Figure S1. Models of different Co ion valence states: (a) BZCT (Co^{2+}) and (b) BZCT (Co^{3+})

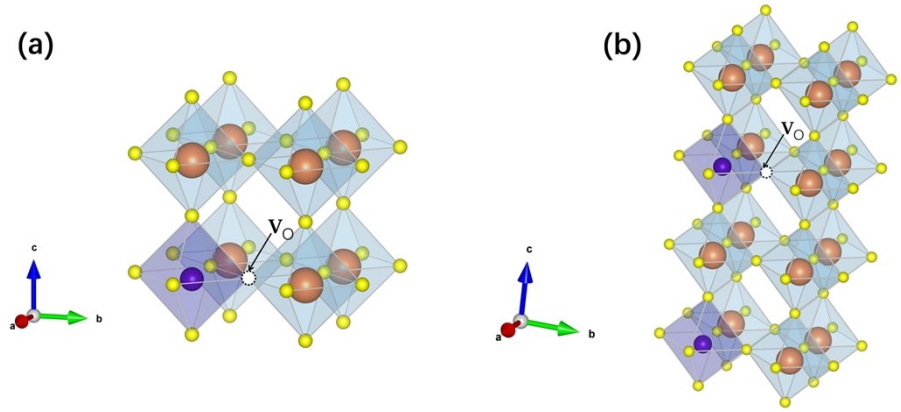


Figure S2. Band structures and density of states for different Co ion valence states:(a) Band structure of BZCT (Co^{2+}), (b) Band structure of BZCT (Co^{3+}), (c) DOS of BZCT (Co^{2+}), (d) DOS of BZCT (Co^{3+})

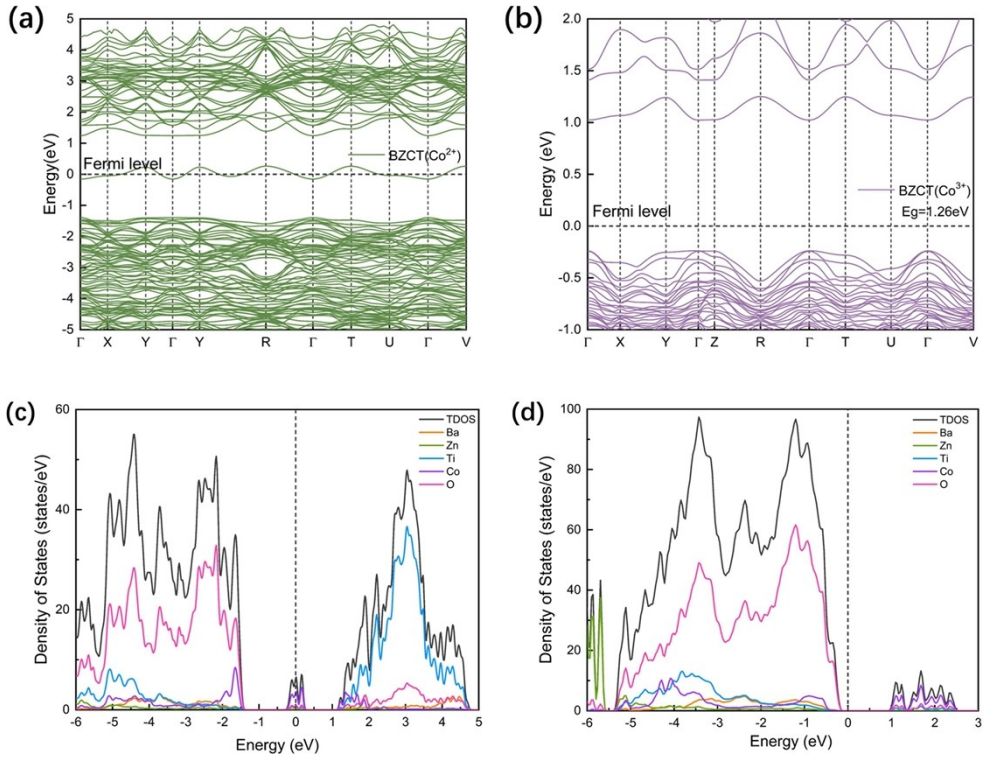


Figure S3. Bond length and bond angle diagrams for (a) BTO and (b) BZCT octahedra

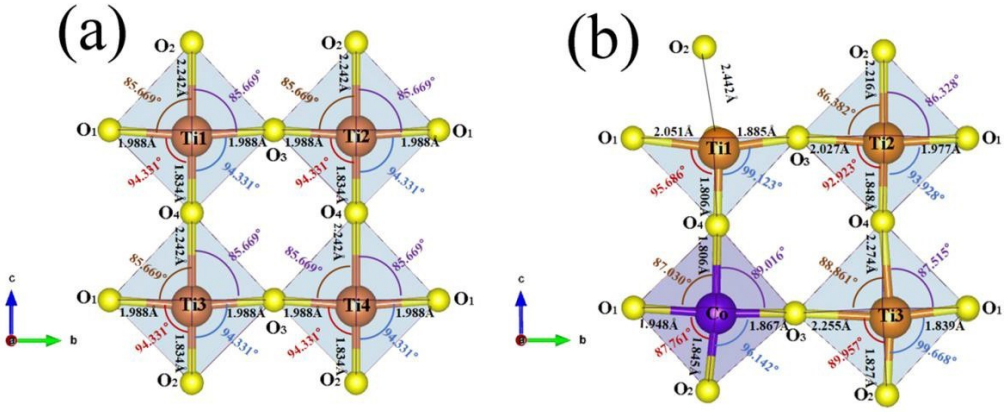


Figure S4. The band structures and band gaps of (a) BZTO and (b) BTCO.

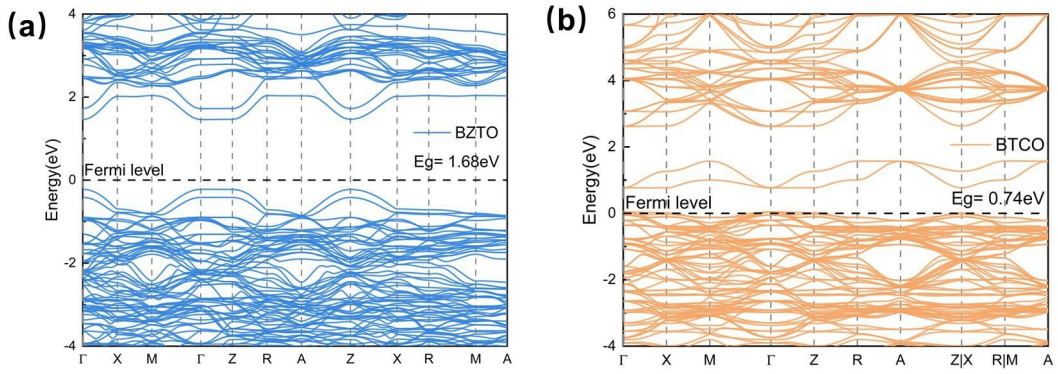
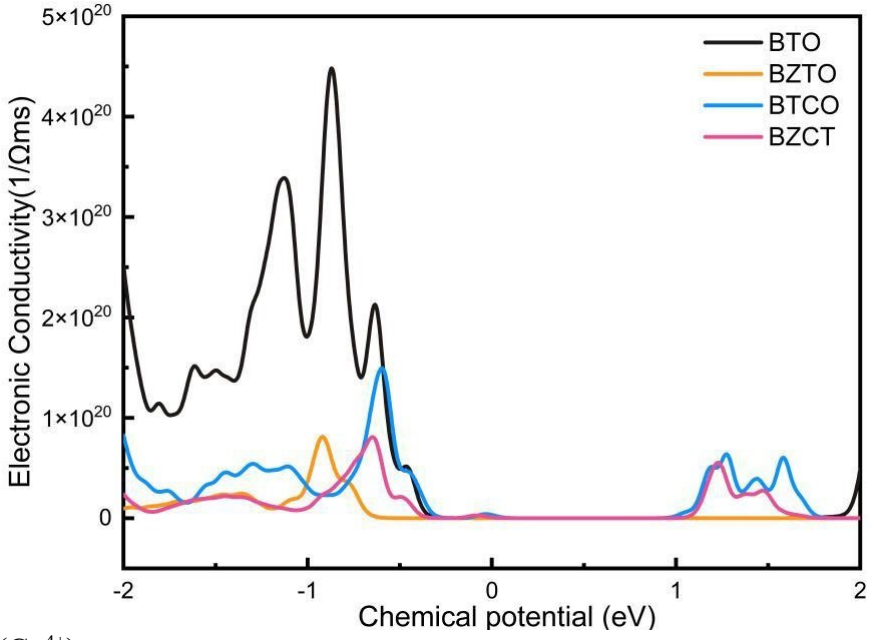


Figure S5. Electrical conductivity of BTO, BZTO, BTCOand BZCT

Table S1. Formation energy (E_f) values of each system BZCT(Co^{2+}), BZCT(Co^{3+})



and BZCT(Co^{4+})

	BZCT(Co^{2+})	BZCT(Co^{3+})	BZCT(Co^{4+})
E_f(eV)	50.5561	96.1053	-4.4917

Table S2. BTO for different supercell sizes.

Supercell size	a=b	c	c/a	Band_Gap(eV)	P_s (μC/cm^2)
1×1×1	3.976	4.048	1.018	1.76	30
2×2×2	3.996	4.217	1.055	1.81	29.57
2×2×2(GGA+U)	3.991	4.041	1.013	3.2	26.86
3×3×3	3.967	4.067	1.025	1.76	——

Table S3. Hubbard U parameter values are chosen for the O-2p, Ti-3d and Ba-5d orbitals of BTO cell, yielding gap energy values in good agreement with the experimental data, by using the GGA-PBE approximation.

U_d(Ba)	U_d(Ti)	U_p(O)	Eg(eV)
0	1	0	1.8029
0	2	0	1.9294
0	3	0	2.1770
0	4	0	2.1962
0	6	0	2.4816
0	7	0	2.6303
0	8	0	2.8885
0	9	0	3.0437
0	10	0	3.2018

Table S4. Convergence tests on cutoff energies in the range of 400-600 eV.

ENCUT(eV)	400	450	500	550	600
TOTEN(eV)	-320.5357	-320.3563	-320.3463	-320.3581	-320.4026
Δ E(eV)	——	0.1793	0.0099	-0.0117	-0.04448

Table S5. K-point grid convergence tests.

KPOINTS	4×4×4	5×5×5	6×6×6	7×7×7
TOTEN(eV)	-320.3061	-320.3463	-320.3463	-320.3464

Table S6. Comparison of GGA+U with Hybrid Functional (HSE06).

	GGA+U	HSE06
E_g(eV)	3.20	3.22

Table S7. Table of energies of individual atoms(μ_{Zn}, μ_{Co}, μ_{Ba}, μ_{Ti}) and substitution energy (E_f) data for systems with different doping sites of the elements. The four identifiers, Zn(Ba), Zn(Ti), Co(Ba) and Co(Ti) are preceded by the individual elements doped, and inside the parentheses are the substituted atomic sites.

Energy/ eV	Zn(Ba)	Zn(Ti)	Co(Ba)	Co(Ti)
E_{doped}	-330.33274827	-321.24961857	-331.81496668	-327.39082757
μ_{Zn}	-10.54035702			
μ_{Co}			-11.35391924	
μ_{Ba}	-3.93582114			
μ_{Ti}	-8.94622768			
E_{pure}	-320.17490499			
E_f	-3.5533074	0.74153405	-4.22196359	-4.8082310

Table S8. Formation energy (E_f) values and the energy of each system(E_{doped}, E_{pure}) and elements (μ_{Zn}, μ_{Co}, μ_{Ba}, μ_{Ti}) .

	Energy(eV)
E_{pure}	-320.39445262
$E_{doped}(Co^{2+})$	-266.38204588

$E_{doped}(Co^{3+})$	-541.22724457
$E_{doped}(Co^{4+})$	-321.42991954

μ_{Zn}	-1.11247205
μ_{Co}	-6.81992599
μ_{Ba}	-3.5469440725
μ_{Ti}	-7.8417359767