

Hydride assisted synthesis of the high temperature thermoelectric phase: $\text{Yb}_{14}\text{MgSb}_{11}$

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ABSTRACT

$\text{Yb}_{14}\text{MnSb}_{11}$ is a p-type high temperature thermoelectric material that has been shown to have a peak zT of 1.3 at 1273 K and stable lifetime testing at that temperature for over 1500 h by NASA. $\text{Yb}_{14}\text{MgSb}_{11}$ is a structural analog, but the highest temperature thermoelectric properties have not yet been reported. $\text{Yb}_{14}\text{MgSb}_{11}$ has been prepared in an environmentally friendly route employing metal hydrides to provide phase pure samples with excellent control of stoichiometry. We present a comparative study employing either MgH_2 or YbH_2 as a reactive precursor that also facilitates milling of the elements. High purity compositions are synthesized, and their high temperature thermoelectric properties were measured on dense pellets. Temperature-dependent thermoelectric properties were measured from 300 to 1273 K. $\text{Yb}_{14}\text{MgSb}_{11}$ exhibited a peak $zT = 1.2$ at 1273 K due to an appreciable power factor and low-lattice thermal conductivity. Carrier concentration and hall mobility were also measured from 300 to 1275 K and ranged from 5.3×10^{20} to $1.3 \times 10^{21} \text{ cm}^{-3}$ and from 4.7 to $0.7 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, respectively.

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INTRODUCTION

High energy ball milling can be a green, energy efficient process that creates a homogeneous powder through the mechanical pulverization of metallic precursors. The product can sometimes be prepared *in situ* or can be reacted to form a product during an annealing step, or directly through spark plasma sintering (SPS). After milling, any one portion of the prereacted powder should have at least the elemental composition of the desired product. Often, due to the malleability of certain metals (Yb, Mg, Ca, Eu, K, etc.), sample compositions become deficient on the cation side as a consequence of materials cold welding or sticking to the surfaces of the vials. There are several different approaches to address this problem such as milling more electronegative elements before adding malleable ones, using binary precursors which are more brittle, or accounting for the loss through elemental excess.¹

Metal hydrides are commercially available as fine powders due to the changed nature of the bonding within the metal. With an increase in surface area and low decomposition temperatures, metal

hydrides show increased reactivity allowing for lower temperature synthesis.^{2,3} The use of hydrides as reactive precursors in the synthesis of thermoelectric materials has been shown to facilitate the formation of otherwise difficult to synthesize Zintl phases and clathrates.^{2,4–10} The metal hydrides provide for stoichiometric reactions to products whereas the use of ductile metals requires a systematic study in stoichiometry adjusted for metal loss. The employment of malleable metals leads to homogeneity issues that depend strongly on the particle size of the starting material, time, and energy of the milling process. Hydrides, on the other hand, can be precisely massed, decompose during annealing, and the hydrogen produced could reduce any oxides present, providing a high quality, oxide-free product.

Zintl phases have shown great potential for thermoelectric applications but many with the highest zT contain Yb, Mg, or other malleable metals.^{11–19} Finding an efficient route to high quality homogeneous materials that is also scalable and reproducible is important for device applications. Thermoelectric generators consist of a heat source and a series of p and n type

semiconductors that are connected electrically in series and thermally in parallel. If their thermal conductivity is low and their electrical conductivity is high, a thermal gradient will be created across the material. This leads to the excitation of carriers on the hot side, which subsequently flow toward the cold side, leading to usable electricity. The efficiency at which a material performs this conversion is directly related to the unitless thermoelectric figure of merit, $zT = S^2\sigma T/\kappa$. Here, S is the Seebeck coefficient, or voltage, created per degree of temperature gradient, σ is the electrical conductivity: the inverse of resistivity (ρ), T is absolute temperature, and κ is the thermal conductivity of the material. In order to maximize efficiencies in a material, all these factors need to be optimized. However, these variables are all inter-related through carrier concentration, which makes optimization difficult.

The $A_{14}MPn_{11}$ family of Zintl phase materials (Fig. 1) has over 30 members ($A = \text{Yb, Eu, Ca, Sr, Ba}$; $M = \text{Mg, Mn, Zn, Cd, In, Al, Ga}$; $Pn = \text{P, As, Sb, Bi}$), some of which have promising thermoelectric properties.¹³ $\text{Yb}_{14}\text{MgSb}_{11}$ is a member of this family and has a reported zT of 1.05 at 1075 K.²⁰ Its crystal structure is defined by 13 Yb^{+2} , Yb^{+3} , $[\text{MgSb}_4]^{-10}$ tetrahedra, Sb_3^{-7} linear unit, 4 Sb^{-3} . In single crystals, it has also been shown that the Yb site can accommodate about 0.2 Mg to yield $\text{Yb}_{13.8}\text{Mg}_{1.2}\text{Sb}_{11}$.²¹ In order to get optimal thermoelectric properties, samples with the $\text{Yb}_{14}\text{MgSb}_{11}$ stoichiometry and minimized side phases are desired. In this paper, we employ MgH_2 and YbH_2 as reactive precursors for the synthesis of high purity $\text{Yb}_{14}\text{MgSb}_{11}$ in order to provide a high quality material with efficiencies beyond a zT of 1 at high temperatures.

SAMPLE SYNTHESIS AND CHARACTERIZATION

In an Ar filled glove box ($\text{H}_2\text{O} < 1$ ppm), stoichiometric amounts of elemental Yb filings (Edge Tech, 99.99%), Sb shot

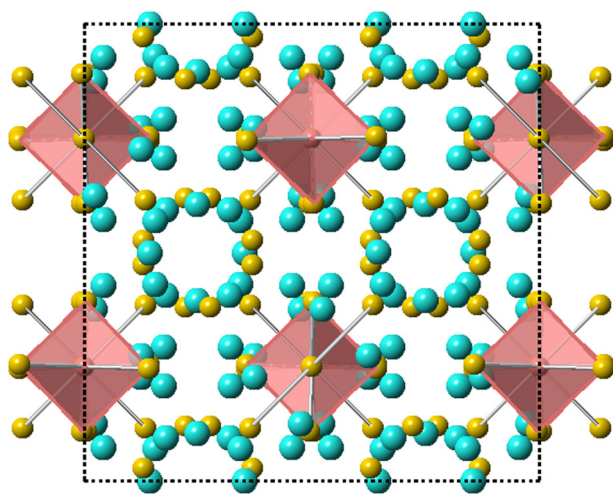


FIG. 1. A view of the $A_{14}MPn_{11}$ structure type (tetragonal, $I4_1/acd$) looking down the c axis. A is shown in cyan, Pn is in gold, and M is in red and centered in the semitransparent red tetrahedra.

(5Nplus, 99.999%), and Mg chips (Strem Chemicals, 99%) were added to a 65 cm^3 stainless steel ball mill with one 12.7 mm diameter stainless steel ball (Spex). Reactions were also performed with either YbH_2 (American Elements, 99.999%, purchased as Yb powder)^{8,9} or MgH_2 (Alfa Aesar, 98%). Reactions were sealed under Ar in Mylar bags and milled for 3 rounds of 30 min each with scraping in between 2nd and 3rd in an Ar(g) filled glovebox. The resultant black powder was transferred to a Nb tube which was sealed at both ends under Ar and jacketed inside an evacuated quartz tube. The tube was annealed for 4 days at 800 °C after which it was removed and quenched at room temperature in air. The reactions are summarized in Table I.

The composition of polycrystalline samples was analyzed by powder X-ray diffraction (PXRD) using a Bruker D8 Eco Advanced with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54$ Å) and a Ni filter to remove $\text{Cu K}\beta$. Diffraction experiments were performed using a zero background off-axis quartz plate at room temperature. Diffraction patterns were analyzed by Rietveld refinement using the JANA 2006 software package.²² Samples were consolidated into pellets using spark plasma sintering (SPS, Dr. Sinter Lab Jr., Fuji Corp.). Powders were loaded under an inert atmosphere into a graphite die with an inner diameter of 12.7 mm, a height of 30 mm, and a 30 mm outer diameter with a hole for thermocouple placement for temperature measurement. The die was heated to 800 °C under dynamic vacuum, and the force was increased from 2 to 7 kN as the sample began to sinter. Resultant pellet densities were greater than 90% of theoretical crystallographic density for those synthesized with YbH_2 and greater than 94% for those with MgH_2 . Thermal diffusivity was measured on densified pellets using Laser Flash Analysis (Netzsch LFA 475 Microflash) under Ar(g) flow. The Seebeck coefficient and resistivity measurements were collected at UC Davis on a Linseis LSR-3 using a 4-probe method with 8 mm probe spacing and a 50 °C thermal gradient. Densified pellets were shaped into $1 \times 1 \times 10$ mm³ rectangular prisms for this measurement. Resistivity and Hall carrier concentrations were measured at the Jet Propulsion Laboratory (JPL) using the Van der Pauw method with a current of 100 mA and a 1.0 T magnet on a specialized high temperature instrument.²³ Seebeck coefficients were measured also at JPL using a custom instrument, which uses the light pipe method with tungsten-niobium thermocouples under high vacuum.²⁴ Elemental analysis was performed using electron probe microanalysis (EPMA) (Cameca SX-100) utilizing backscattered electron mode and x-ray elemental mapping using MgO , Sb , and a $\text{Yb}_{14}\text{MgSb}_{11}$ single crystal as standards.

RESULTS AND DISCUSSION

Synthesis and PXRD

Bulk polycrystalline samples of $\text{Yb}_{14}\text{MgSb}_{11}$ were synthesized by the reaction of stoichiometric amounts of the powders employing YbH_2 (YBH) as described above over 4 days at 800 °C, lower than what has been previously reported for the same compound. A large (1.5) excess of Mg was required in order to avoid the formation of a common side phase, $\text{Yb}_{11}\text{Sb}_{10}$, in this reaction. The resultant product provided diffraction patterns that were well refined by Rietveld refinement and were indexed fully as the tetragonal phase pure compound, $\text{Yb}_{14}\text{MgSb}_{11}$ (Rp: 6.78, wRp: 8.92; see the

TABLE I. A summary of reaction compositions, milling schemes, and annealing profiles.

Sample	Reactants	Milling	Anneal
YBH $\text{Yb}_{14}\text{MgSb}_{11}$	13 Yb + 1 YbH_2 + 1.5 Mg + 11 Sb	3 × 30 min	800 °C for 4 days in Nb
MGH $\text{Yb}_{14}\text{MgSb}_{11}$	14 Yb + 1.2 MgH_2 + 11 Sb	3 × 30 min	800 °C for 4 days in Nb

[supplementary material](#)). The unit cells of samples prepared with YbH_2 are $a = 16.6159(1) \text{ \AA}$, $c = 22.2539(1) \text{ \AA}$, and $V = 6144.1(1) \text{ \AA}^3$. The lattice parameters are consistent with those previously reported for single crystals [$a = 16.625(1) \text{ \AA}$, $c = 22.24(1) \text{ \AA}$, $V = 6147(1) \text{ \AA}^3$] but larger than those reported for polycrystalline [$a = 16.602(1) \text{ \AA}$, $c = 22.233(1) \text{ \AA}$, $V = 6128(1) \text{ \AA}^3$].²⁰ After densification by SPS, small amounts (less than 5% by mass) of $\text{Yb}_{11}\text{Sb}_{10}$ can become evident due to the vaporization of Mg and the crystallization of amorphous side phases (Rp: 5.95, wRp: 7.85). However, crystalline impurities are not evident in the samples prepared with YbH_2 , presumably due to the large magnesium excess (50%) employed in the synthesis.

Bulk polycrystalline samples of $\text{Yb}_{14}\text{MgSb}_{11}$ were also synthesized employing MgH_2 (MGH) as described above over 4 days at 800 °C. Due to the increased surface area and reactivity of MgH_2 , a smaller excess was required to synthesize phase pure materials at lower temperatures. The resultant product provided diffraction patterns that were well refined by Rietveld refinement and could be

fully indexed and refined with a slight (0.5%) Yb_2O_3 impurity (Rp: 7.45, wRp: 9.67). The unit cells of samples prepared with MgH_2 were $a = 16.6081(1) \text{ \AA}$, $c = 22.2436(1) \text{ \AA}$, and $V = 6135.5(1) \text{ \AA}^3$ (Fig. 2). Those synthesized with MgH_2 show a slight reduction in all parameters and are consistent with those previously reported for polycrystalline samples. After densification by SPS, small amounts (less than 5% by mass) of $\text{Yb}_{11}\text{Sb}_{10}$ became evident in the powder pattern of the sample prepared with MgH_2 (Rp: 7.36, wRp: 9.37). Although some impurities may have significant effects on the material properties, $\text{Yb}_{11}\text{Sb}_{10}$ is reported to have a small Seebeck coefficient and low resistivity at temperatures relevant for $\text{Yb}_{14}\text{MgSb}_{11}$.^{20,25} It has also been reported as present in some of the best samples of $\text{Yb}_{14}\text{MnSb}_{11}$ with minimal impact on the thermoelectric properties.^{11,14} At low mass percent, the contribution due to the $\text{Yb}_{11}\text{Sb}_{10}$ impurity is considered negligible. Patterns of milled, annealed, and SPSed powders can be found in the [supplementary material](#).

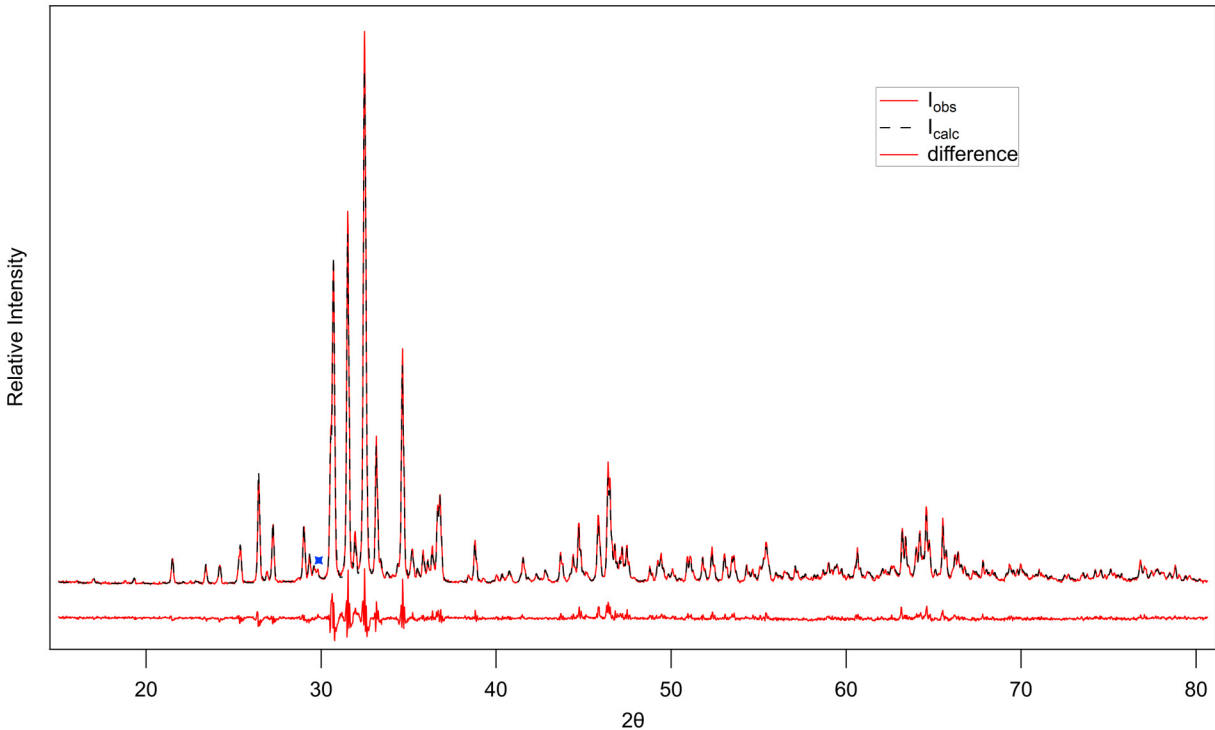


FIG. 2. Powder X-ray diffraction pattern of $\text{Yb}_{14}\text{MgSb}_{11}$ (MGH) synthesized using MgH_2 and Rietveld refinement showing a small (0.5%) Yb_2O_3 impurity marked by the blue dot around 30 2θ (Rp: 7.45, wRp: 9.67).

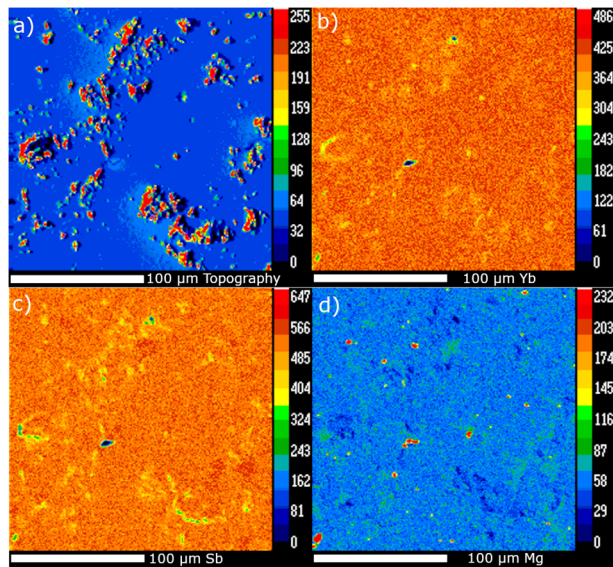


FIG. 3. EPMA topography (a) and X-ray elemental mapping of Yb (b), Sb (c), and Mg (d) of Yb₁₄MgSb₁₁ made with YbH₂ (YBH).

Elemental analysis

Pieces of densified pellet were set in epoxy and analyzed by electron probe microanalysis (EPMA). Samples appear to be phase pure with no evident regions of impurity, see Figs. 3 (YBH) and

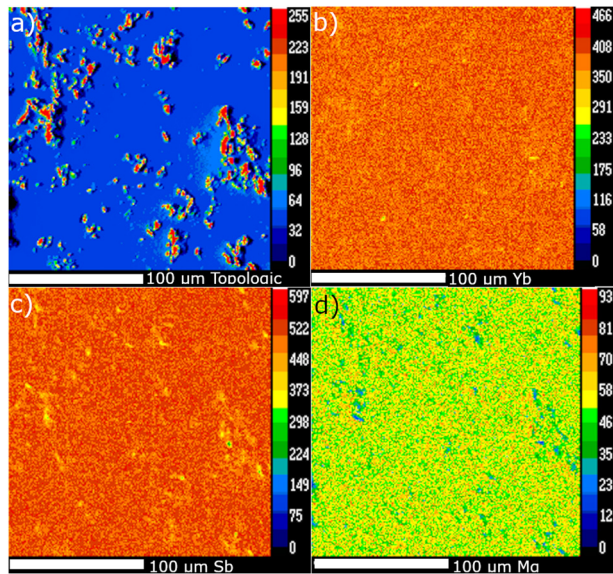


FIG. 4. EPMA topography (a) and X-ray elemental mapping of Yb (b), Sb (c), Mg (d) Yb₁₄MgSb₁₁ made with MgH₂ (MGH).

4 (MGH). Some deviation from uniform counts in the elemental maps corresponds to topographical inconsistencies. These inconsistencies are attributed to surface roughness: providing a surface that is not in the proper orientation with relation to the electron beam and detector, leading to improper elemental X-ray mapping at those points. However, for YBH, there are high Mg counts apparent in the Mg elemental map that are not related to the topographical inconsistencies indicated by the red spots in Fig. 3(d). This suggests that Mg is present, presumably at the grain boundary in this sample. Porosity of the sample is also evident (low counts in the elemental mapping) consistent with lowered density observed for this sample. The porosity may be attributed to the relative thermal stability of YbH₂. The kinetics of hydride decomposition are not reported for YbH₂ and it is possible that some residual subhydride was still present before SPS consolidation (although not evident via PXRD), giving rise to more porosity. It is also possible that the additional Mg present contributes to porosity if it sublimates during the SPS densification.

Elemental analysis (Table II) shows deficiency in Yb and Sb and an excess in Mg for the YBH sample. Although this could suggest Mg incorporation into the Yb sites, the unit cell volume from PXRD does not match that of those found in the single crystal study of Yb_{13.85}Mg_{1.15}Sb₁₁ ($V = 6079 \text{ \AA}^3$).²¹ When the data are reanalyzed by forcing Yb stoichiometry to be 14, Sb content returns to that expected, and the Mg content becomes slightly less than what was originally loaded [1.3(2)]. The elemental mapping and elemental analysis support the idea that there is Mg at the grain boundaries of this sample.

The overall composition of the sample synthesized using MgH₂ (MGH) is shown to be stoichiometric with low standard deviation in the magnesium composition (Table II). Figure 4 shows some topography, but overall the elemental maps are much more uniform. Starting with a powered reagent of the low stoichiometry element for this compound leads to a more homogeneous product through better dispersion. Indeed, better dispersion lowers the solid state diffusion path length of Mg atoms, increasing reactivity, and hence requiring less elemental excess.³

Carrier concentration and Hall mobility

Hall mobility and carrier concentration of the two samples were measured up to 1273 K (see the supplementary material). For Yb₁₄MgSb₁₁ synthesized using YbH₂, carrier concentrations ranged from 5.7×10^{20} to $1.5 \times 10^{21} \text{ cm}^{-3}$ and mobilities from 2.3

TABLE II. EPMA elemental analysis of Yb₁₄MgSb₁₁ made with YbH₂ (YBH) and MgH₂ (MGH).

Element ^a	YBH ^b	YBH ^c	MGH ^b
Yb	13.8(2)	14.0	14.0(2)
Mg	1.3(2)	1.3(2)	1.02(2)
Sb	10.9(1)	11.1(1)	11.0(2)

^aValues are the average of 10 individual points.

^bDetermined assuming 26 atoms/formula unit.

^cDetermined by restricting Yb = 14.0.

to $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. The carrier concentration at 300 K is in agreement with what has previously been reported.²⁰ The lower mobility of the YbH_2 is most likely due to the presence of Mg at the grain boundaries. The sample synthesized using MgH_2 showed similar carrier concentrations ranging from 5.3×10^{20} to

$1.3 \times 10^{21} \text{ cm}^{-3}$ and higher mobilities from 4.7 to $0.7 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. The lower mobility of the samples synthesized using YbH_2 could be due to the presence of excess Mg at grain boundaries, which is avoided in MgH_2 samples due to improved dispersity and reaction kinetics.

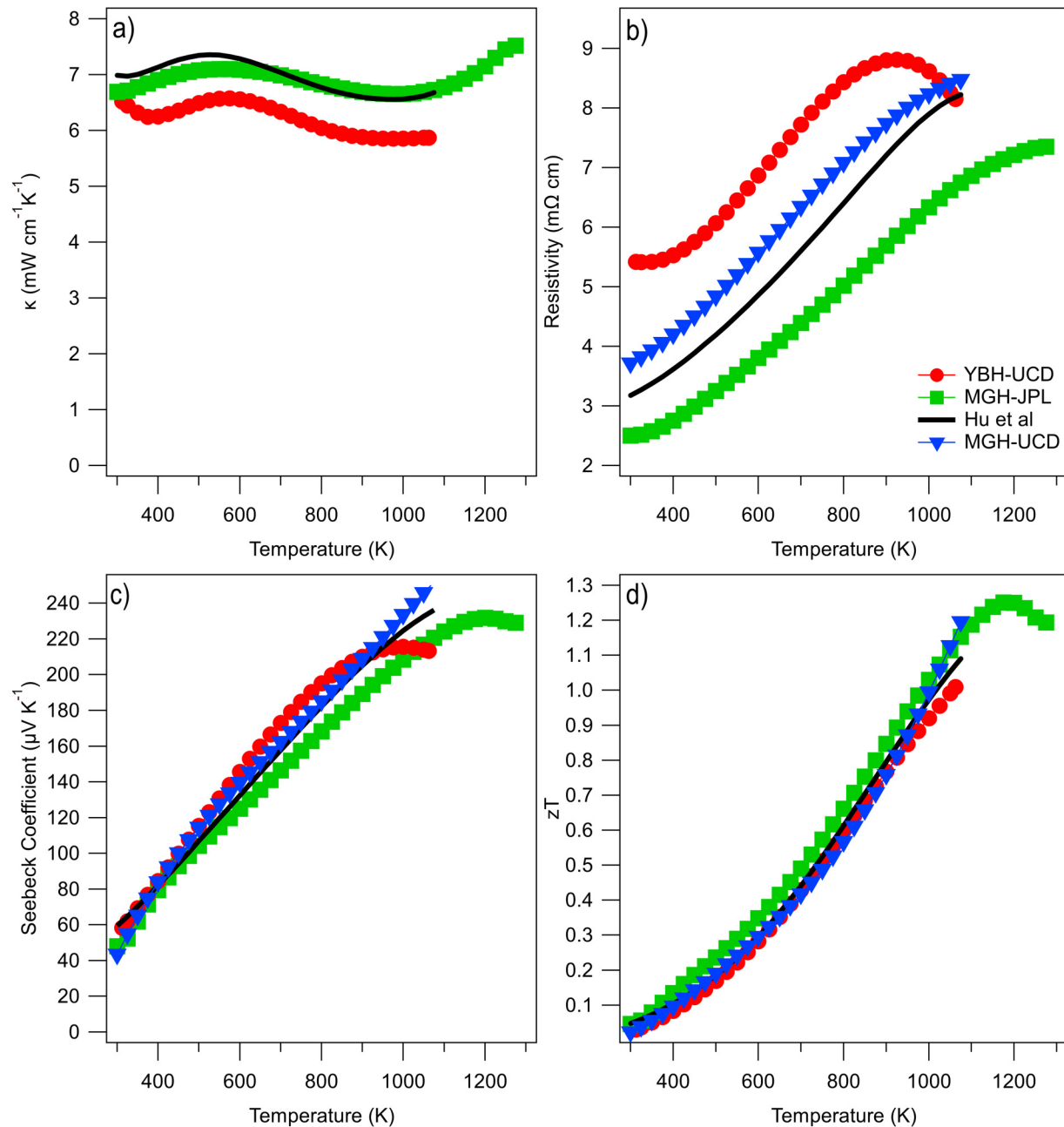


FIG. 5. The thermal conductivity (a), electrical resistivity (b), Seebeck coefficient (c), and zT (d) of $\text{Yb}_{14}\text{MgSb}_{11}$ made with YbH_2 (YBH) and MgH_2 (MGH) measured at UCD and JPL. Data in black reproduced from Hu *et al.*²⁰

Thermoelectric properties

Thermoelectric properties are shown in Fig. 5. Thermal diffusivity was measured on densified pellets. The thermal conductivity was then calculated using $\kappa = C_p \rho D$, where κ is the thermal conductivity, C_p is the specific heat capacity, ρ is the density, and D is the thermal diffusivity. Thermal conductivity consists of two parts: a lattice component (κ_l) which is the contribution due to the material's structure and an electrical component (κ_e) which considers the thermal energy transferred by charge carriers. This leads to the equation $\kappa = \kappa_l + \kappa_e$. The sample synthesized with YbH_2 (YBH) has a slightly lowered thermal conductivity ($6.13 \text{ mW cm}^{-1} \text{ K}^{-1}$), which may be due to the lower density of this sample along with the increased electrical resistivity, lowering both the lattice and the electronic contributions of thermal conductivity. With low density samples, there is an increased percent of void space present in the sample. These voids lead to increased phonon scattering and lower lattice thermal conductivity. $\text{Yb}_{14}\text{MgSb}_{11}$ synthesized using MgH_2 (MGH) had a thermal conductivity comparable to that previously published (6.719 and $6.68 \text{ mW cm}^{-1} \text{ K}^{-1}$ at 1075 K , respectively).²⁰ Because both samples have comparable densities, their thermal conductivity are expected to be similar.

Resistivity and the Seebeck coefficient of $\text{Yb}_{14}\text{MgSb}_{11}$ synthesized with YbH_2 (YBH) were measured by the off axis 4-probe method. This sample showed a relatively high resistivity ($8.7 \text{ m}\Omega \text{ cm}$ at 900 K), which rolls over before reaching peak temperatures. This high resistivity is attributed to Mg's presence at the grain boundaries. It is possible that the metallic boundary from Mg leads to bending of the $\text{Yb}_{14}\text{MgSb}_{11}$ bands and an increase in resistivity. There is no evidence for sample decomposition or melting after measurement. The Seebeck coefficient of YBH is similar to that of those synthesized with elemental reagents or MgH_2 (MGH). Both the Seebeck coefficient and electrical resistivity of the sample bend over around 900 K . This coincides closely with the melting point of elemental Mg and may suggest the presence of Mg at grain boundaries.

The electrical resistivity and the Seebeck coefficient of $\text{Yb}_{14}\text{MgSb}_{11}$ synthesized with MgH_2 (MGH) were also measured by the off axis 4-probe method. Resistivity of the sample measured by this technique was similar to what was previously published (8.4 and $8.2 \text{ m}\Omega \text{ cm}$, respectively). The Seebeck coefficient measured by the 4-probe method was $251 \mu\text{V/K}$ at 1075 K , higher than that previously reported. This difference in the Seebeck coefficient at higher temperatures could be attributed to possible cold finger effect.¹ Overall, the properties measured at UC Davis resulted in a calculated zT of 1.19 at 1075 K . Because of these promising results, $\text{Yb}_{14}\text{MgSb}_{11}$ made with MgH_2 (MGH) was measured up to higher temperatures (1273 K) at JPL. In comparison to samples synthesized with elemental reagents, MGH exhibited significantly reduced resistivity, peaking at $7.39 \text{ m}\Omega \text{ cm}$ at 1275 K . Because of the higher surface area and increased dispersity of the hydride, it is more reactive during annealing, leading to less elemental Mg at grain boundaries. Additionally, the hydrogen rich environment during annealing reduces any minor oxides present. As a result of the reduced electrical resistivity, the Seebeck coefficient of MGH is reduced but still reaches peak values of $232 \mu\text{V/K}$ before rolling over at 1200 K . The turnover temperature in the Seebeck coefficient correlates with the beginning of the turnover in the resistivity. This

suggests that the turnover in electronic properties is due to bipolar conduction at high temperatures. Due to the presence of the Yb^{+3} , $\text{Yb}_{14}\text{MgSb}_{11}$ is closer to a full charge compensated Zintl phase. This leads to a smaller bandgap in comparison to $\text{Yb}_{14}\text{MnSb}_{11}$. This Seebeck coefficient and temperature correspond to a bandgap of 0.56 eV by the Goldsmid-Sharp equation.^{1,26} This agrees well with the previously determined value of 0.6 eV determined by computational methods.²⁰ Overall, the reduction in electrical resistivity overcomes the small drop in the Seebeck coefficient to give samples synthesized using MgH_2 (MGH) a peak zT of 1.26 at 1200 K . The differences in properties between what was measured at UC Davis and JPL can be attributed to a combination of the cold finger effect, which can result in exaggerated Seebeck coefficient values and slight differences in sample composition between two halves of the same consolidated sample.¹

CONCLUSIONS

Metal hydrides have proven to be highly effective as reactive precursors for malleable or low atomic percent metals. Due to the increase in surface area and better dispersity within the milled powder, there is an increase in reactivity, allowing for lower temperature synthesis, which requires less energy. Additionally, the increase in reactivity of MgH_2 compared with YbH_2 leads to a pure product with less Mg at grain boundaries. Samples of $\text{Yb}_{14}\text{MgSb}_{11}$ prepared with MgH_2 showed increased thermoelectric efficiencies, reaching a peak zT of 1.26 at 1200 K , which is comparable to efficiencies reported by Grebenkemper *et al.* and the ATEC project for $\text{Yb}_{14}\text{MnSb}_{11}$.^{14,19}

SUPPLEMENTARY MATERIAL

See the supplementary material for powder diffraction patterns, carrier concentration and Hall mobility as a function of temperature and a plot of Power Factor.

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