Supporting Information

Tunable threshold voltage of ZnTe-based ovonic switching devices via isovalent cation-exchange

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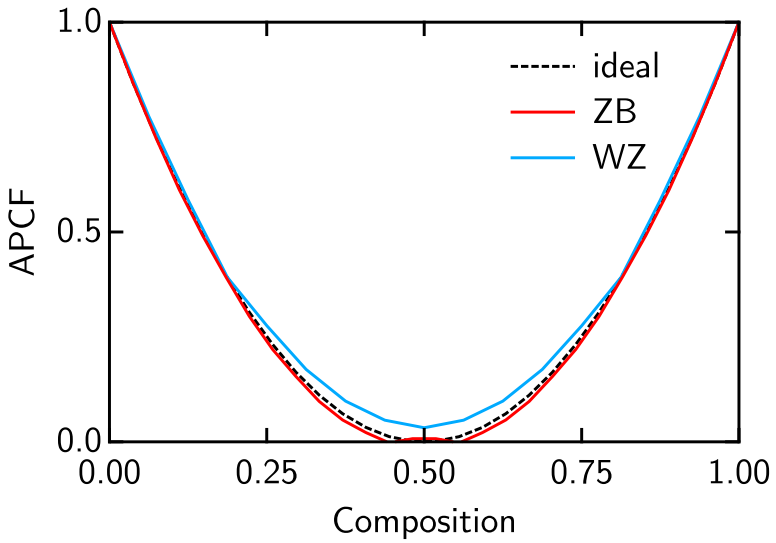

Figure S1: The atomic pair correlation functions (APCF) of zincblende and wurtzite structures as a function of composition. The black dashed line represent APCF of fully random configuration. The red and cyan lines show APCF values of zincblende (ZB) and wurtzite (WZ) structures, respectively.

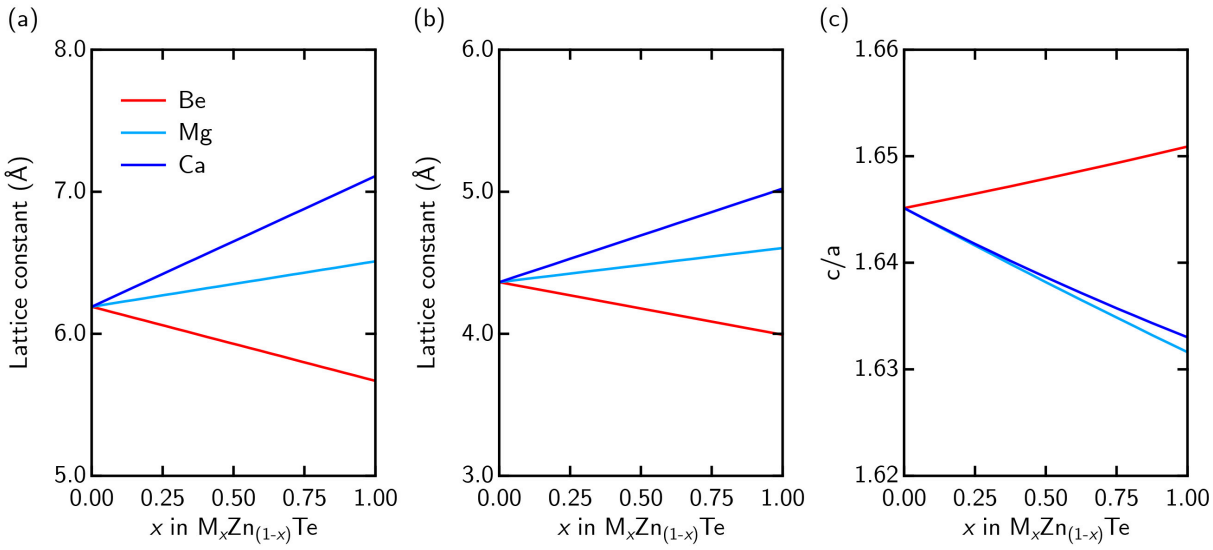

Figure S2: Calculated lattice constants of $Zn_{1-x}M_xTe$ (M = Be, Mg, and Ca) alloys. Lattice constants a of (a) zincblende and (b) wurtzite structures and (c) c/a for wurtzite structures are plotted as a function of composition x. The red, cyan and blue lines represent the exchanged cations Be, Mg, and Ca, respectively.

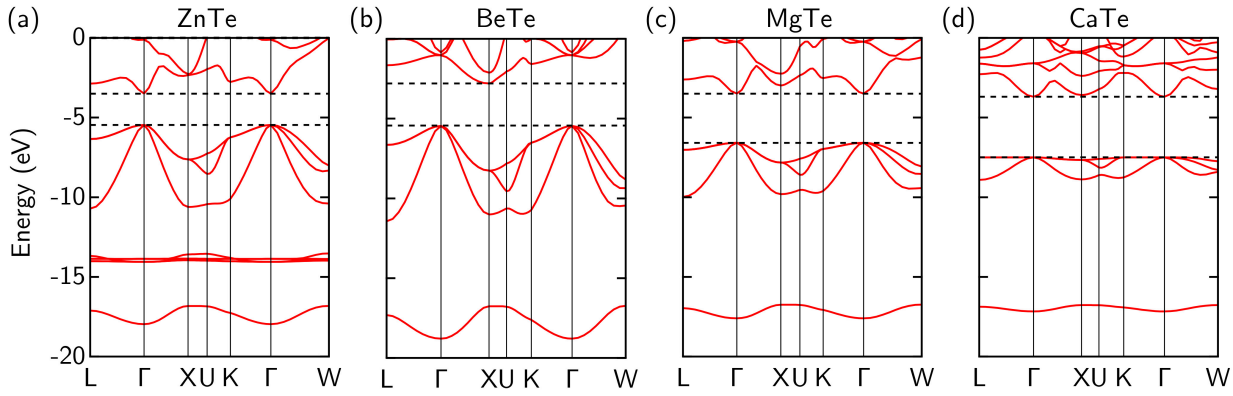

Figure S3: HSE06-derived electronic band structures of binary tellurides: (a) ZnTe, (b) BeTe, (c) MgTe, and (d) CaTe. All energies are aligned with respect to the vacuum level (i.e., 0 eV). The band edges (i.e., VBM and CBM) are indicated by the horizontal dashed black lines.

Table S1: Calculated lattice constants a (in Å) of zincblende $Zn_{1-x}M_xTe$ (M = Be, Mg, and Ca) alloys as a function of composition x. The GGA-PBE exchange-correlation functional used here.

x	Be	Mg	Ca
0.00	4.378	4.378	4.378
0.04	4.364	4.386	4.402
0.07	4.351	4.395	4.426
0.11	4.337	4.403	4.450
0.15	4.323	4.411	4.474
0.19	4.309	4.420	4.498
0.22	4.296	4.428	4.522
0.26	4.282	4.436	4.547
0.30	4.268	4.445	4.571
0.33	4.255	4.453	4.595
0.37	4.241	4.462	4.619
0.41	4.227	4.470	4.643
0.44	4.214	4.478	4.667
0.48	4.200	4.487	4.691
0.52	4.186	4.495	4.715
0.56	4.173	4.503	4.739
0.59	4.159	4.512	4.763
0.63	4.145	4.520	4.787
0.67	4.132	4.529	4.811
0.70	4.118	4.537	4.836
0.74	4.104	4.545	4.860
0.78	4.091	4.554	4.884
0.81	4.077	4.562	4.908
0.85	4.063	4.570	4.932
0.89	4.050	4.579	4.956
0.93	4.036	4.587	4.980
0.96	4.022	4.596	5.004
1.00	4.008	4.604	5.028

Table S2: Calculated lattice constants a and c in (in Å) of wurtzite $Zn_{1-x}M_xTe$ (M = Be, Mg, and Ca) alloys as a function of composition x. The GGA-PBE exchange-correlation functional used here.

	Be		Mg		Ca	
x	a	c	a	c	a	c
0.00	4.364	7.180	4.364	7.180	4.364	7.180
0.06	4.341	7.143	4.379	7.201	4.405	7.244
0.13	4.318	7.107	4.394	7.222	4.447	7.308
0.19	4.295	7.070	4.409	7.242	4.488	7.372
0.25	4.272	7.033	4.424	7.263	4.529	7.436
0.31	4.248	6.996	4.439	7.284	4.570	7.499
0.38	4.225	6.960	4.454	7.305	4.611	7.563
0.44	4.202	6.923	4.469	7.326	4.652	7.627
0.50	4.179	6.886	4.484	7.346	4.694	7.691
0.56	4.156	6.849	4.500	7.367	4.735	7.755
0.63	4.132	6.813	4.515	7.388	4.776	7.819
0.69	4.109	6.776	4.530	7.409	4.817	7.883
0.75	4.086	6.739	4.545	7.430	4.858	7.947
0.81	4.063	6.703	4.560	7.451	4.899	8.011
0.88	4.040	6.666	4.575	7.471	4.940	8.074
0.94	4.016	6.629	4.590	7.492	4.982	8.138
1.00	3.993	6.592	4.605	7.513	5.023	8.202

Table S3: PBE-derived mixing Gibbs free energies (ΔG_{mix}) of zincblende $Zn_{1-x}M_xTe$ (M = Be, Mg, and Ca) alloys at 300, 600, 900 K as a function of composition x.

	Be			Mg			Ca		
x	300 K	600 K	900 K	300 K	600 K	900 K	300 K	600 K	900 K
0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.04	0.002	-0.002	-0.007	0.000	-0.004	-0.008	0.021	0.016	0.012
0.07	0.005	-0.001	-0.008	0.002	-0.005	-0.012	0.041	0.035	0.028
0.11	0.009	0.000	-0.009	0.003	-0.006	-0.015	0.058	0.049	0.040
0.15	0.011	0.000	-0.011	0.004	-0.007	-0.018	0.071	0.061	0.050
0.19	0.014	0.001	-0.011	0.005	-0.007	-0.019	0.085	0.072	0.060
0.22	0.018	0.004	-0.010	0.007	-0.007	-0.021	0.098	0.084	0.070
0.26	0.019	0.004	-0.011	0.008	-0.007	-0.022	0.105	0.090	0.075
0.30	0.022	0.006	-0.009	0.009	-0.007	-0.023	0.111	0.096	0.080
0.33	0.025	0.008	-0.008	0.009	-0.007	-0.023	0.116	0.099	0.083
0.37	0.027	0.010	-0.007	0.010	-0.007	-0.024	0.117	0.100	0.083
0.41	0.029	0.011	-0.006	0.010	-0.007	-0.025	0.121	0.103	0.086
0.44	0.030	0.012	-0.006	0.010	-0.007	-0.025	0.120	0.102	0.084
0.48	0.029	0.011	-0.007	0.010	-0.008	-0.026	0.117	0.099	0.081
0.52	0.029	0.011	-0.007	0.010	-0.008	-0.026	0.117	0.099	0.081
0.56	0.031	0.013	-0.004	0.010	-0.008	-0.025	0.117	0.099	0.081
0.59	0.031	0.014	-0.004	0.010	-0.008	-0.025	0.112	0.094	0.077
0.63	0.029	0.012	-0.005	0.009	-0.008	-0.025	0.107	0.089	0.072
0.67	0.029	0.013	-0.004	0.008	-0.008	-0.025	0.099	0.083	0.066
0.70	0.027	0.012	-0.004	0.007	-0.009	-0.024	0.088	0.073	0.057
0.74	0.024	0.009	-0.006	0.006	-0.009	-0.024	0.079	0.064	0.049
0.78	0.023	0.009	-0.004	0.005	-0.009	-0.022	0.071	0.057	0.044
0.81	0.019	0.006	-0.006	0.004	-0.009	-0.021	0.060	0.048	0.036
0.85	0.015	0.004	-0.006	0.003	-0.008	-0.019	0.049	0.038	0.028
0.89	0.013	0.004	-0.005	0.002	-0.007	-0.016	0.039	0.030	0.021
0.93	0.009	0.002	-0.005	0.000	-0.006	-0.013	0.026	0.019	0.012
0.96	0.003	-0.001	-0.005	0.000	-0.004	-0.009	0.012	0.008	0.004
1.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table S4: PBE-derived mixing Gibbs free energies (ΔG_{mix}) of wurtzite $Zn_{1-x}M_xTe$ (M = Be, Mg, and Ca) alloys at 300, 600, 900 K as a function of composition x.

	Be			Mg			Ca		
x	300 K	600 K	900 K	300 K	600 K	900 K	300 K	600 K	900 K
0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.06	0.005	-0.002	-0.008	0.001	-0.005	-0.011	0.037	0.031	0.025
0.13	0.010	0.000	-0.009	0.004	-0.006	-0.015	0.067	0.057	0.047
0.19	0.018	0.006	-0.007	0.006	-0.006	-0.018	0.093	0.081	0.068
0.25	0.021	0.007	-0.008	0.009	-0.006	-0.020	0.111	0.096	0.082
0.31	0.026	0.010	-0.007	0.009	-0.007	-0.023	0.109	0.093	0.077
0.38	0.029	0.012	-0.005	0.010	-0.007	-0.024	0.121	0.103	0.086
0.44	0.031	0.013	-0.004	0.012	-0.006	-0.024	0.132	0.114	0.096
0.50	0.032	0.015	-0.003	0.011	-0.007	-0.025	0.120	0.102	0.084
0.56	0.034	0.016	-0.002	0.011	-0.007	-0.024	0.120	0.103	0.085
0.63	0.031	0.014	-0.003	0.009	-0.008	-0.025	0.104	0.087	0.070
0.69	0.029	0.013	-0.003	0.008	-0.008	-0.024	0.093	0.077	0.061
0.75	0.027	0.012	-0.002	0.007	-0.008	-0.023	0.077	0.062	0.048
0.81	0.024	0.011	-0.001	0.005	-0.008	-0.020	0.063	0.050	0.038
0.88	0.015	0.006	-0.004	0.002	-0.008	-0.017	0.041	0.031	0.021
0.94	0.008	0.002	-0.004	0.000	-0.006	-0.012	0.022	0.016	0.010
1.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

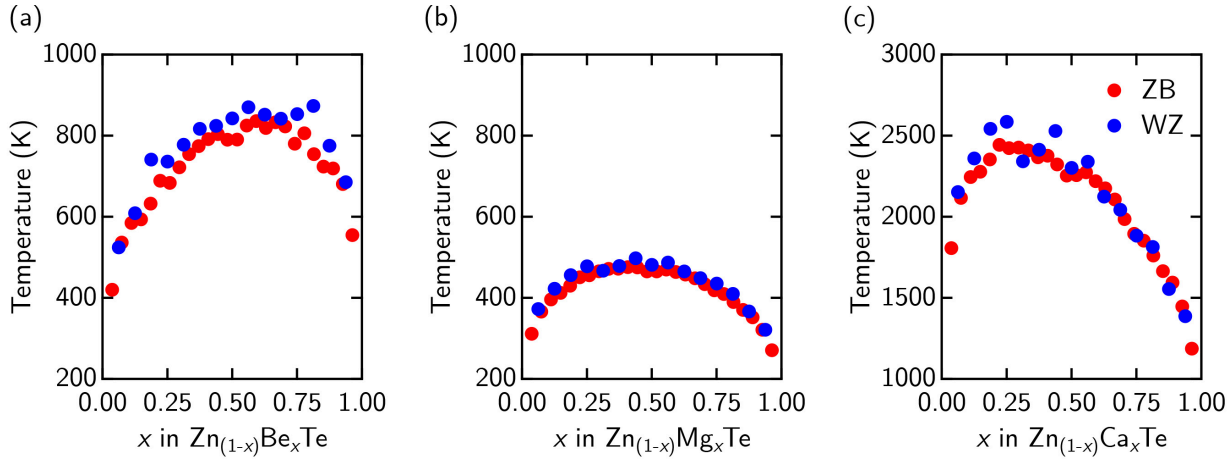

Figure S4: Calculated temperatures at which the mixing Gibbs free energy becomes zero (i.e., $\Delta G_{\mathrm{mix}} = 0$) for (a) $Zn_{(1-x)}Be_xTe$, (b) $Zn_{(1-x)}Mg_xTe$, and (c) $Zn_{(1-x)}Ca_xTe$. The temperatures for ZB and WZ structures are indicated by red and blue markers, respectively.

Table S5: HSE06-derived electronic band gap energies (in eV) as a function of composition x for zincblende (ZB) and wurtzite (WZ) $Zn_{1-x}M_xTe$ (M = Be, Mg, and Ca).

	ZB				WZ		
x	Be	Mg	Ca	x	Be	Mg	Ca
0.00	1.90	1.90	1.90	0.00	1.96	1.96	1.96
0.04	2.10	1.94	2.00	0.06	2.18	1.98	2.02
0.07	2.12	1.94	1.98	0.13	2.28	2.02	1.98
0.11	2.20	1.96	1.96	0.19	2.38	2.06	1.96
0.15	2.28	2.00	1.96	0.25	2.48	2.10	1.98
0.19	2.38	2.02	1.96	0.31	2.48	2.16	2.08
0.22	2.44	2.02	1.94	0.38	2.46	2.20	2.08
0.26	2.52	2.08	1.98	0.44	2.56	2.24	2.10
0.30	2.58	2.10	2.00	0.50	2.52	2.30	2.12
0.33	2.66	2.12	2.02	0.56	2.50	2.38	2.28
0.37	2.76	2.14	2.10	0.63	2.50	2.42	2.18
0.41	2.74	2.20	2.14	0.69	2.48	2.46	2.28
0.44	2.76	2.22	2.16	0.75	2.54	2.60	2.54
0.48	2.78	2.28	2.24	0.81	2.60	2.66	2.64
0.52	2.76	2.32	2.28	0.88	2.66	2.80	3.00
0.56	2.66	2.32	2.24	0.94	2.70	2.90	3.10
0.59	2.68	2.36	2.30	1.00	2.86	3.12	3.90
0.63	2.68	2.42	2.42				
0.67	2.64	2.46	2.50				
0.70	2.64	2.50	2.56				
0.74	2.68	2.58	2.74				
0.78	2.64	2.62	2.78				
0.81	2.64	2.68	2.88				
0.85	2.64	2.76	3.00				
0.89	2.62	2.80	3.04				
0.93	2.62	2.88	3.14				
0.96	2.64	2.98	3.40				
1.00	2.68	3.06	3.82				

Table S6: HSE06-derived electronic band edges (in eV), taken with respect to the vacuum level (as 0 eV), for zincblende (ZB) and wurtzite (WZ) binary tellurides. Here, ϵ_{VBM} and ϵ_{CBM} are the valence band maximum and conduction band minimum, respectively.

	ZB		WZ	
	ϵ_{VBM}	ϵ_{CBM}	ϵ_{VBM}	ϵ_{CBM}
ZnTe	−5.46	−3.56	−5.45	−3.47
BeTe	−5.43	−2.75	−4.77	−1.91
MgTe	−6.61	−3.55	−6.61	−3.46
CaTe	−7.56	−3.74	−7.57	−3.67

Table S7: Experimental values for the band gap, ϵ_{gap} (in eV), threshold voltage, V_{th} (in V), film thickness (in nm). Their references are listed accordingly.

	Band gap (ϵ_{gap})	Threshold voltage (V_{th})	Film thickness	Reference
Bi doped GeSe (4.79 at.%)	1.02	3.55	100	1
Bi doped GeSe (6.68 at.%)	0.96	3.36	100	1
Bi doped GeSe (9.40 at.%)	0.85	3.10	100	1
$Ge_{0.6}Se_{0.4}$	0.95	3.24	100	2
$Sb_{0.08}(Ge_{0.6}Se_{0.4})_{0.92}$	0.85	2.49	100	2
$Sb_{0.10}(Ge_{0.6}Se_{0.4})_{0.90}$	0.89	2.73	100	2
$Sb_{0.17}(Ge_{0.6}Se_{0.4})_{0.83}$	0.78	2.66	100	2
$Sb_{0.22}(Ge_{0.6}Se_{0.4})_{0.78}$	0.78	2.17	100	2
Ga_2Te_3	1.00	1.62	100	3
N doped Ga_2Te_3 (0.3 at.%)	0.96	1.36	100	3
N doped Ga_2Te_3 (1.0 at.%)	0.95	1.23	100	3
N doped Ga_2Te_3 (2.4 at.%)	0.93	1.15	100	3
$Zn_{0.20}Te_{0.80}$	1.23	0.84	10	4
$Zn_{0.35}Te_{0.65}$	1.60	1.05	10	4
$Zn_{0.50}Te_{0.50}$	1.58	1.18	10	4
$Zn_{0.60}Te_{0.40}$	1.47	0.81	10	4
$Zn_{0.70}Te_{0.30}$	0.60	0.73	10	4
ZnTe	2.20	1.20	20	5

Table S8: Predicted threshold voltage, V_{th} (in V) as a function of the composition x for both zincblende (ZB) and wurtzite (WZ) $Zn_{1-x}M_xTe$ (where M = Be and Mg).

	x	0.00	0.04	0.07	0.11	0.15	0.19	0.22	0.26	0.30	0.33	0.37	0.41	0.44	0.48	0.52	0.56	0.59	0.63	0.67	0.70	0.74	0.78	0.81	0.85	0.89	0.93	0.96	1.00
ZB	$Zn_{1-x}Be_xTe$	1.11	1.17	1.18	1.20	1.23	1.26	1.28	1.31	1.33	1.35	1.38	1.38	1.38	1.39	1.38	1.35	1.36	1.36	1.34	1.34	1.36	1.34	1.34	1.34	1.34	1.34	1.34	1.35
	$Zn_{1-x}Mg_xTe$	1.11	1.12	1.12	1.13	1.14	1.15	1.15	1.17	1.17	1.18	1.18	1.20	1.21	1.23	1.24	1.24	1.26	1.27	1.29	1.30	1.33	1.34	1.36	1.38	1.40	1.42	1.45	1.48

	x	0.00	0.06	0.013	0.19	0.25	0.31	0.38	0.44	0.50	0.56	0.63	0.69	0.75	0.81	0.88	0.94	1.00
WZ	$Zn_{1-x}Be_xTe$	1.13	1.20	1.23	1.26	1.29	1.29	1.29	1.32	1.31	1.30	1.30	1.29	1.31	1.33	1.35	1.36	1.42
	$Zn_{1-x}Mg_xTe$	1.13	1.13	1.15	1.16	1.17	1.19	1.20	1.22	1.24	1.26	1.27	1.29	1.33	1.35	1.40	1.43	1.50

References

(1) Seo, J.; Ahn, H.-W.; Shin, S.-Y.; Cheong, B.-K.; Lee, S. Anomalous Reduction of the Switching Voltage of Bi-Doped $Ge_{0.5}Se_{0.5}$ Ovonic Threshold Switching Devices. *Appl. Phys. Lett.* **2014**, *104*, 153503.

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