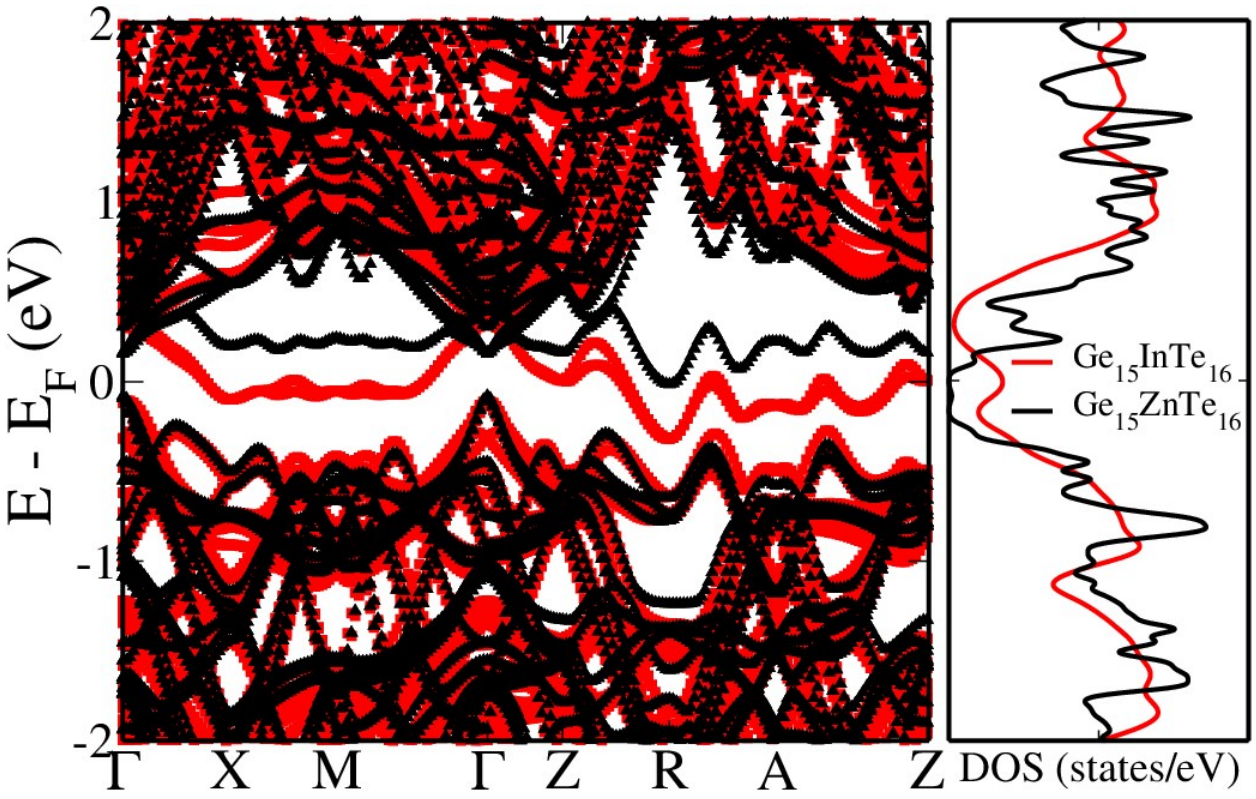

Figure S3. Electronic structure and DOS of $Ge_{15}ZnTe_{16}$ (black) and $Ge_{15}InTe_{16}$ (red). The energy levels are shifted with respect to the Fermi level which is set to zero. Resonance states are clearly visible as split off band from the valence band touching the conduction band in the electronic structure and as peaks around the Fermi level in the DOS plot. It is observed that the dominance of heavy hole valence band is seen only in the case of *Zn* doping while in the case of *In* doping mere valence band convergence occurs.

Table S1. Energy gaps in pristine and *Zn* doped GeTe

Configuration		$Ge_{16}Te_{16}$	$Ge_{15}ZnTe_{16}$
Band Gap	**ΔE_{Γ} (eV)**	0.19	0.24
$E_{\Gamma} - E_{Z+\delta}$	**ΔE_{VB_1} (eV)**	0.21	- 0.25
	ΔE_{VB_2} (eV)	0.21	0.21
$E_{\Gamma} - E_{\Gamma+\delta'}$	**ΔE_{VB_1} (eV)**	0.07	-0.22
	ΔE_{VB_2} (eV)	0.07	0.17
$E_{\Gamma} - E_{Z+\delta}$	**ΔE_{CB} (eV)**	0.21	0.19

ΔE_{VB_1} represents the energy difference between the highest light hole valence band and highest heavy hole valence band. ΔE_{VB_2} represents the energy difference between the second highest light hole valence band and second highest heavy hole valence band. Negative sign indicates the heavy hole valence band is higher than the light hole valence band. $E_{Z+\delta}$ denotes energy at that point in Z→R direction. $E_{\Gamma+\delta'}$ denotes energy at that point in Γ→X direction in the Brillouin zone of the supercell.

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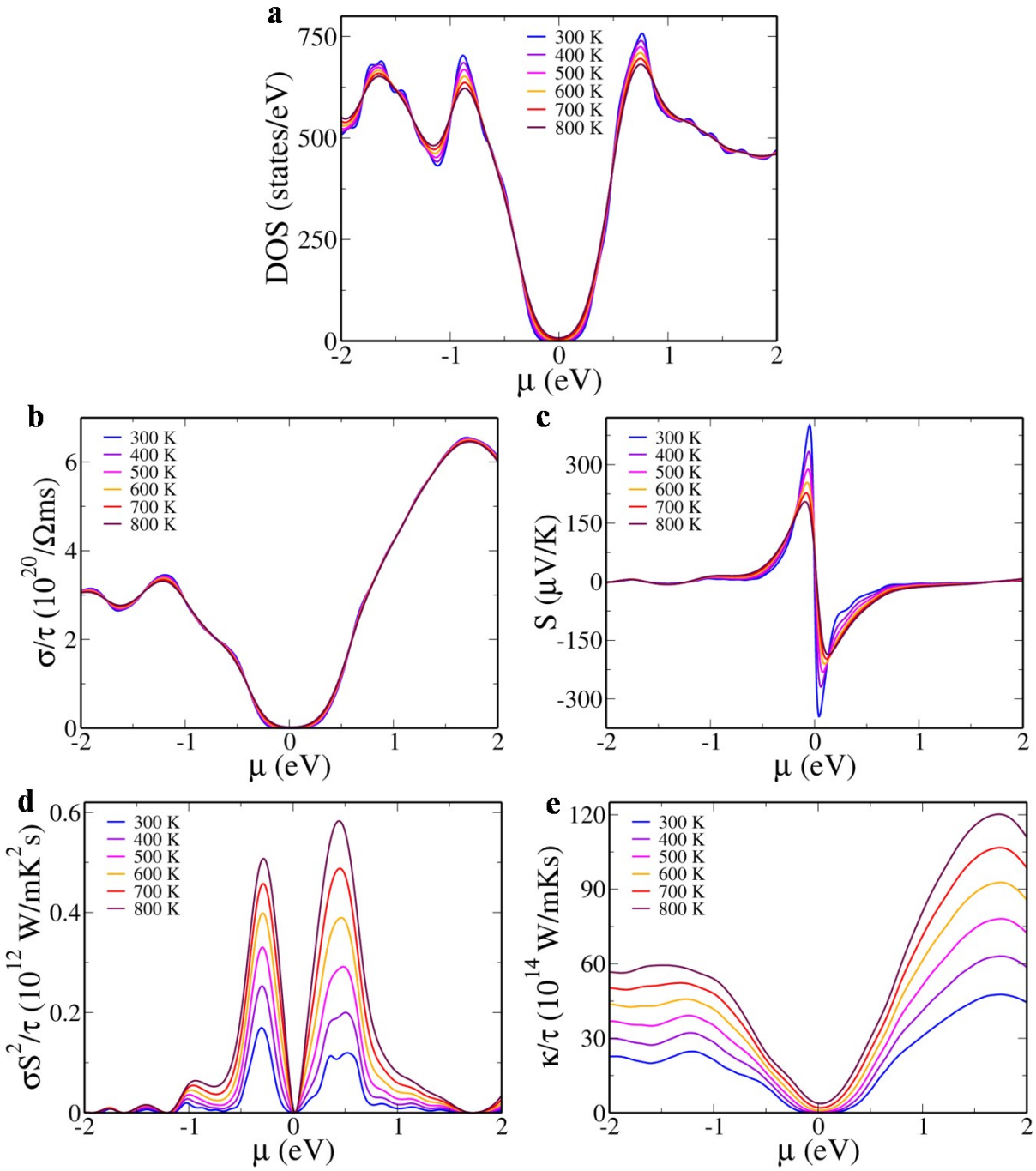

Figure S4. a) DOS; b) Electrical conductivity; c) Seebeck co-efficient; d) Power factor and e) Thermal conductivity of $Ge_{16}Te_{16}$ as a function of chemical potential at various temperatures. Electrical conductivity, power factor and thermal conductivity are reported by scaling them with τ.