Optimization of thermoelectric properties in f-electron cage-like intermetallic compounds

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ABSTRACT

We report on efforts to enhance the thermoelectric properties of the f-electron cage-like intermetallic compounds YbT_2Zn_{20} (T = Co, Rh, Ir), which were previously shown to exhibit a large figure of merit ($ZT = S^2\sigma T/k$) at low temperatures [1]. The factors that define ZT are the Seebeck coefficient S, electrical conductivity σ, and thermal conductivity k, all of which are set by the unusual crystal structure and stoichiometry of these materials: they are 'electron crystal/phonon glass' materials [2]. To some extent, all materials with mobile electrons exhibit thermoelectric properties but in most cases it is too weak to be of practical use. These '1-2-20' materials provide counter examples, where the presence of *f*-electron states near the Fermi energy results in enhanced S, the abundant conduction electrons produces a large σ, and the large unit cell with a cage like structure minimizes the lattice component of k. By varying the stoichiometry in these compounds through chemical substitution on the Yb-site, we seek to further optimize these quantities.

INTRODUCTION

An effective approach to uncovering materials with enhanced thermoelectric properties is to focus on heavy fermion compounds based on Ce and Yb with large or cage-like structures. The expectation that the Seebeck coefficient is high in these compounds stems from the fact that they sometimes feature a large and rapidly changing density of states near the Fermi energy [3, 4]. The crystal structure is also expected to yield a reduced lattice component of the thermal conductivity. We attempted to produce single crystals of $Yb_{1-x}Ce_xCo_2Zn_{20}$ and $Yb_{1-x}Co_2Zn_{20}$, both of which would increase disorder (lower lattice thermal conductivity) and vary the Kondo lattice energy scale (tune the Seebeck coefficient), by comparison to $YbCo_2Zn_{20}$. We analyzed their properties using energy-dispersive X-ray spectroscopy, magnetic susceptibility (χ), electrical conductivity (σ), thermal conductivity (κ), and Seebeck coefficient (S). These measurements show that small amounts of Yb → Ce is readily substituted into $YbCo_2Zn_{20}$ and that this varies the total effective magnetic moment while preserving the Curie-Weiss behavior. In the intermediate x-range the stoichiometry varies dramatically from the 1-2-20 ratio, suggesting the formation of an unexpected phase.

SAMPLE SYNTHESIS

$Yb_{1-x}Ce_xCo_2Zn_{20}$ and $Yb_{1-x}Co_2Zn_{20}$ crystals were synthesized using the molten metallic flux growth technique. The starting materials were Yb chunks (99.9%, Ames Labs), Ce rods (99.9%, Ames Labs), Co ingots (99.99%, Alfa Aesar), and Zn shot (99.999%, Alfa Aesar). Elements were combined in the atomic ratios Yb:Co:Zn = 0.1:2:60, 0.05:2:60, 0.025:2:60 and Yb:Ce:Co:Zn = 0.75:0.25:2:60, 0.5:0.5:2:60, 0.25:0.75:2:60, 0:1:2:60. The elements were loaded into 2-ml alumina Canfield crucibles and sealed under vacuum in quartz tubes. The quartz tubes were placed in a resistive box furnace then heated to 300°C at a rate of 50°C/hour, held at 300°C for 2 hours, heated to 1050°C at a rate of 50°C/hour, held at 1050°C for 72 hours, then cooled to 700°C at a rate of 4°C/hour, held at 700°C for 48 hours. At this temperature, the samples were removed from the furnace and centrifuged to separate the remaining flux from the precipitated crystals.

CRYSTAL STRUCTURE

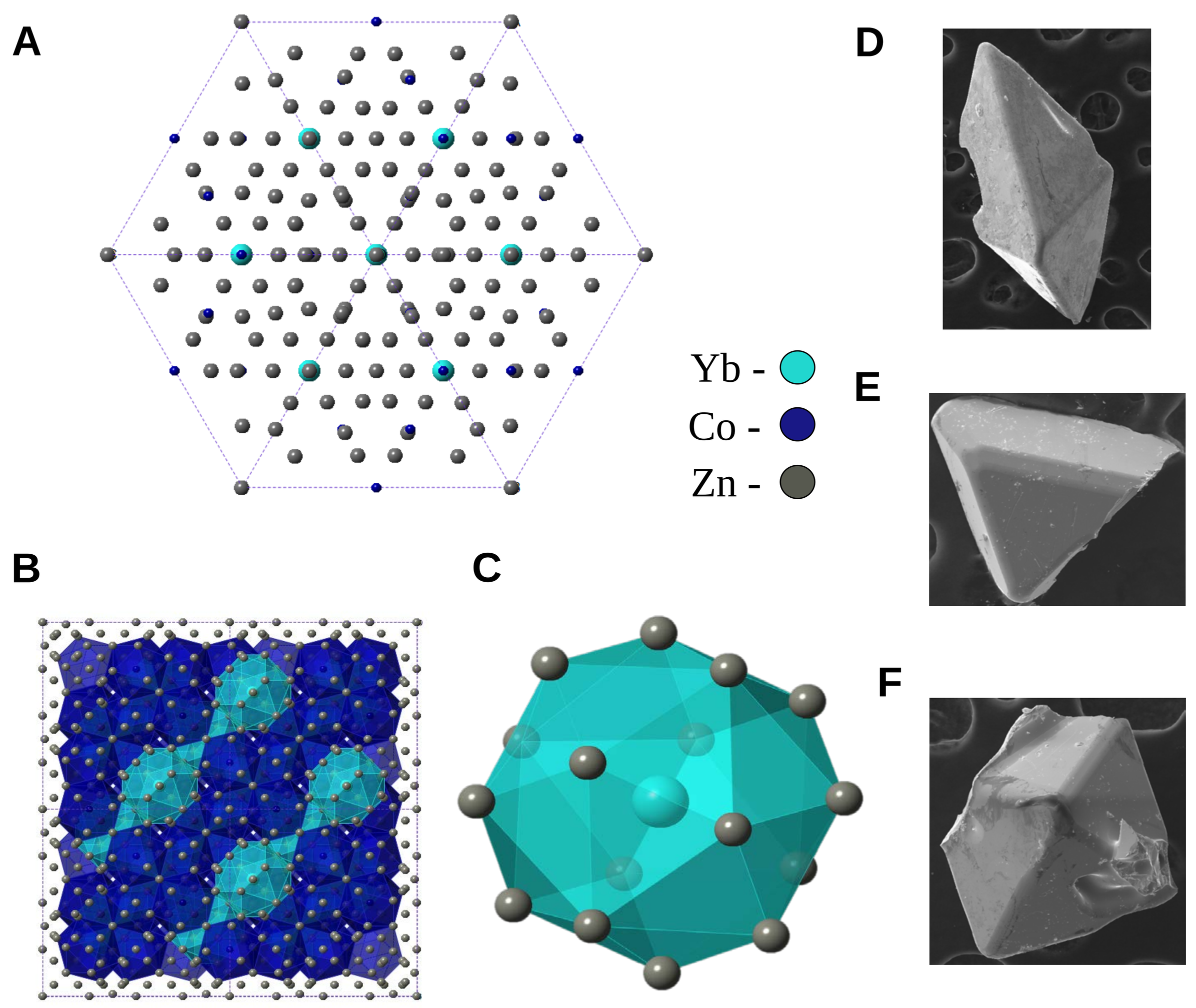

Figure 1: **(A)** [111] directional view of one unit cell of $YbCo_2Zn_{20}$. **(B)** [100] directional view of polyhedron unit cells. **(C)** Single ytterbium ion surrounded by a zinc cage-like structure. The images of the single crystals of $YbCo_2Zn_{20}$ **(D)**, **(E)**, and **(F)** were captured using a Scanning Electron Microscopy (**SEM**).

MAGNETIC SUSCEPTIBILITY

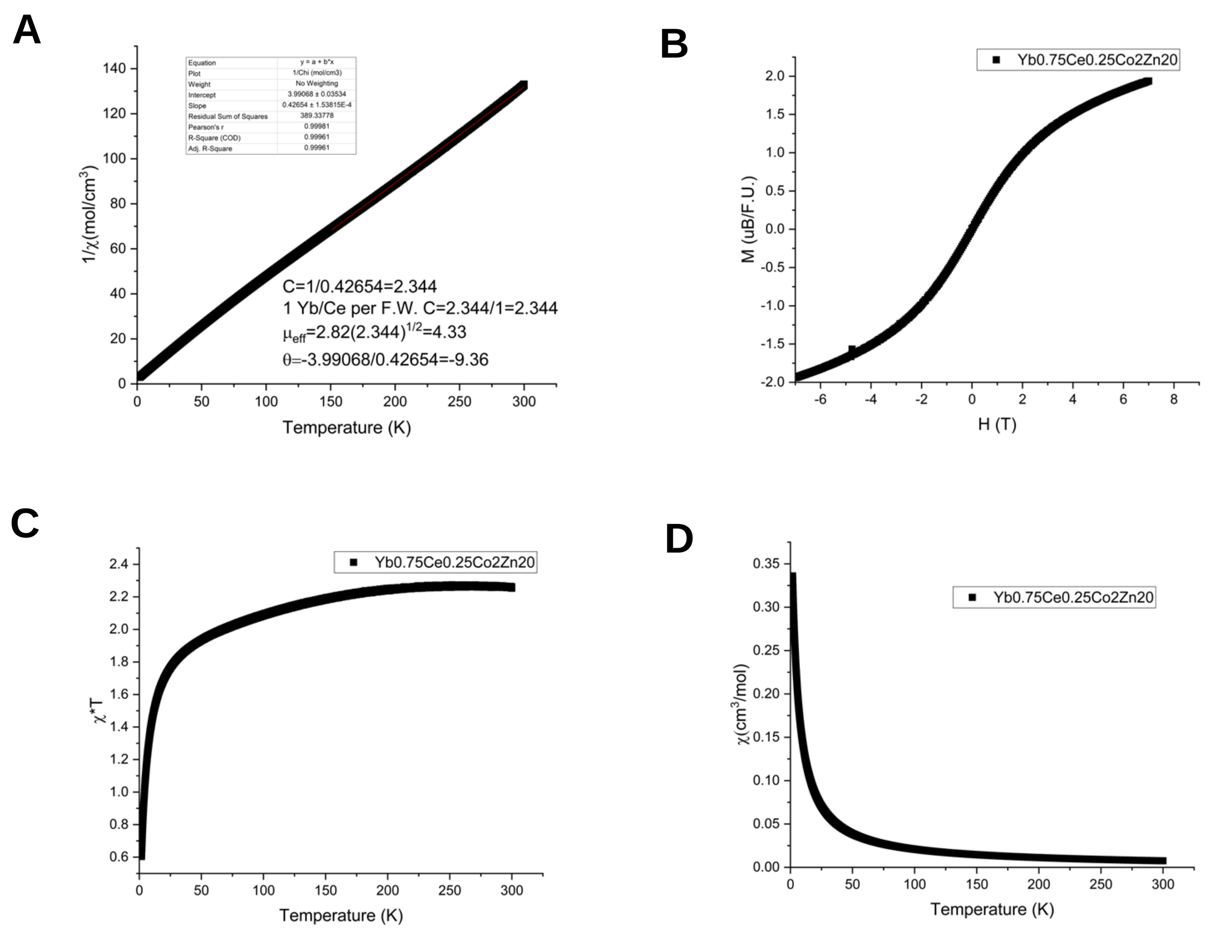

Figure 3: Temperature and field dependent magnetization measurements performed using a Quantum Design VSM Magnetic Property Measurement System (**MPMS**). **(A)** represents the inverse magnetic susceptibility 1/χ vs. temperature T, where the straight line is a Curie-Weiss fit to the data. **(B)** represents magnetization M vs field H. **(C)** represents the product of magnetic susceptibility and temperature χT vs T. **(D)** χ vs T.

THERMOELECTRICS

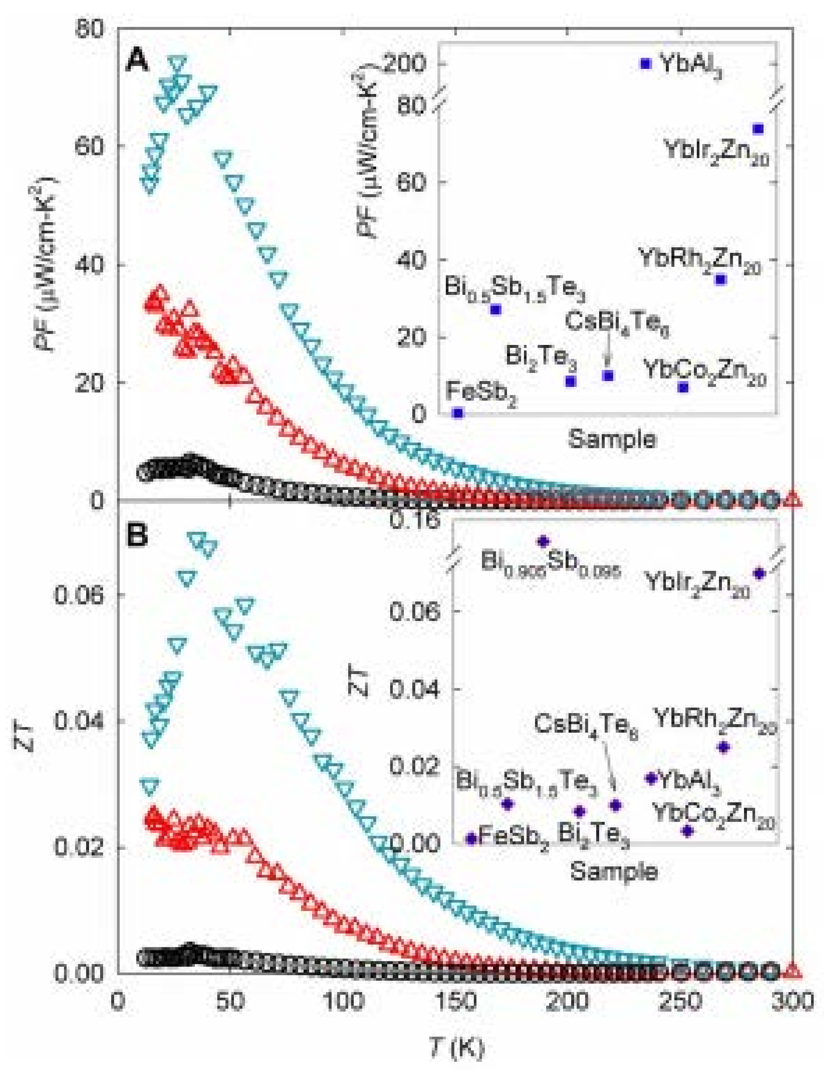

Figure 2: Temperature-dependent **(A)** power factor and **(B)** thermoelectric figure of merit from parent compounds [1]. YbCo2Zn20 (circle), YbRh2Zn20 (up-triangle), and YbIr2Zn20 (down-triangle).

CHEMICAL ANALYSIS

Table A	Target Composition %				EDS Composition %			
Sample #	Yb	Ce	Co	Zn	Yb	Ce	Co	Zn
BS-3	3.26	1.09	8.7	86.96	3.54	1.09	9.03	86.12
BS-4	2.17	2.17	8.7	86.96	1.04	9.925	2.2	86.84
BS-5	1.09	3.26	8.7	86.96	0.56	10.03	2.28	87.14
BS-6	0	4.38	8.7	86.96	0.58	9.87	2.25	87.3
BS-10	3.26	1.09	8.7	86.96	4.01	0.79	9.03	86.17

Table B	Target Composition %			EDS Compostion %		
Sample #	Yb	Co	Zn	Yb	Co	Zn
BS-7	4.24	8.7	86.96	4.85	9.24	85.92
BS-8	4.13	8.7	86.96	4.79	9.13	86.09
BS-9	3.91	8.7	86.96	4.86	9.04	86.11

Figure 4: Energy-dispersive X-ray spectroscopy (**EDS**) used to determine chemical composition. **(Table A)** represents the comparison between the target composition percentage verses the measured EDS composition percentage in $Yb_{1-x}Ce_xCo_2Zn_{20}$. **(Table B)** represents the comparison between the target composition percentage verses the measured EDS composition percentage in $Yb_{1-x}Co_2Zn_{20}$.

PHENOMENOLOGICAL THEORY

Thermoelectric Figure of Merit

$$ZT = \frac{S^2\sigma}{\kappa}T$$

- S - Seebeck coefficient
- T - absolute temperature
- κ - thermal conductivity
- σ - electrical conductivity

Seebeck coefficient

$$S = \frac{\Delta V}{\Delta T}$$

- S - Seebeck coefficient
- V – electric potential
- T - temperature

Power Factor

$$PF = \frac{S^2}{\rho}$$

- S - Seebeck coefficient
- ρ - electrical resistivity

CONCLUSIONS

- Based on EDS data, the target concentrations of Yb and Ce were successfully substituted for the $Yb_{0.75}Ce_{0.25}Co_2Zn_{20}$ compound.
- Magnetic susceptibility data from $Yb_{0.75}Ce_{0.25}Co_2Zn_{20}$ proves that the total effective magnetic moment value varies from the Yb standard of $4.5\mu_B$ to the measured $4.33\mu_B$, while retaining the Curie-Weiss behavior.
- The stoichiometry alters dramatically from the target compositions at ratios other than $Yb_{0.75}Ce_{0.25}Co_2Zn_{20}$, this indicates the formation of an unexpected phase in BS-4, BS-5, and BS-6.

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FUTURE WORK

- Measure the temperature-dependent power factor and thermoelectric figure of merit for BS-10 and BS-9 to determine weather the disorder has caused enhanced thermoelectric properties.
- Further characterize the BS-4, BS-5, and BS-6 compounds that provided an unexpected phase.

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