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Article

First-Principles Calculations of Thermoelectric Transport Properties of Quaternary and Ternary Bulk Chalcogenide Crystals

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Citation: Hasan, S.; San, S.; Baral, K.; Li, N.; Rulis, P.; Ching, W.-Y. First-Principles Calculations of Thermoelectric Transport Properties of Quaternary and Ternary Bulk Chalcogenide Crystals. *Materials* **2022**, *15*, 2843. https://doi.org/10.3390/ma15082843

Academic Editors: Irena Jankowska-Sumara and Magdalena Krupska-Klimczak

Received: 18 February 2022
Accepted: 9 April 2022
Published: 13 April 2022

1. The Supplementary Tables

Table S1. The fully optimized structures with the corresponding experimental lattice parameters of 30 chalcogenide crystals.

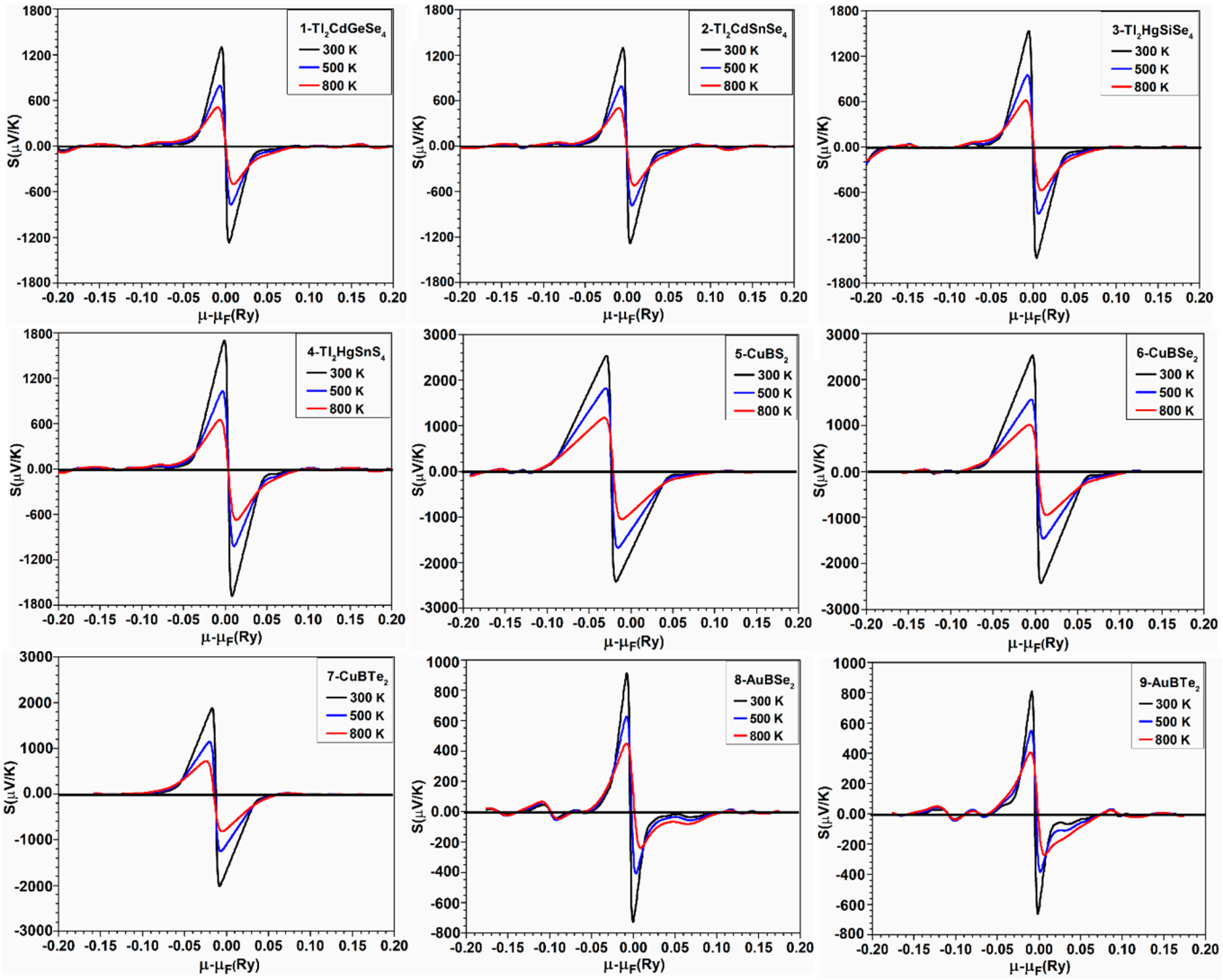
#	Crystal	Space group	Lattice parameters (our calculations) a, b, c(Å), α, β, γ(degree)	Lattice parameters(experimental) a, b, c(Å), α, β, γ(degree)
1	$Tl_2CdGeSe_4$	Tet, I-4 2 m(121)	8.1791, 8.1791, 6.8532, 90.00, 90.00, 90.00	8.0145, 8.0145, 6.7234, 90.00, 90.00, 90.00[1]
2	$Tl_2CdSnSe_4$	Tet, I-4 2 m(121)	8.2291, 8.2291, 6.9925, 90.00, 90.00, 90.00	8.0490, 8.0490, 6.8573, 90.00, 90.00, 90.00[1]
3	$Tl_2HgSiSe_4$	Tet, I-4 2 m(121)	8.1599, 8.1599, 6.8546, 90.00, 90.00, 90.00	8.0032, 8.0032, 6.6879, 90.00, 90.00, 90.00[2]
4	Tl_2HgSnS_4	Tet, I-4 2 m(121)	7.9589, 7.9589, 6.8578, 90.00, 90.00, 90.00	7.8571, 7.85716.6989, 90.00, 90.00, 90.00[3]
5	$CuBS_2$	Tet, I-42d(122)	5.0203, 5.0203, 9.0696, 90.00, 90.00, 90.00	5.044, 5.044, 8.948056, 90.00, 90.00, 90.00[4]
6	$CuBSe_2$	Tet, I-42d(122)	5.3328, 5.3328, 9.7364, 90.00, 90.00, 90.00	5.782, 5.782, 11.4021, 90.00, 90.00, 90.00[4]
7	$CuBTe_2$	Tet, I-42d(122)	5.7218, 5.7218, 10.7973, 90.00, 90.00, 90.00	5.616, 5.616, 10.6479, 90.00, 90.00, 90.00[4]
8	$AuBSe_2$	Tet, I-42d(122)	5.6726, 5.6726, 9.6556, 90.00, 90.00, 90.00	5.676, 5.676, 9.6776, 90.00, 90.00, 90.00[5]
9	$AuBTe_2$	Tet, I-42d(122)	5.9911, 5.9911, 10.8396, 90.00, 90.00, 90.00	6.011, 6.011, 10.7897, 90.00, 90.00, 90.00[5]
10	$AuAlTe_2$	Tet, I-42d(122)	6.3156, 6.3156, 12.3673, 90.00, 90.00, 90.00	6.244, 6.244, 12.5692, 90.00, 90.00, 90.00[5]
11	$AuGaTe_2$	Tet, I-42d(122)	6.3232, 6.3232, 12.4756, 90.00, 90.00, 90.00	6.2990, 6.2990, 12.4720, 90.00, 90.00, 90.00[5]
12	$AuInTe_2$	Tet, I-42d(122)	6.5064, 6.5064, 13.0550, 90.00, 90.00, 90.00	6.4840, 6.4840, 12.9745, 90.00, 90.00, 90.00[5]
13	$CuAlSe_2$	Tet, I-42d(122)	5.6526, 5.6526, 11.1557, 90.00, 90.00, 90.00	5.602, 5.602, 10.944, 90.00, 90.00, 90.00[6]
14	$CuAlTe_2$	Tet, I-42d(122)	6.0944, 6.0944, 12.1101, 90.00, 90.00, 90.00	5.964, 5.964, 11.780, 90.00, 90.00, 90.00[6]
15	$AgAlSe_2$	Tet, I-42d(122)	6.0324, 6.0324, 11.1150, 90.00, 90.00, 90.00	5.95, 5.95, 10.7457, 90.00, 90.00, 90.00[7]
16	$AgAlTe_2$	Tet, I-42d(122)	6.4134, 6.4134, 12.2311, 90.00, 90.00, 90.00	6.29, 6.29, 11.8252, 90.00, 90.00, 90.00[7]
17	$CuGaS_2$	Tet, I-42d(122)	5.3824, 5.3824, 10.6673, 90.00, 90.00, 90.00	5.347, 5.347, 10.974, 90.00, 90.00, 90.00[8]
17	$CuGaSe_2$	Tet, I-42d(122)	5.6782, 5.6782, 11.2749, 90.00, 90.00, 90.00	5.607, 5.607, 10.990, 90.00, 90.00, 90.00[8]
19	$CuGaTe_2$	Tet, I-42d(122)	6.0999, 6.0999, 12.1799, 90.00, 90.00, 90.00	5.994, 5.994, 11.912, 90.00, 90.00, 90.00[8]
20	$AgGaS_2$	Tet, I-42d(122)	5.7803, 5.7803, 10.6678, 90.00, 90.00, 90.00	5.755, 5.755, 10.283, 90.00, 90.00, 90.00[8]
21	$AgGaSe_2$	Tet, I-42d(122)	6.0507, 6.0507, 11.2857, 90.00, 90.00, 90.00	5.985, 5.985, 10.901, 90.00, 90.00, 90.00[8]
22	$AgGaTe_2$	Tet, I-42d(122)	6.4089, 6.4089, 12.3514, 90.00, 90.00, 90.00	6.301, 6.301, 11.962, 90.00, 90.00, 90.00[8]

23	$CuInS_2$	Tet, I-42d(122)	5.594, 5.594, 11.273, 90.00, 90.00, 90.00	5.522, 5.522, 11.132, 90.00, 90.00, 90.00[8]
24	$CuInSe_2$	Tet, I-42d(122)	5.879, 5.879, 11.829, 90.00, 90.00, 90.00	5.785, 5.785, 11.570, 90.00, 90.00, 90.00[8]
25	$CuInTe_2$	Tet, I-42d(122)	6.302, 6.302, 12.648, 90.00, 90.00, 90.00	6.179, 6.179, 12.360, 90.00, 90.00, 90.00[8]
26	$AgInS_2$	Tet, I-42d(122)	5.936, 5.936, 11.567, 90.00, 90.00, 90.00	5.827, 5.827, 11.190, 90.00, 90.00, 90.00[8]
27	$AgInSe_2$	Tet, I-42d(122)	6.197, 6.197, 12.123, 90.00, 90.00, 90.00	6.098, 6.098, 11.708, 90.00, 90.00, 90.00[8]
28	$AgInTe_2$	Tet, I-42d(122)	6.571, 6.571, 13.021, 90.00, 90.00, 90.00	6.443, 6.443, 12.636, 90.00, 90.00, 90.00[8]
29	$NaInSe_2$	Tet, I-42d(122)	6.7103, 6.7103, 11.2860, 90.00, 90.00, 90.00	6.418, 6.418, 12.644, 90.00, 90.00, 90.00[9]
30	$NaInTe_2$	Tet, I-42d(122)	7.1943, 7.1943, 12.2738, 90.00, 90.00, 90.00	6.599, 6.599, 12.276, 90.00, 90.00, 90.00[9]

Table S2. Energy gap (Eg) (calculated in our previous works), the Seebeck coefficients (S) and figure of merit (ZT) as a function of chemical potential at room temperature (300 K), and the TBOD for these 30 chalcogenide crystals. In the previous published works (Refs. 79 and 80 in the main text), OLCAO code was used to calculate the energy band gap. Spin-Orbit Coupling (SOC) effect was not included in the calculations.

#	Crystal	Eg(eV)	S(μV/K)	S(μV/K)	Highest ZT	TBOD (e^-/ Å 3)
1	$Tl_2CdGeSe_4$	0.814(D)	1300	—	1.01	0.0085
2	$Tl_2CdSnSe_4$	0.810(D)	1250	—	1.0	0.0080
3	$Tl_2HgSiSe_4$	0.992(D)	1500	—	1.02	0.0067
4	Tl_2HgSnS_4	1.105(D)	1660	—	1.0	0.0066
5	$CuBS_2$	1.8(D)	2600	2295[4]	1.01	0.0363
6	$CuBSe_2$	1.6(D)	2500	2527[4]	1.02	0.0293
7	$CuBTe_2$	1.2(D)	1800	1704[4]	1.0	0.0250
8	$AuBSe_2$	1.78(ID)	925	—	0.96	0.0228
9	$AuBTe_2$	1.40(ID)	825	—	0.98	0.0202
10	$AuAlTe_2$	1.60(D)	600	—	0.94	0.0151
11	$AuGaTe_2$	0.646(D)	205	—	0.60	0.0144
12	$AuInTe_2$	0.635(D)	190	—	0.54	0.0125
13	$CuAlSe_2$	1.20(D)	1600	—	1.0	0.0209
14	$CuAlTe_2$	1.70(ID)	1800	—	1.0	0.0182
15	$AgAlSe_2$	1.45(D)	2050	—	1.005	0.0170
16	$AgAlTe_2$	1.81(D)	1900	—	1.01	0.0149
17	$CuGaS_2$	0.80(D)	850	—	0.96	0.0234
18	$CuGaSe_2$	0.39(D)	700	—	0.82	0.0198
19	$CuGaTe_2$	0.85(D)	550	—	0.90	0.0176
20	$AgGaS_2$	1.05(D)	1100	—	1.01	0.0185
21	$AgGaSe_2$	0.60(D)	480	—	0.90	0.0160
22	$AgGaTe_2$	0.90(D)	500	860[10]	0.91	0.0144
23	$CuInS_2$	0.240(D)	390	370[11]	0.84	0.0191
24	$CuInSe_2$	0.146(D)	260	240[11]	0.70	0.0166
25	$CuInTe_2$	0.754(D)	460	325[11], 00[12]	0.88	0.0153
26	$AgInS_2$	0.651(D)	770	—	0.98	0.0152
27	$AgInSe_2$	0.453(D)	390	—	0.84	0.0135
28	$AgInTe_2$	1.001(D)	525	500[13], 750[14]	0.92	0.0125
29	$NaInSe_2$	1.54(D)	2400	—	1.01	0.0111
30	$NaInTe_2$	1.80(D)	2100	—	1.02	0.00942

2. The Supplementary Figures



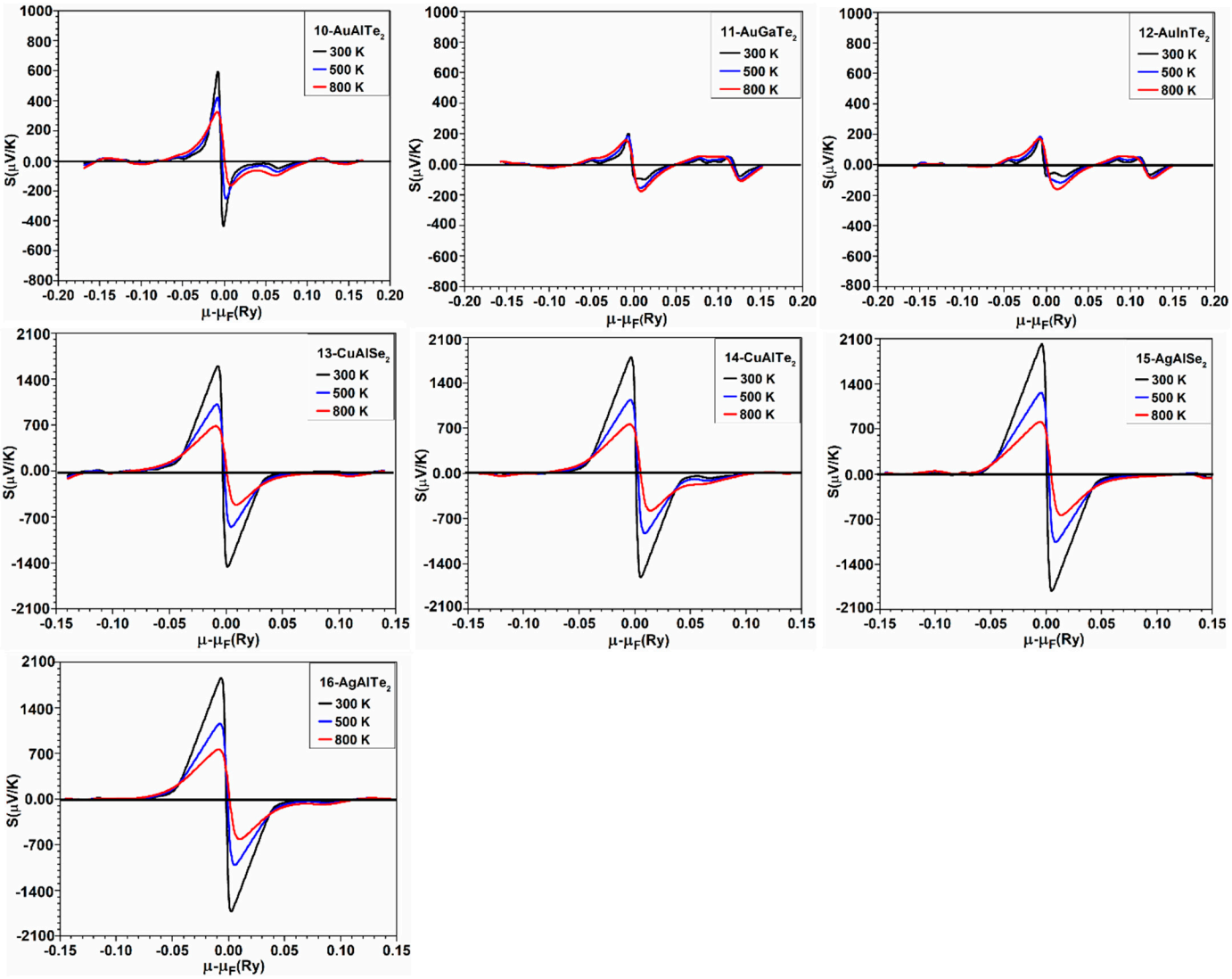
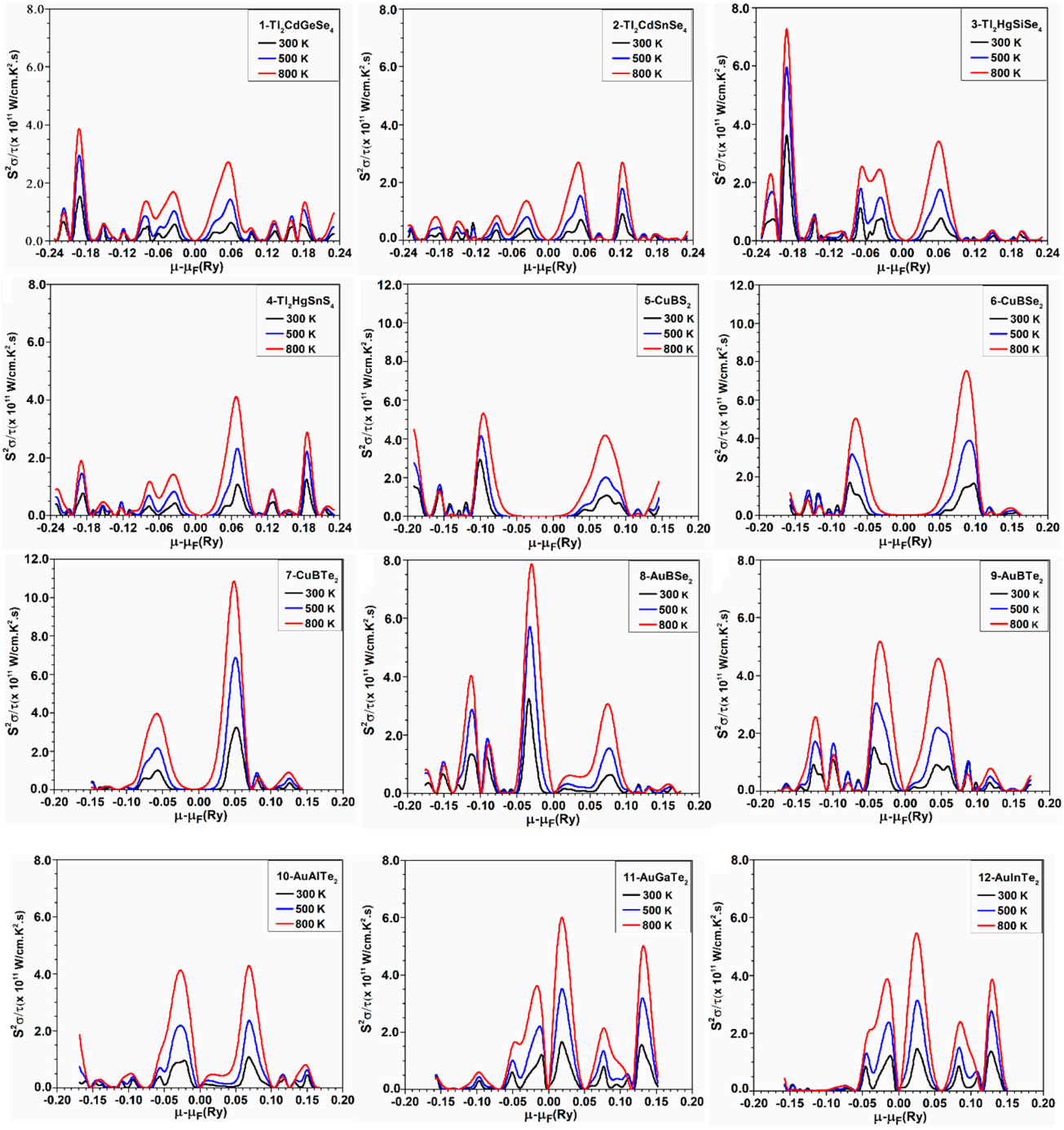


Figure S1. Calculated Seebeck coefficient(S) versus the chemical potential for the crystals from 1-Tl_2CdGeS_4 to 16-$AgAlTe_2$.


1-Tl2CdGeSe4
2-Tl2CdSnSe4
3-Tl2HgSiSe4
4-Tl2HgSnS4
5-CuBS2
6-CuBSe2
7-CuBTe2
8-AuBSe2
9-AuBTe2
10-AuAlTe2
11-AuGaTe2
12-AuInTe2
300 K
500 K
800 K
S2σ/τ(x 10^11 W/cm.K2.s)
μ-μF(Ry)

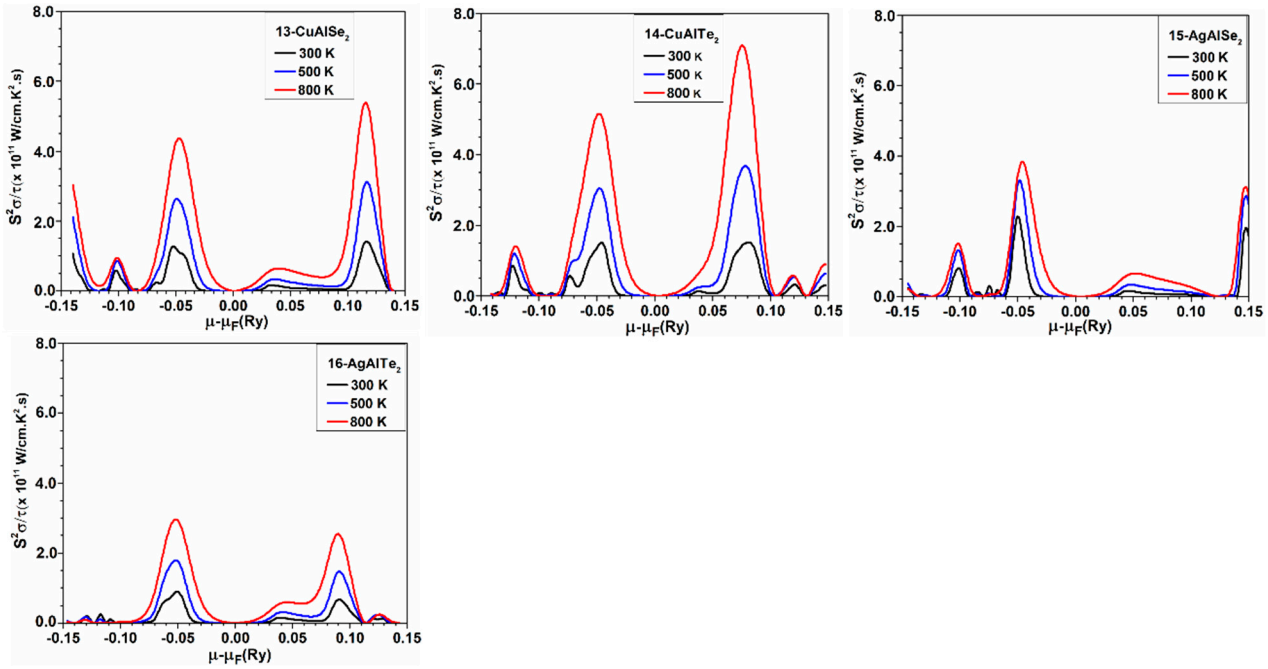
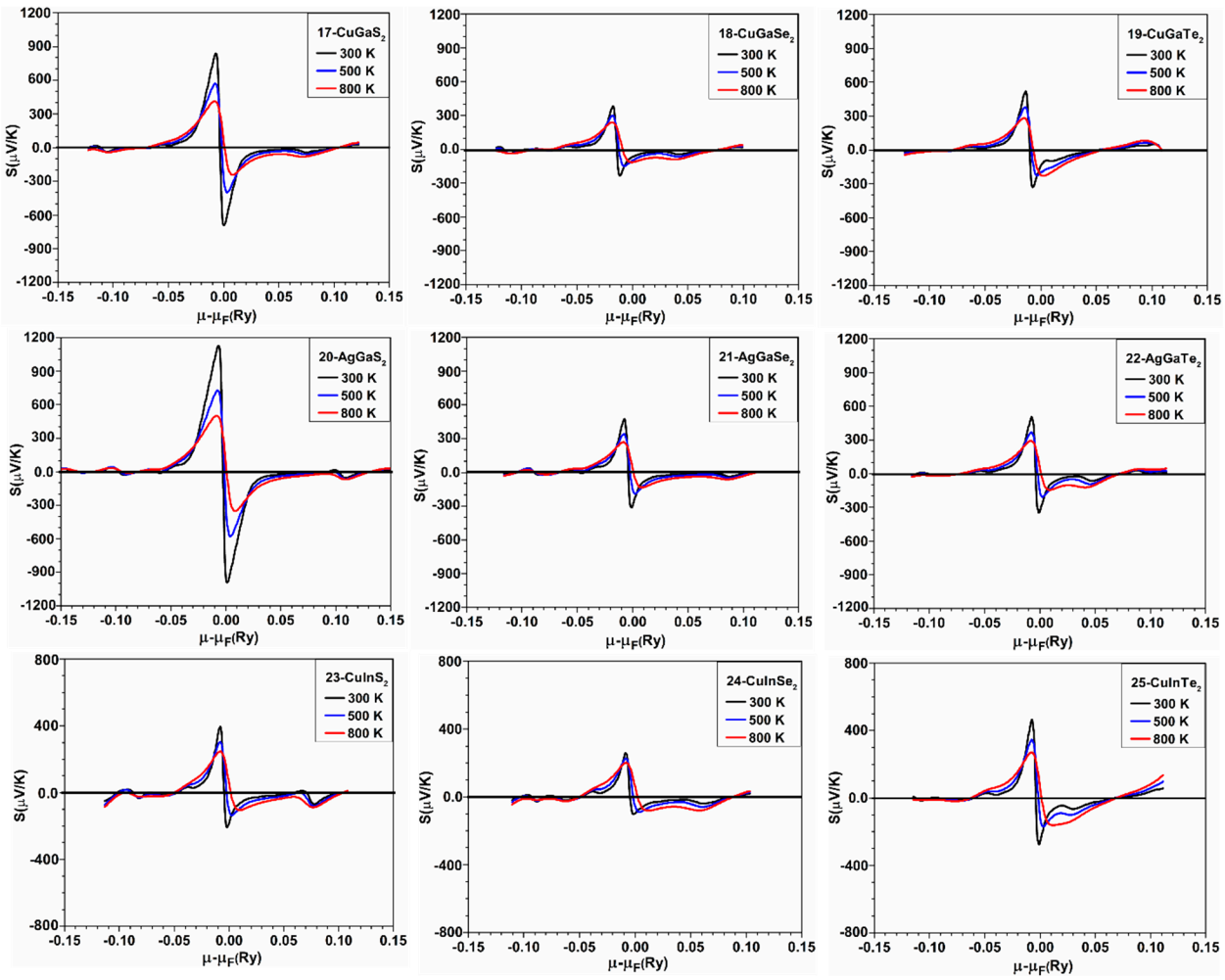


Figure S2. Calculated PF versus the chemical potential for the crystals from 1-Tl2CdGeS4 to 16-AgAlTe2.



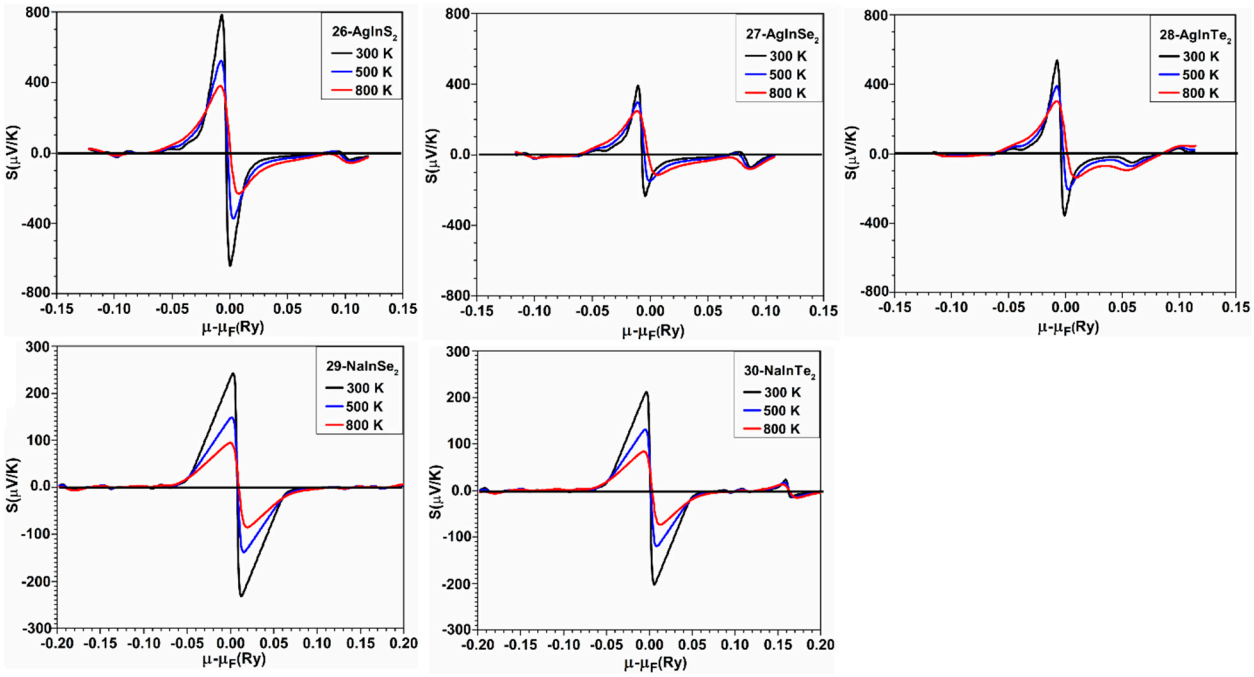
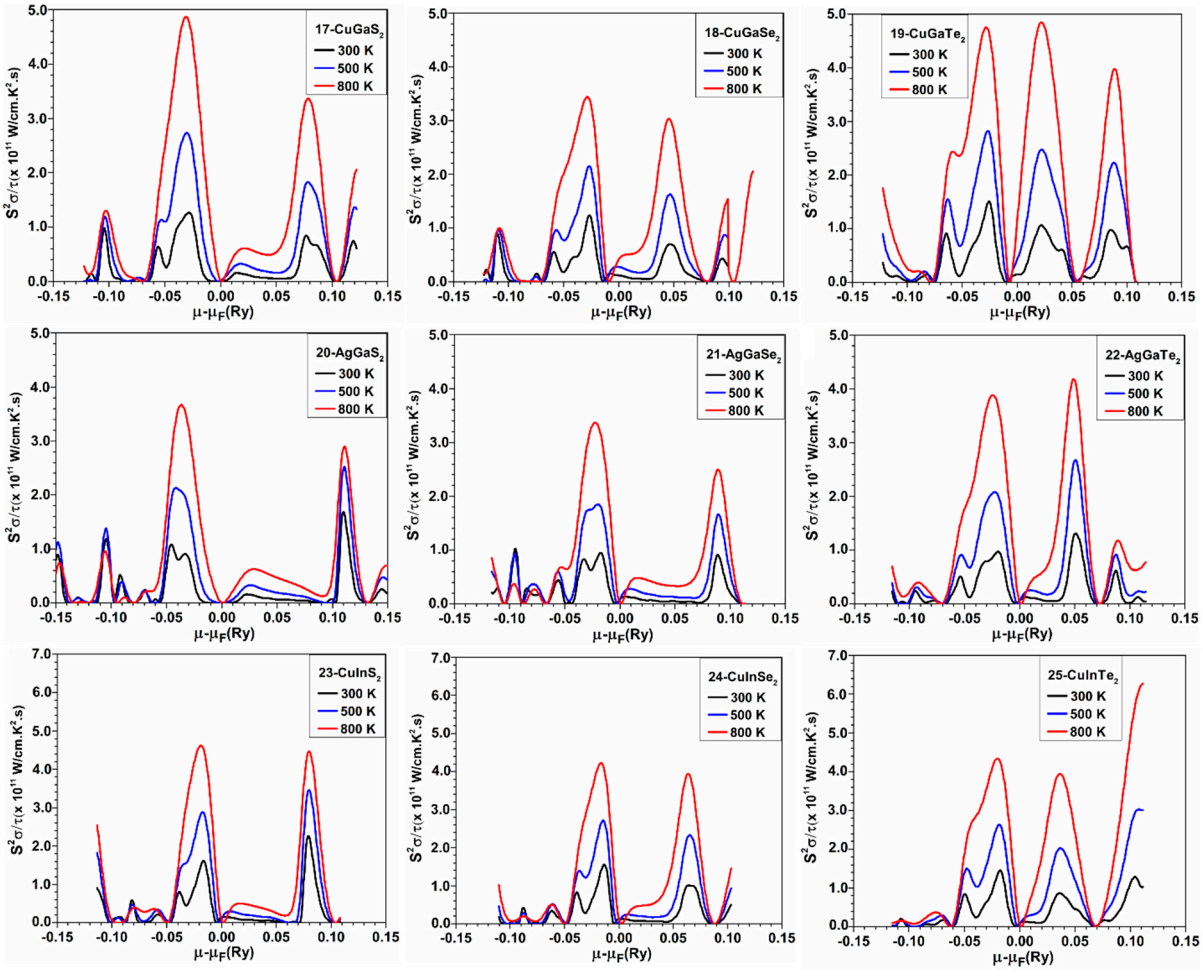


Figure S3. Calculated Seebeck coefficient(S) versus the chemical potential for the crystals from 17-$CuGaS_2$ to 30-$NaInTe_2$.



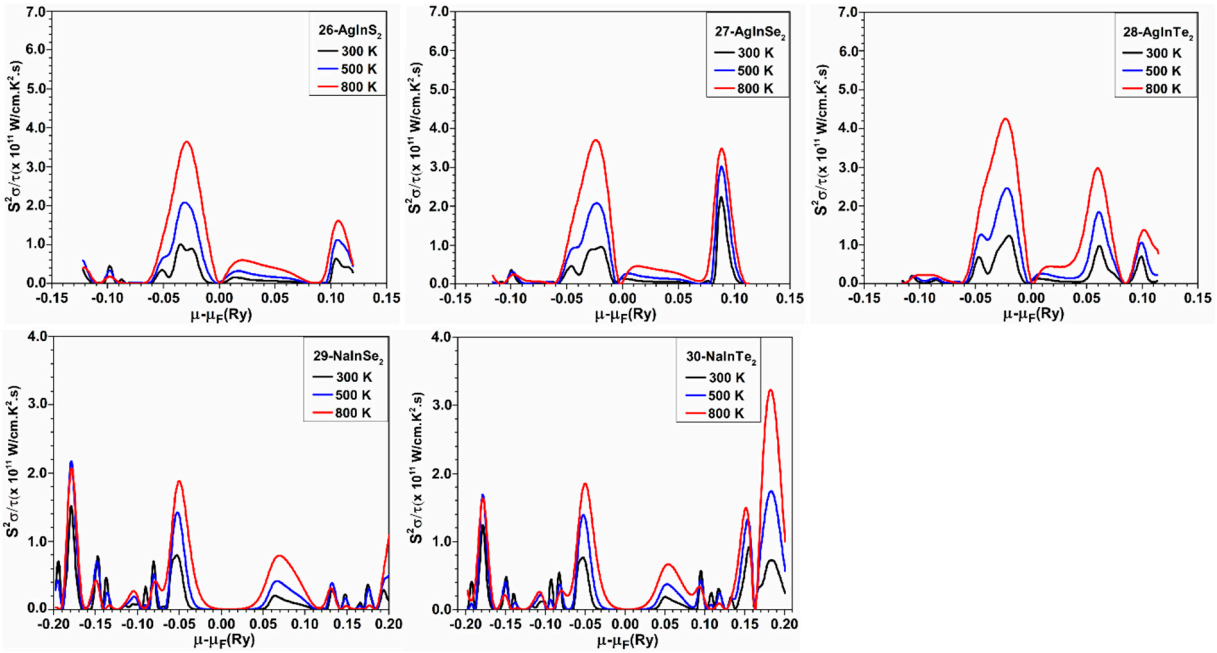
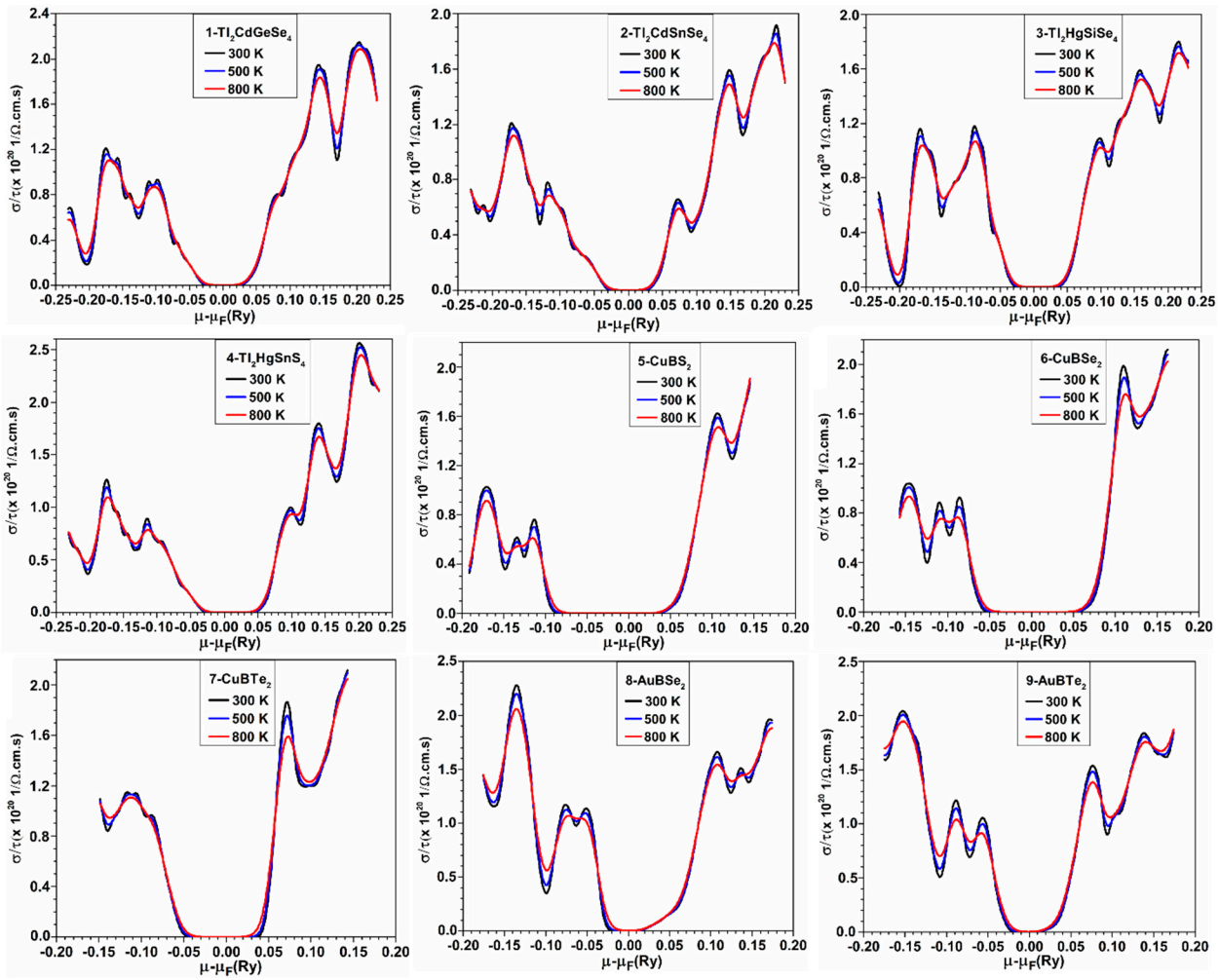
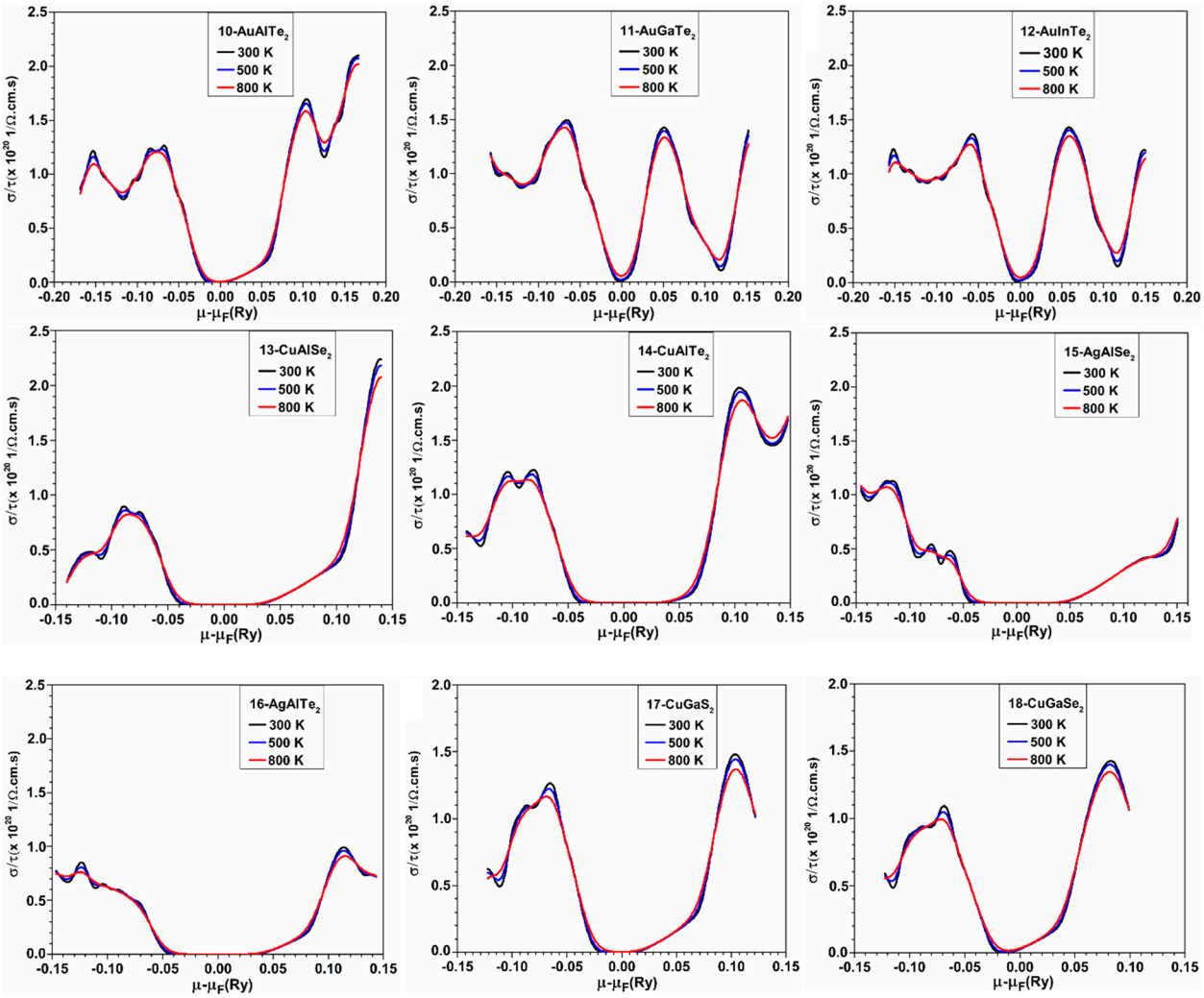


Figure S4. Calculated PF versus the chemical potential for the crystals from 17-$CuGaS_2$ to 30-$NaInTe_2$.




10-AuAlTe2
11-AuGaTe2
12-AuInTe2
13-CuAlSe2
14-CuAlTe2
15-AgAlSe2
16-AgAlTe2
17-CuGaS2
18-CuGaSe2
300 K
500 K
800 K
σ/τ(x 10^20 1/Ω.cm.s)
μ-μF(Ry)

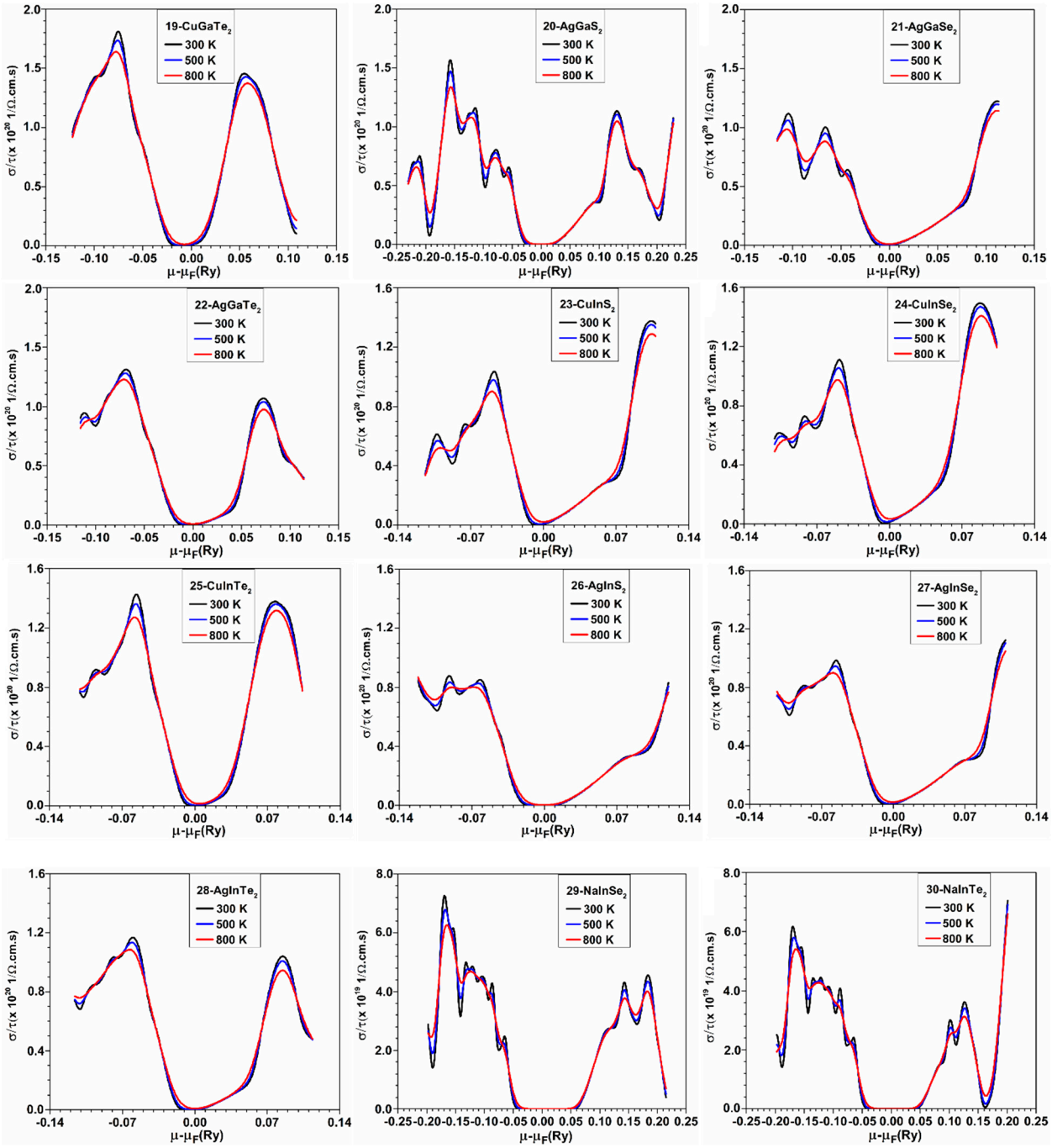
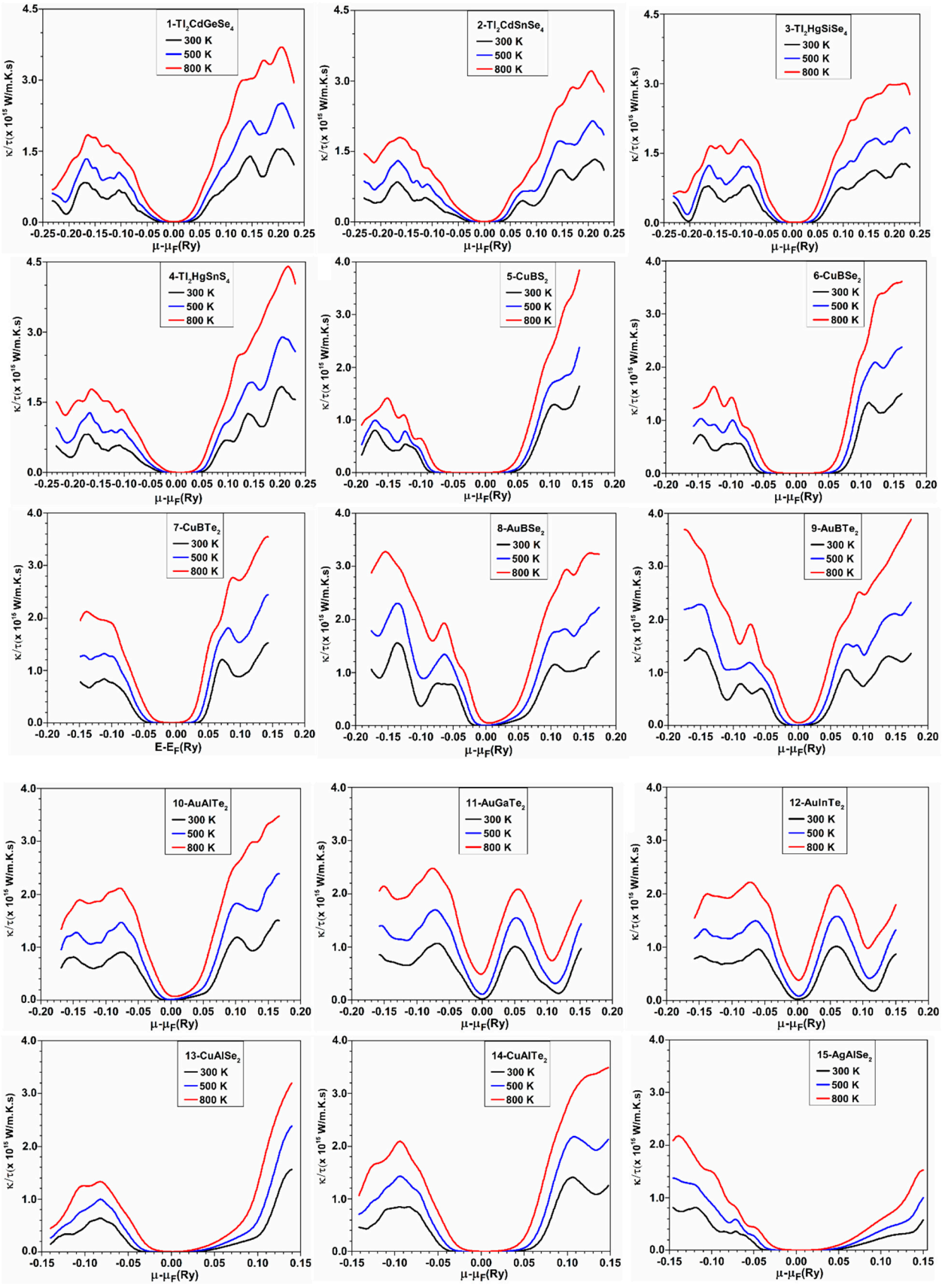


Figure S5. Calculated σ/τ versus the chemical potential for the 30 crystals.


1-Tl2CdGeSe4
2-Tl2CdSnSe4
3-Tl2HgSiSe4
4-Tl2HgSnS4
5-CuBS2
6-CuBSe2
7-CuBTe2
8-AuBSe2
9-AuBTe2
10-AuAlTe2
11-AuGaTe2
12-AuInTe2
13-CuAlSe2
14-CuAlTe2
15-AgAlSe2
300 K
500 K
800 K
κ/τ(x 10^15 W/m.K.s)
μ-μF(Ry)
E-EF(Ry)

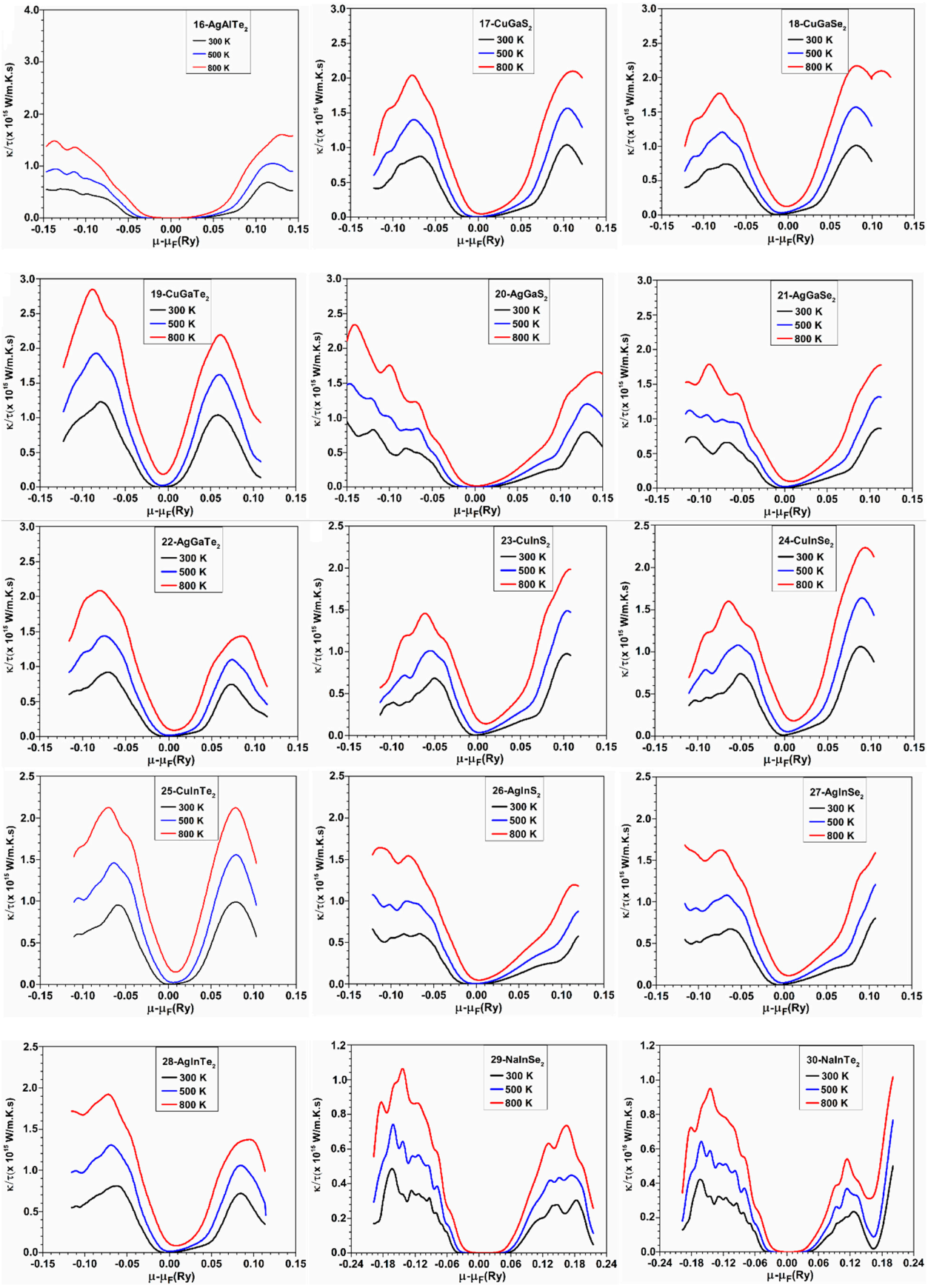
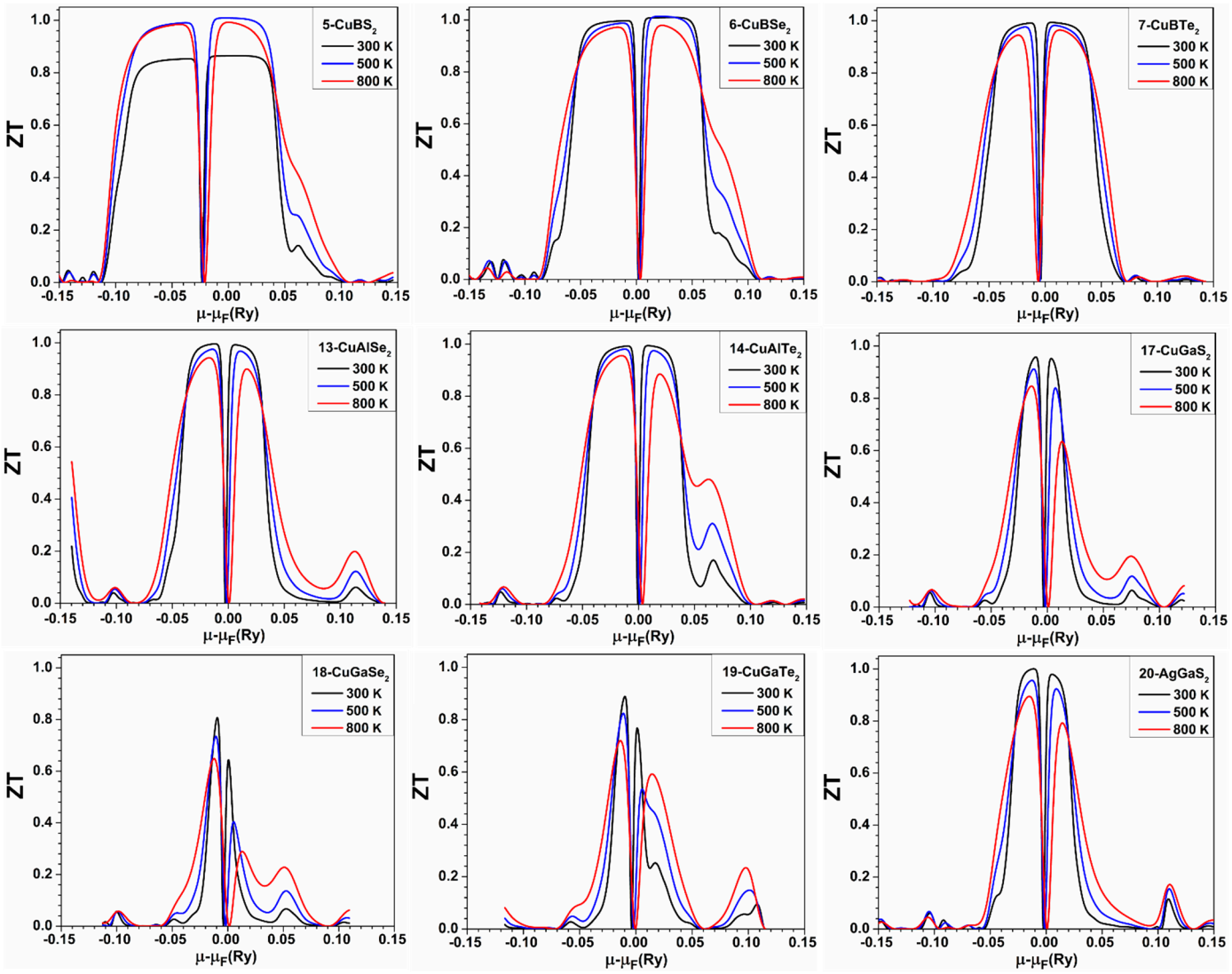


Figure S6. Calculated κ/τ versus the chemical potential for the 30 crystals.


5-CuBS2
6-CuBSe2
7-CuBTe2
13-CuAlSe2
14-CuAlTe2
17-CuGaS2
18-CuGaSe2
19-CuGaTe2
20-AgGaS2
300 K
500 K
800 K
ZT
μ-μF(Ry)

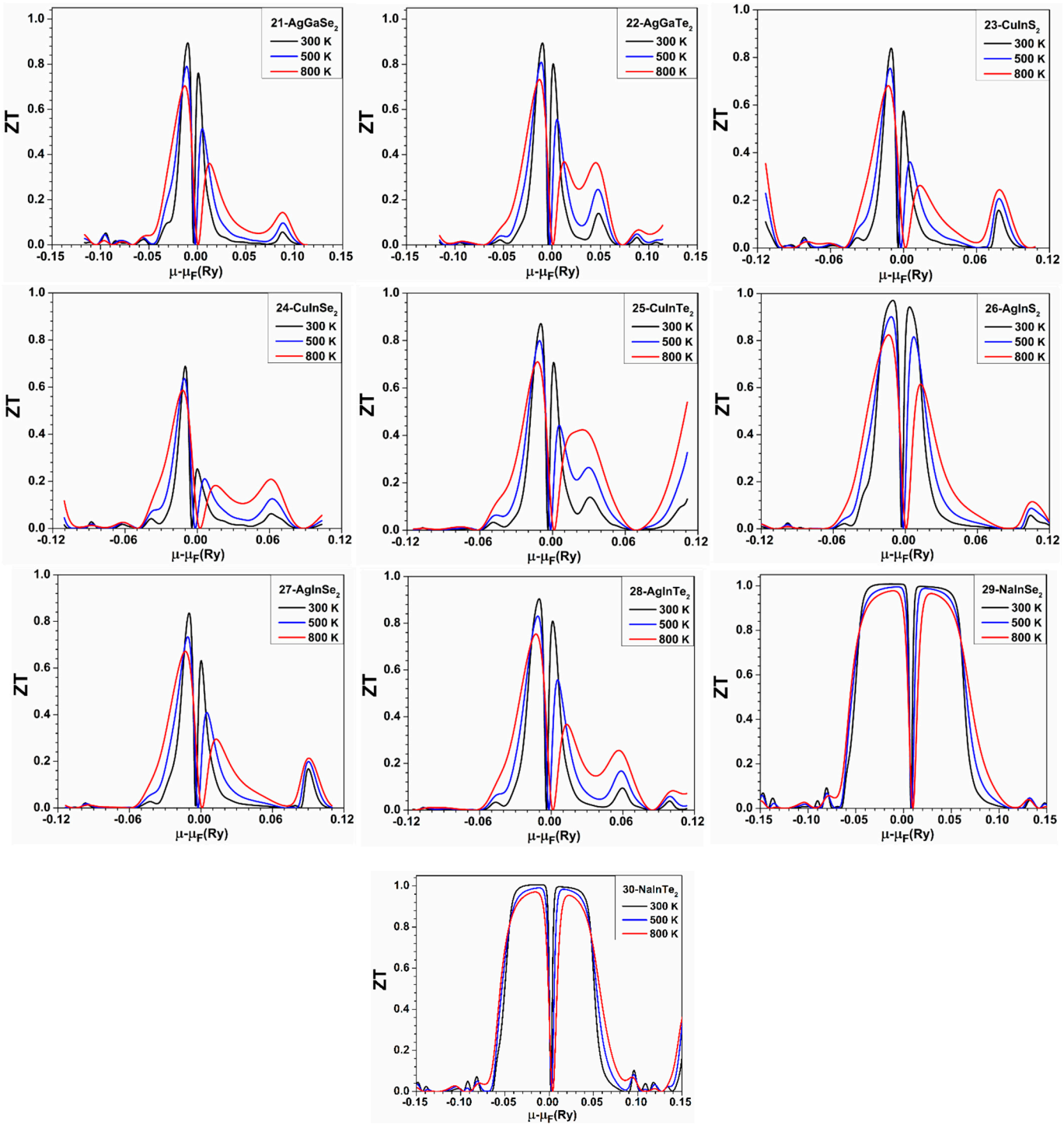


Figure S7. Calculated ZT versus the chemical potential.

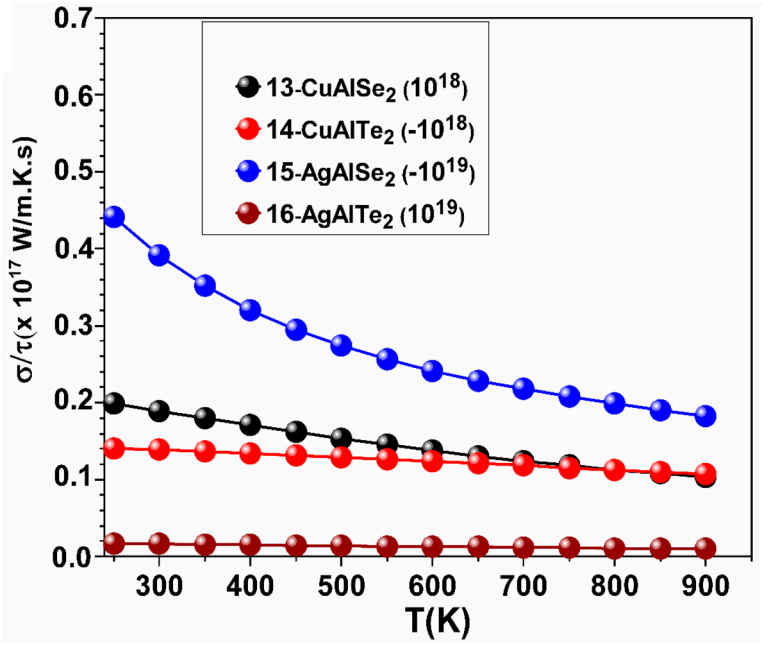


Figure S8. Calculated σ/τ versus the temperature for the crystals 13–16.

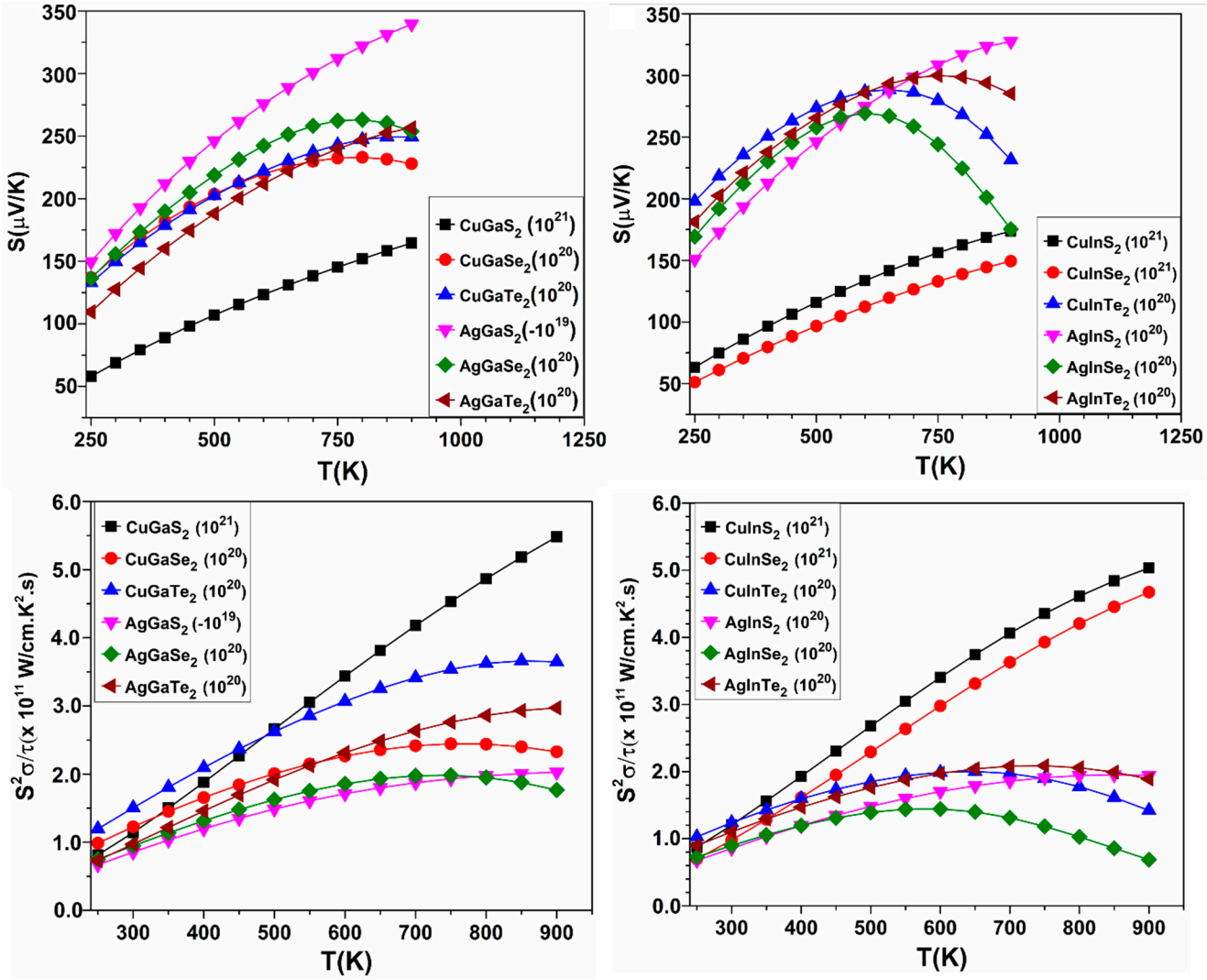


Figure S9. Calculated S and PF versus the temperature for the crystals from 17 to 30.

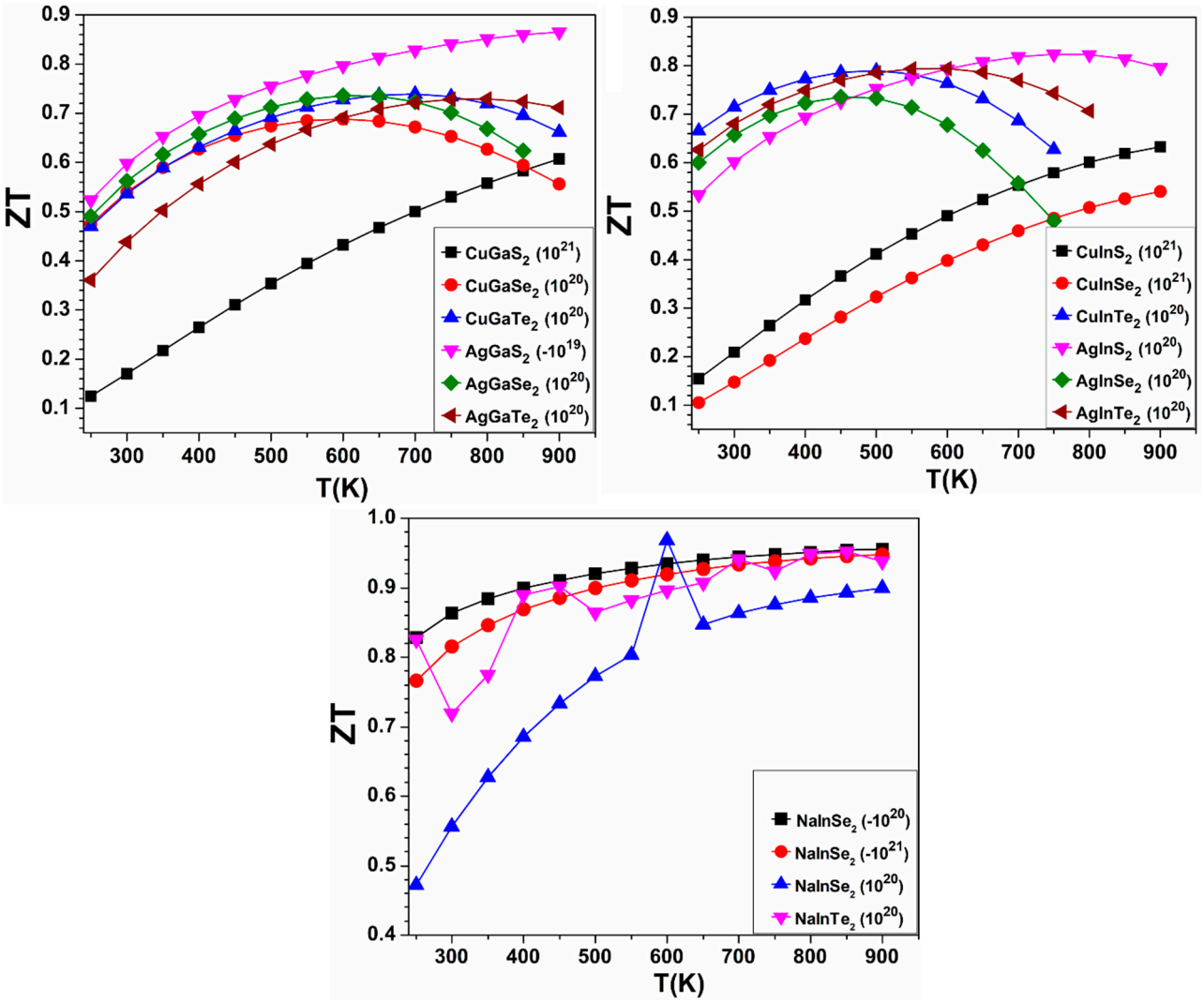


Figure S10. Calculated ZT versus the temperature for the crystals from 17 to 30.

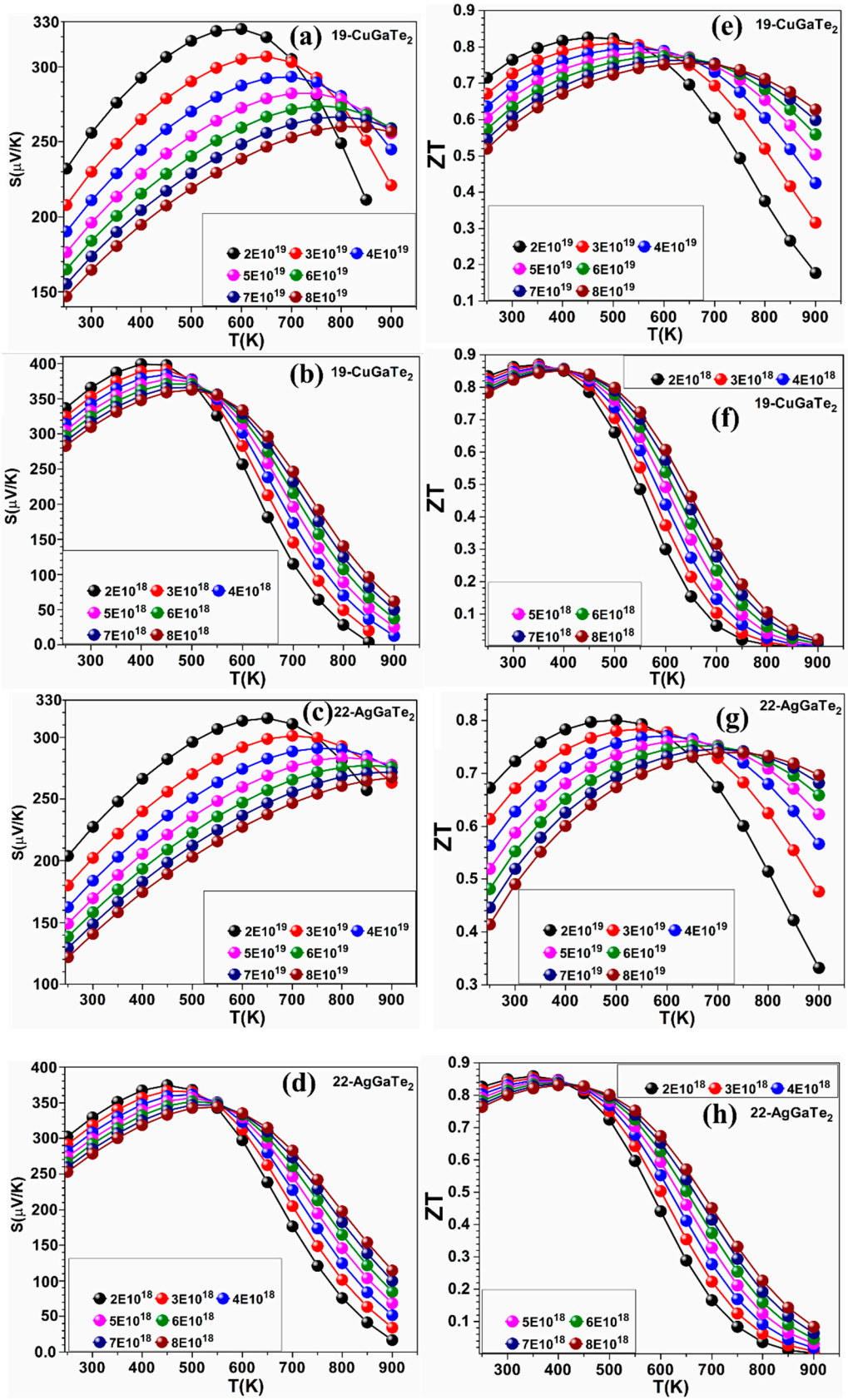


Figure S11. S and ZT versus the temperature for the crystals: (a,b,e,f) are for 19-CuGaTe2 crystal, and (c,d,g,h) are for 22-AgGaTe2 crystal at two different ranges of n.

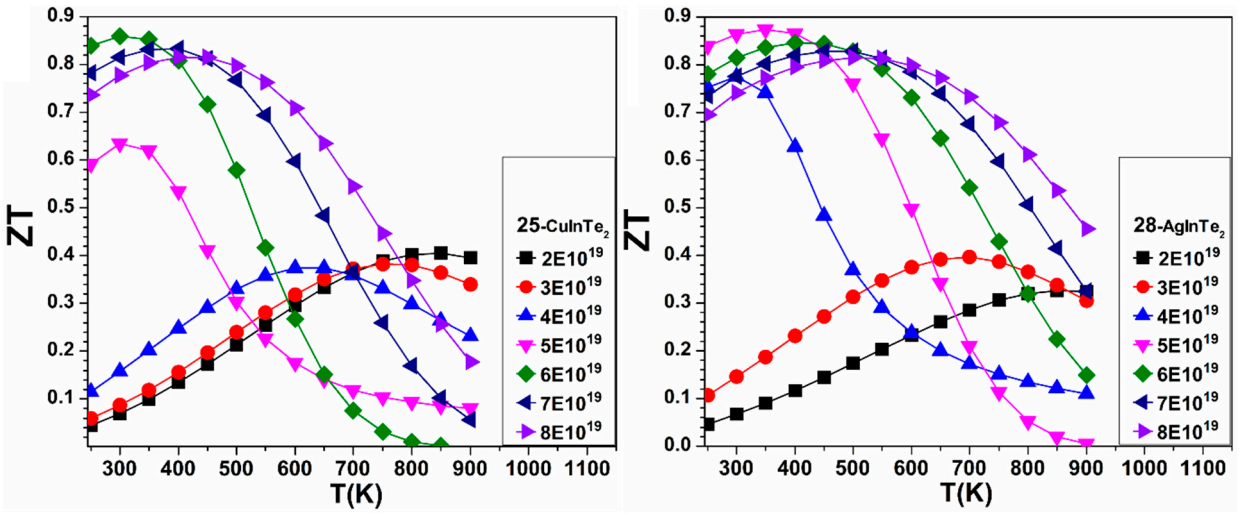


Figure S12. Shows our results for ZT versus temperature at range of n:(+2x10[19], +8x10[19] in e-/cm[3]) for the crystals 25-CuInTe2 and 28-AgInTe2

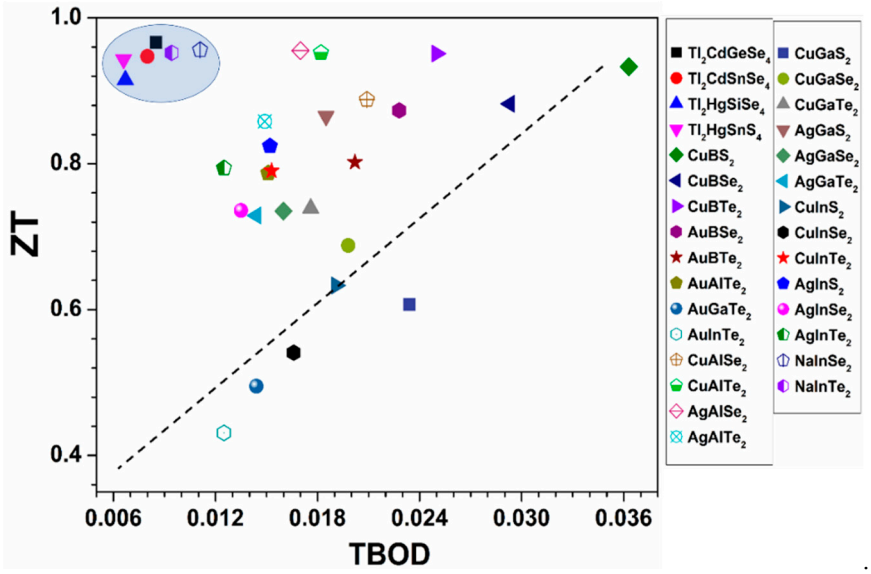


Figure S13. Calculated TBOD versus ZT for the 30 crystals.

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