Electronic Supplementary Information (ESI)

Observation of Valence Band Crossing: The Thermoelectric Properties of the $CaZn_2Sb_2$-$CaMg_2Sb_2$ Solid Solution

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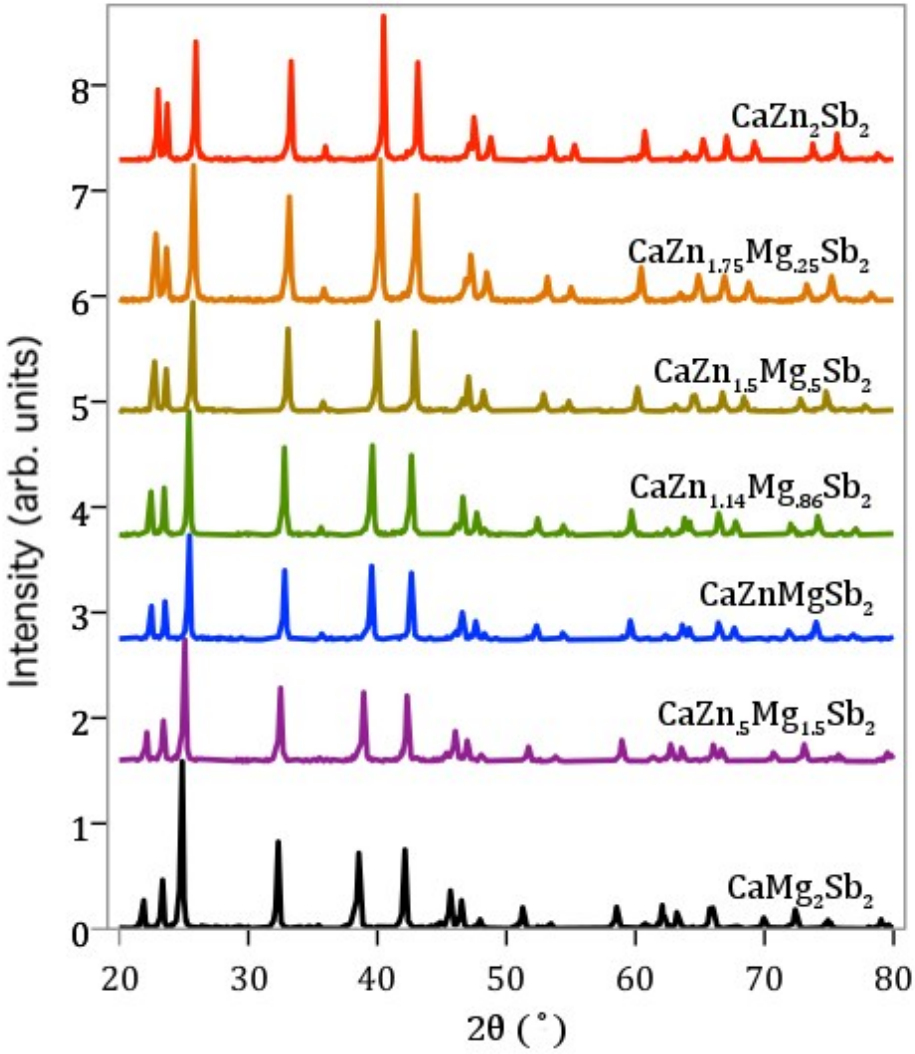

Figure S1. XRD patterns of $CaZn_{2-x}Mg_xSb_2$ samples. Peak shifting due to changing lattice parameter is linear with respect to composition in both the *a* and *c* axes.

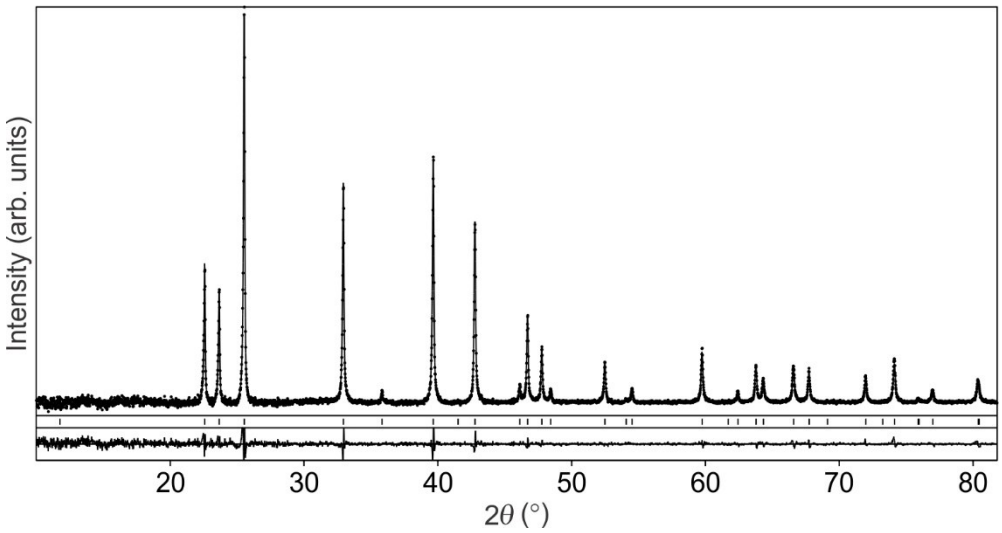

Figure S2: Rietveld fit of $CaZnMgSb_2$ (Cu-K_{a1} radiation). Ticks mark the calculated reflection positions of this Zintl phase while the baseline corresponds to the residuals of a Rietveld refinement ($R_i = 0.03$, $R_p = 0.12$, $R_{wp} = 0.09$) based on the reported crystal structure data [1] [2]. No preferred orientation was observed based on the texture analysis.

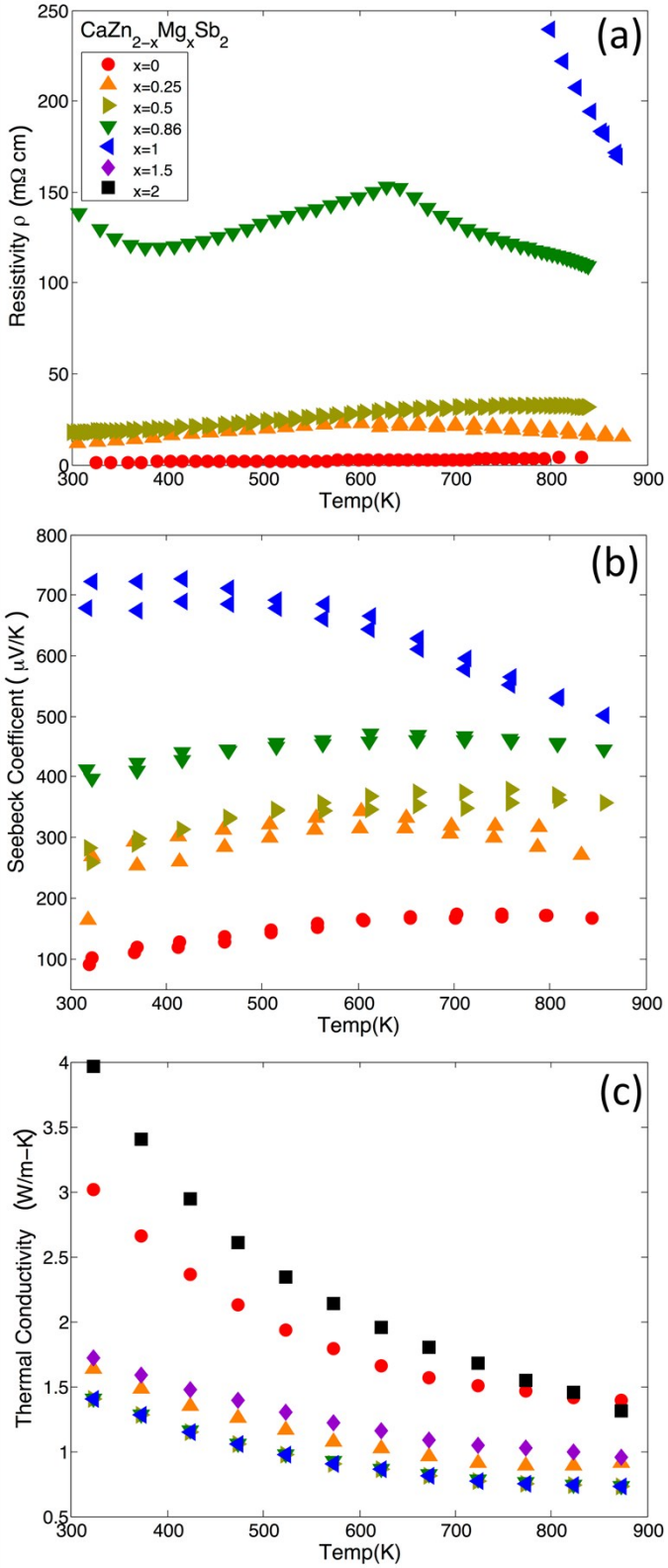

Figure S3. (a) Resistivity, (b) Seebeck, and (c) thermal conductivity data for samples without Na doping.

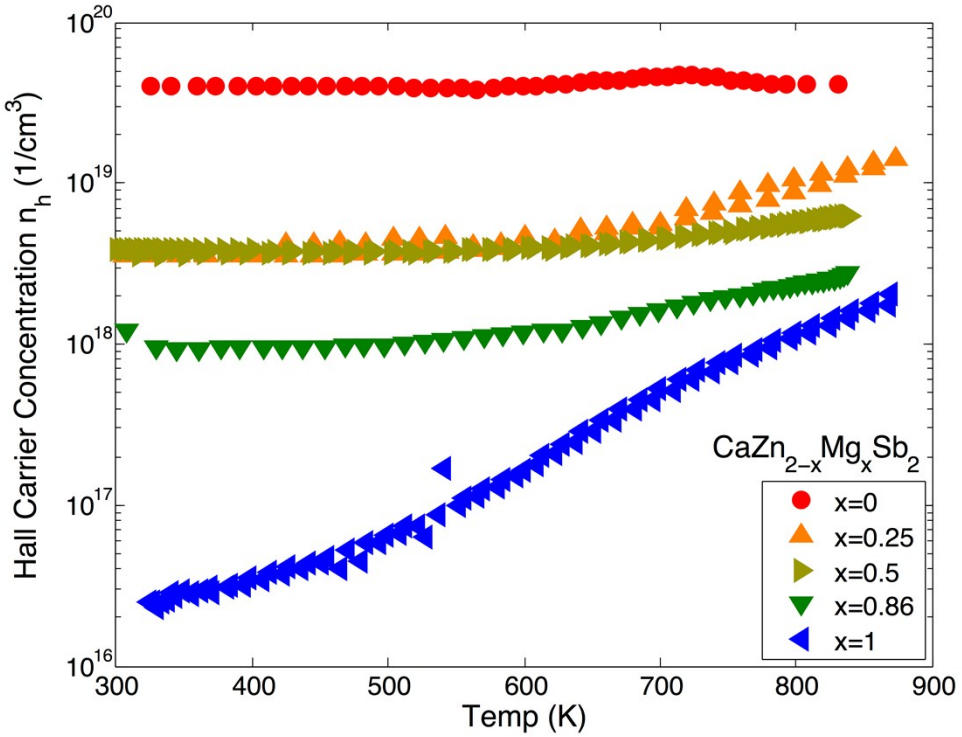

Figure S4. Hall Carrier Concentration for compounds $CaZn_{2-x}Mg_xSb_2$ (x = 0, .25, .5, .86, 1)

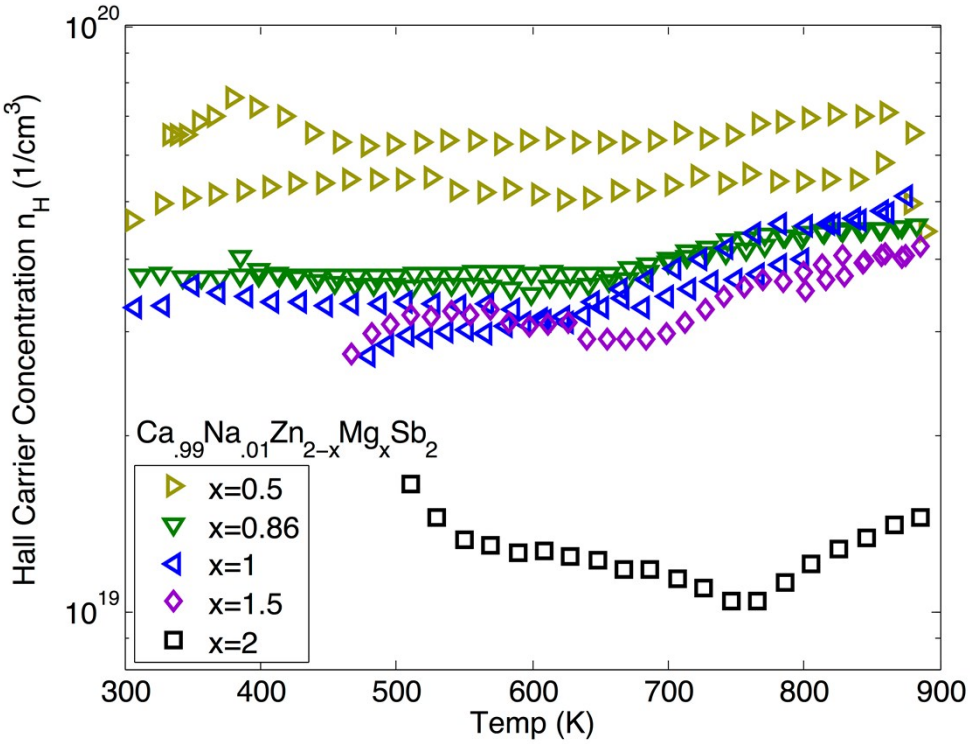

Figure S5. Hall Carrier Concentration for compounds $Ca_{.99}$ $Na_{.01}$ $Zn_{2-x}Mg_xSb_2$ (x = .5, .86, 1, 1.5,2)

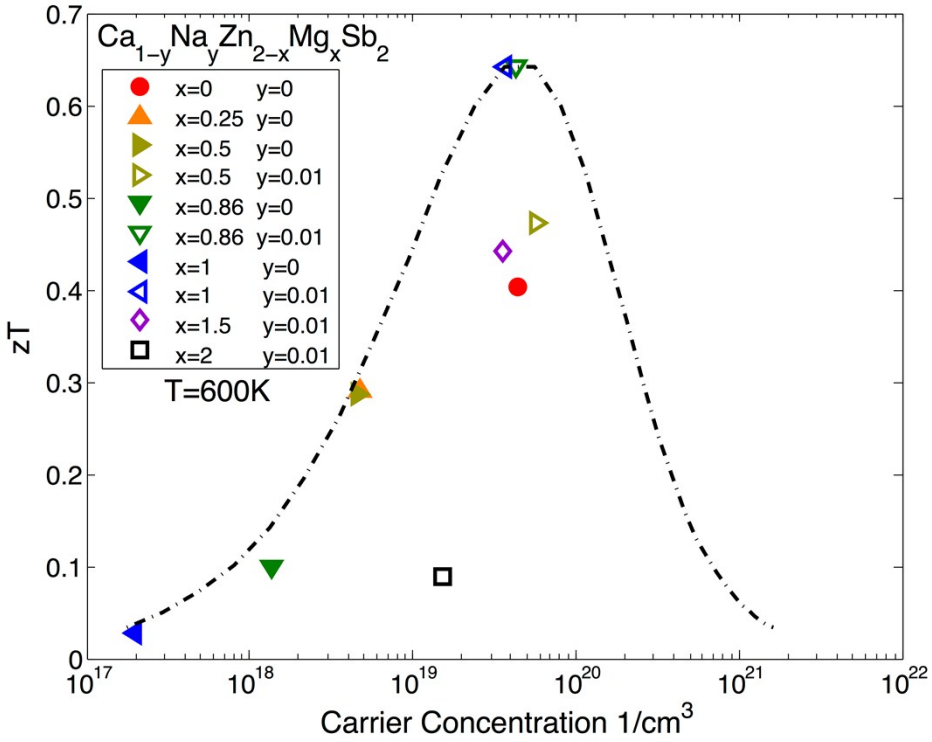

Figure S6. zT vs carrier concentration at 600 K for all samples measured. The calculated curve is based on the sample $Ca_{.99}Na_{.01}MgZnSb2$ that has a unit-less quality factor .218 and an effective mass of $1.011m_e$.

Table 1: Atomic coordinates, displacement parameters (in Å^2) and site occupancy factor (*SOF*) of $CaZnMgSb_2$ (Cu-K_{a1} radiation) in *P*-3*m*1 (R_i = 0.03; R_p = 0.12, R_{wp} = 0.09). Standard deviations are provided in parentheses.

Atom	**Site**	***x***	***y***	***z***	U_{iso}	***SOF***
Ca	1*a*	0	0	0	0.016(5)	1
Zn/Mg	2*d*	1/3	2/3	0.6311(9)	0.015(3)	0.47(2) / 0.53(2)
Sb	2*d*	1/3	2/3	0.2501(6)	0.015(1)	1

References:

1. Mewis, A., *Ab2x2 Compounds with Caal2si2 Structure .4. Crystal-Structure of Cazn2sb2, Cacd2sb2, Srzn2sb2, and Srcd2sb2.* Zeitschrift Fur Naturforschung Section B-a Journal of Chemical Sciences, 1978. **33**(4): p. 382-384.
2. Deller, K. and B. Eisenmann, *Ternary Alkaline Earth Element(V)-Compounds Amg2b2 with a = Ca, Sr, Ba and B = as, Sb, Bi.* Zeitschrift Fur Naturforschung Section B-a Journal of Chemical Sciences, 1977. **32**(6): p. 612-616.