Supporting Information

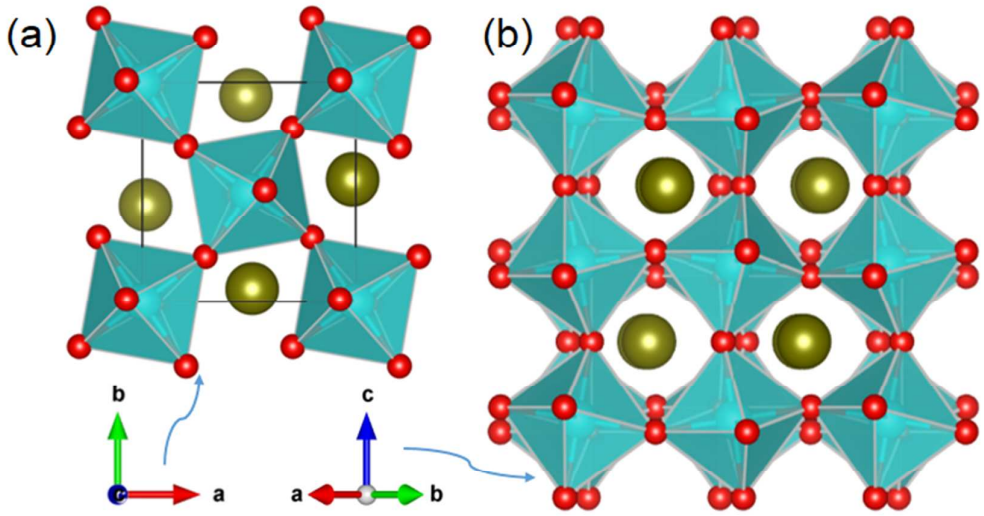

Figure S1. Structure of distorted $BaZrS_3$: (a) top view along the [001] direction and (b) side view along the [110] direction. Yellow, blue and red balls indicate Ba, Zr and S atoms, respectively.

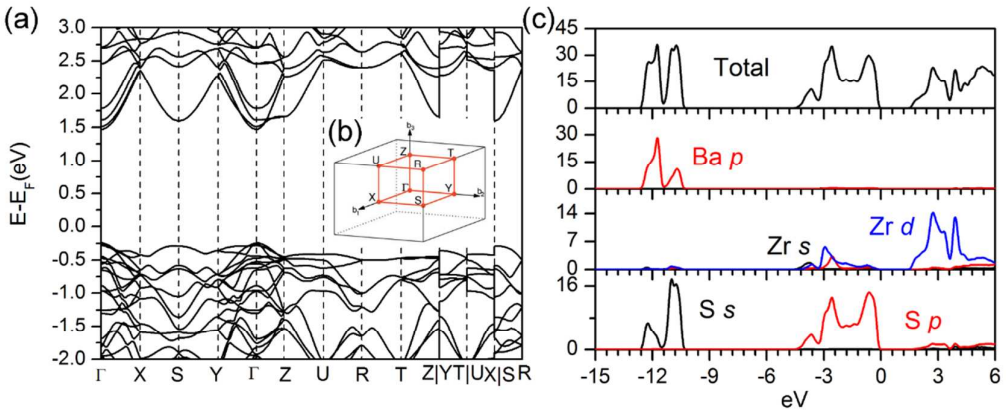

Figure S2. GGA+*U* calculated band structure and density of states (DOS) for $BaZrS_3$.

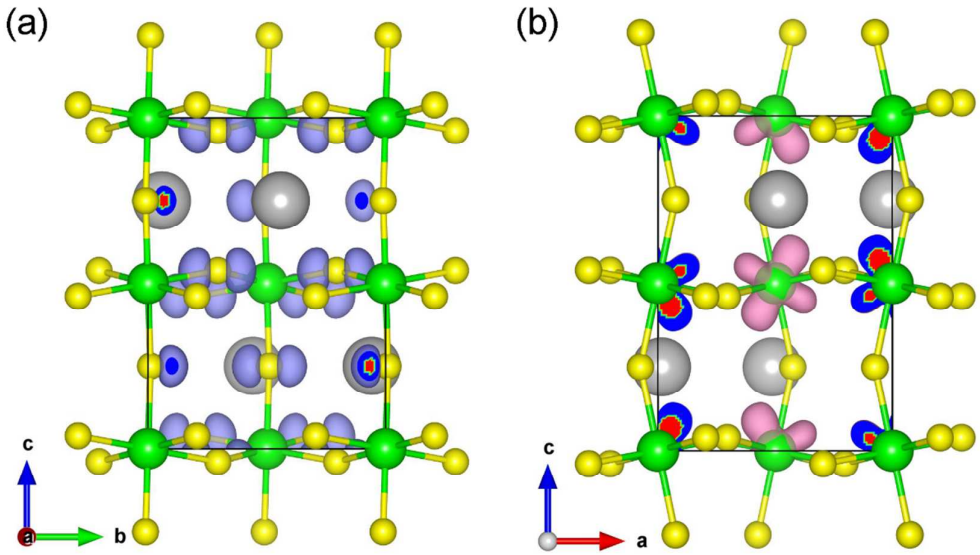

Figure S3. Calculated $BaZrS_3$ charge density map for (a) VBM, blue color and (b) CBM, pink color. Ba, Zr and S atoms are represented by grey, green and yellow balls, respectively.

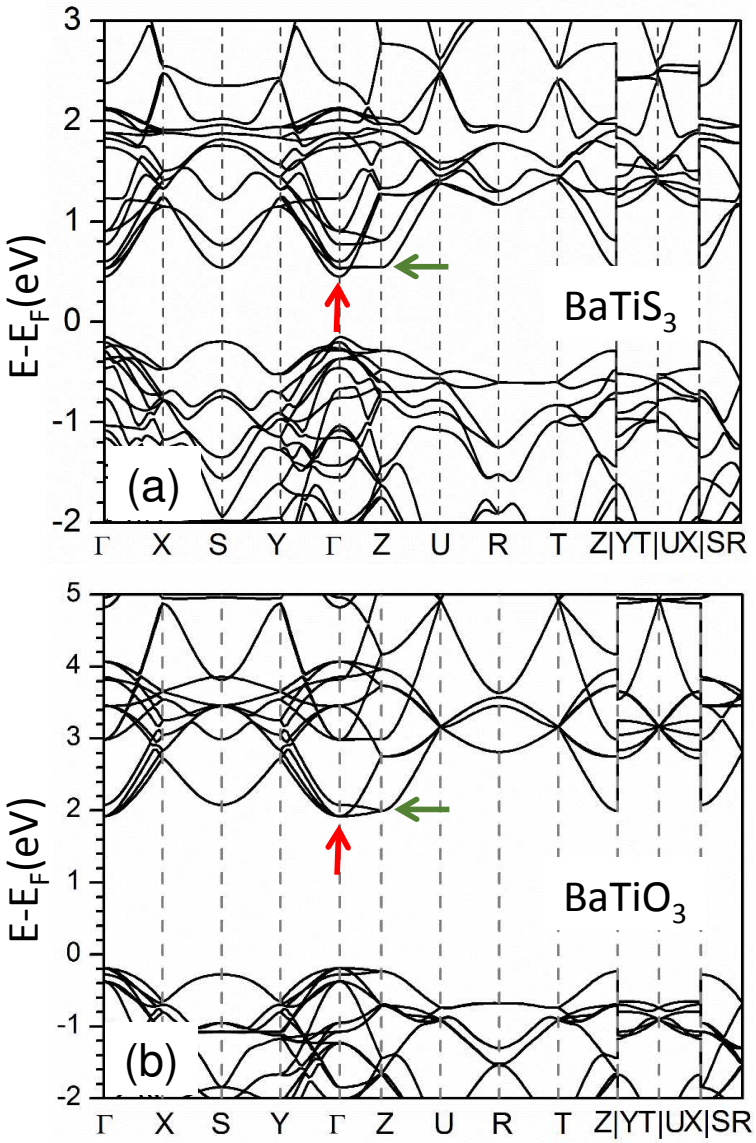

Figure S4. Calculated band structures of (a) $BaTiS_3$ and (b) $BaTiO_3$ perovskites.

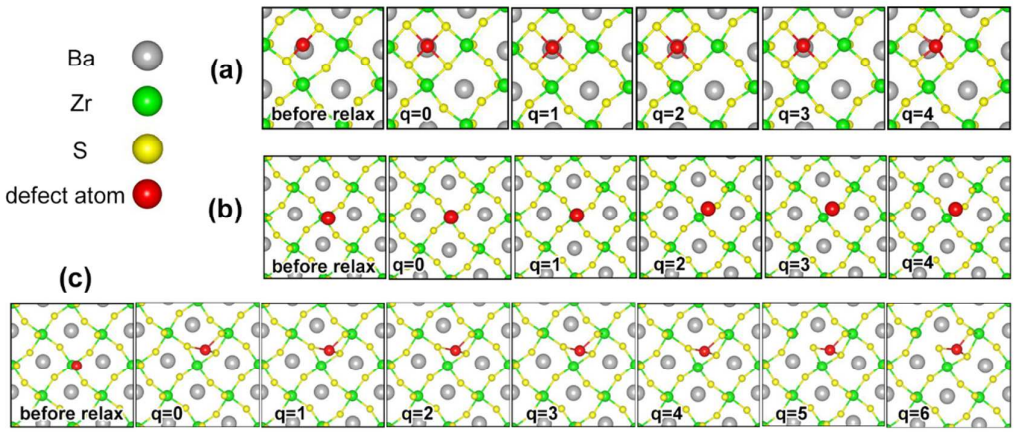

Figure S5. Configurations of three defects with multiple charge states before and after ionic relaxation: (a) Zr_i, (b) Ba_S and (c) Zr_S. *q* equals positive charge state. Red color atoms are the defect atoms.

Table S1. Comparison of GGA+U and HSE06 calculated bandgaps.

		HSE06	GGA+*U*
Bandgap (eV)	$BaZrS_3$-perovskite	1.72	1.62 (U_{eff}=4.0 eV)
			1.76 (U_{eff}=4.5 eV)
			1.87 (U_{eff}=5.0 eV)
	$BaTiS_3$-perovskite	0.53	0.41 (U_{eff}=3 eV)
			0.60 (U_{eff}=4 eV)
			0.76 (U_{eff}=5 eV)

Table S2. Calculated PBE total energies of three $BaTiS_3$ phases. The energies are referred to that of the hexagonal phase.

Phase	Hexagonal phase	Perovskite phase	Needle-like phase
Total Energy (eV/formula)	0	0.237	0.250