The Effects of Ag on the Thermoelectric Properties of Higher Manganese Silicide

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Higher manganese silicide (HMS) possesses electron transport properties suitable for thermoelectric generators and Peltier coolers, but its slightly large lattice thermal conductivity prevented us from utilizing it in practical applications. HMS containing 5 at % heavy elements such as Ta, W and Re shows reduced lattice thermal conductivity, despite the materials being metastable and decomposing at high temperatures. It is preferable to make bulk samples of these materials without the formation of precipitate. We found that small amounts of Ag works as "glue" to help obtain bulk samples with lower sintering temperature. Therefore, in this study, the addition of Ag to n-type and p-type HMS on the thermoelectric properties of HMS-based materials are being intensively investigated. The process to create the materials consists of (1) measuring out the elements, (2) mixing them into homogenous powders, (3) arc melting the pressed powders together to create an ingot consisting of several phases, (4) making single phased ribbons using a liquid quenching or melt spinning machine, (5) mixing the obtained ribbons with different amounts of Ag, and (6) creating bulk samples using spark plasma sintering. The thermoelectric properties, Seebeck coefficient, electrical resistivity, and thermal conductivity were measured in a wide temperature range from 300 K to 900 K. This allows us to figure out the best Ag concentrations that lead to the best thermoelectric, non-toxic and cheap HMS materials. As a result of this investigation, we succeeded in obtaining p-type HMS and n-type HMS in the form of bulk and these bulk samples showed $ZT = 0.82$ and 0.65, respectively. These values are very close to that of practical thermoelectric materials consisting of toxic, expensive elements.

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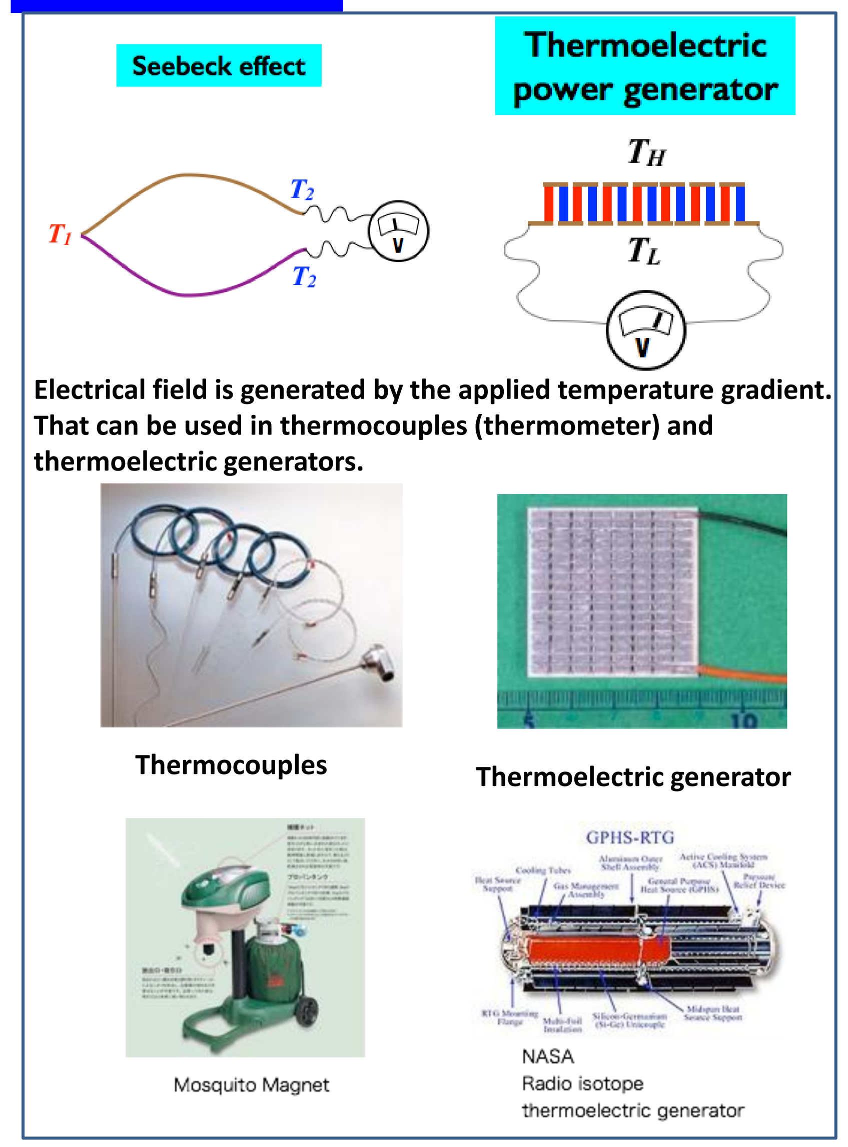
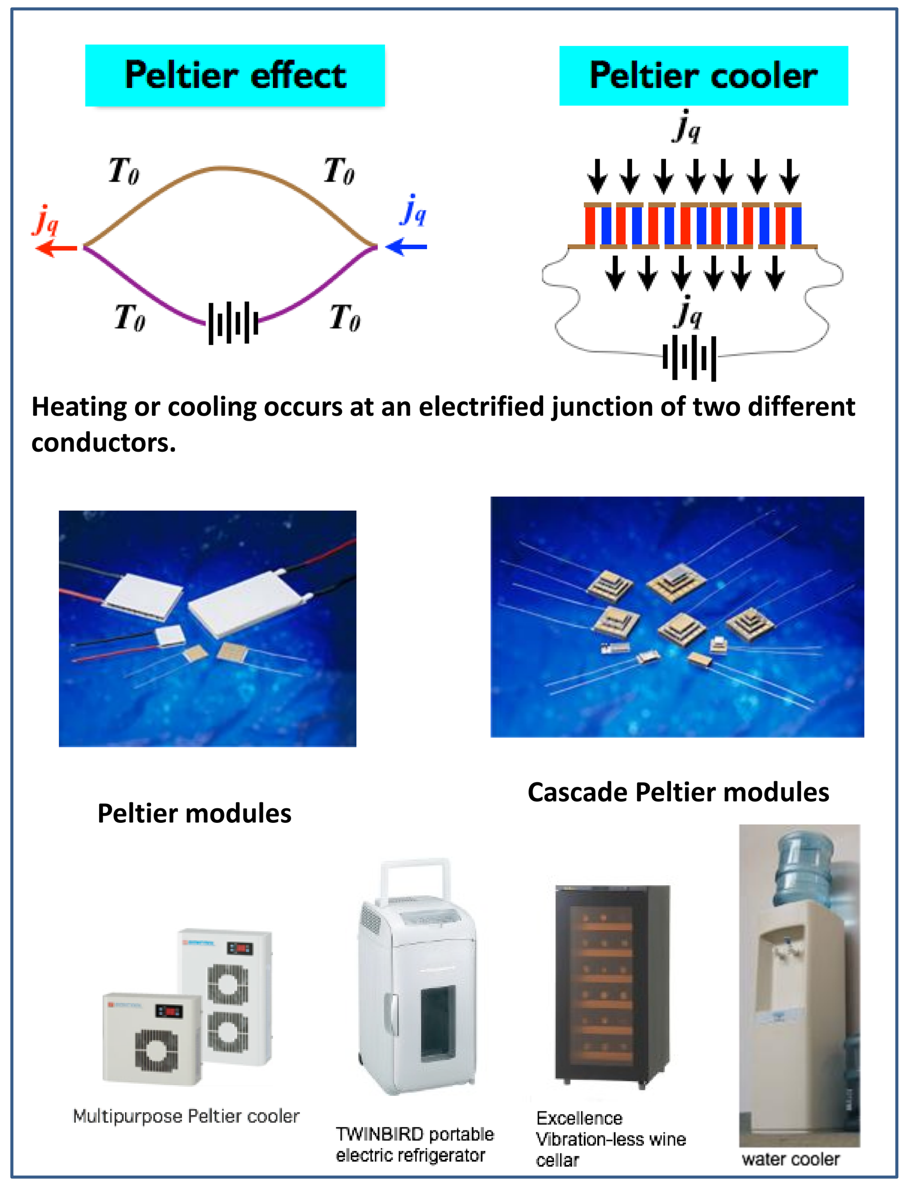
Introduction



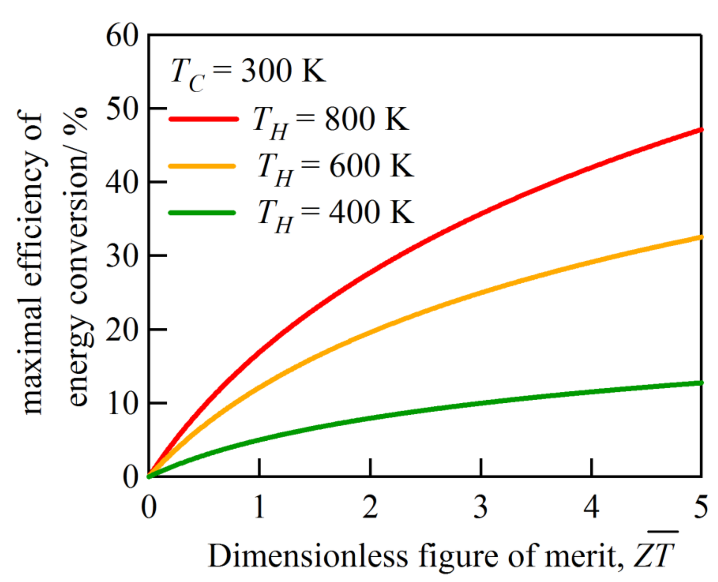


Dimensionless figure of merit

$$ZT = \frac{TS^2}{\rho\kappa}$$

S = thermopower (V/K)
ρ = electrical resistivity (Ωcm)
κ = thermal conductivity (W/cmK)
T = temperature (K)

Efficiency of energy conversion of thermoelectric generators



$$\eta = \left(\frac{T_H - T_C}{T_H}\right) \cdot \frac{\sqrt{1+ZT_{avg}} - 1}{\sqrt{1+ZT_{avg}} + (T_C / T_H)}$$

A large *ZT* is obtainable for heavily doped semiconductors that have a:

- wide band gap,
- narrow peak in the electronic density of states near the band edge, and
- small value of lattice thermal conductivity.

The higher manganese silicide (HMS) stabilizing at $MnSi_{1.73}$ possess the following, provided that some manganese atoms are substituted with heavy 5d such as Re, Ta, & W:

- low decomposing temperature,
- forming unwanted precipitate. and
- preventing the formation of bulk samples.

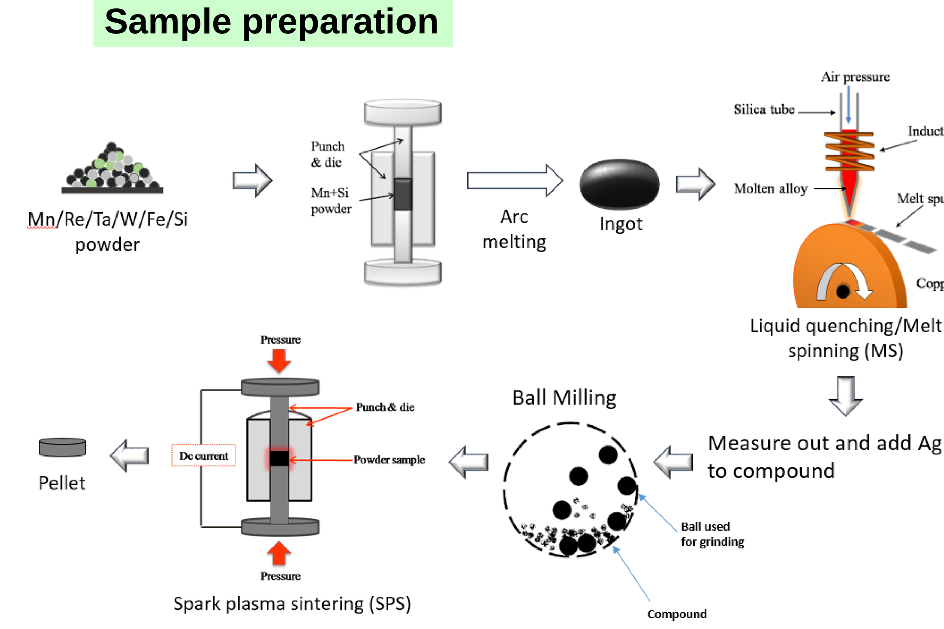
Solution: Slight amounts of Ag work as a "glue" to help obtain bulk samples with lower temperature sintering, the pressure used to heat and make bulk samples.

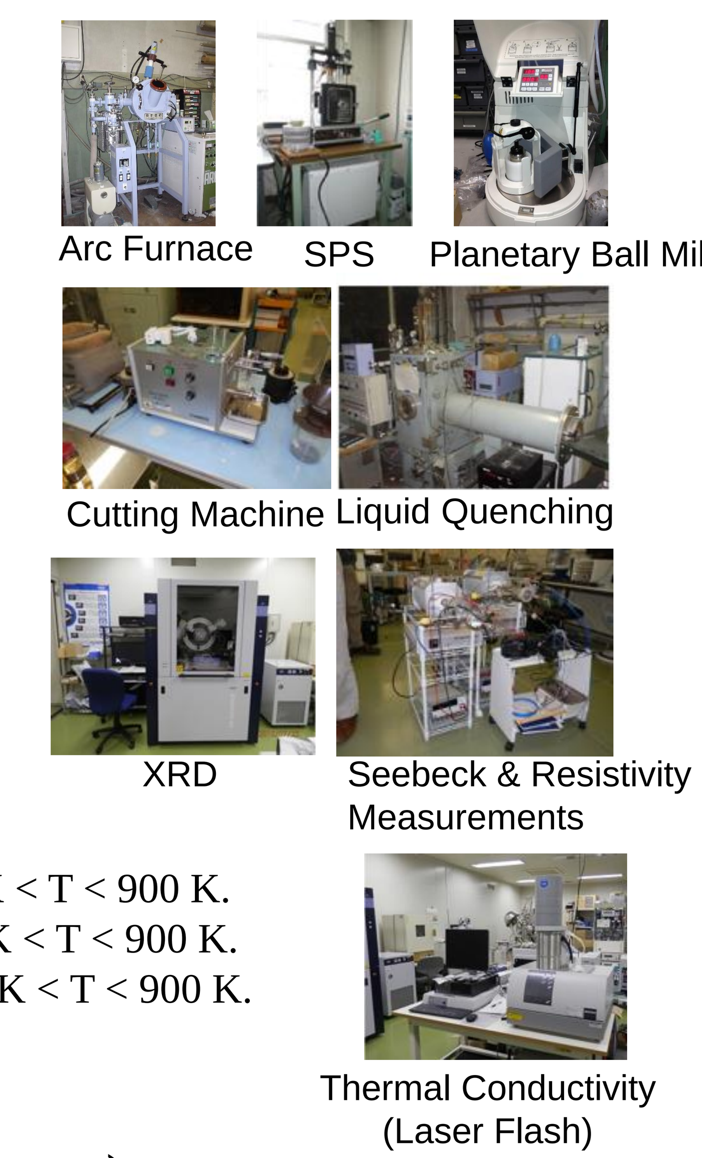
Purpose of this study

Investigate the effects of Ag on the thermoelectric properties of HMS to develop bulk shaped, high performance materials. We tried to make n- type and p-type bulk materials because both are to used in thermoelectric modules.

Experimental Procedure

Sample preparation



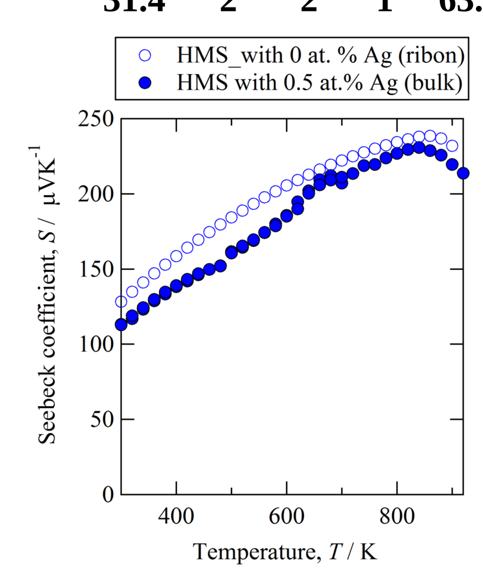


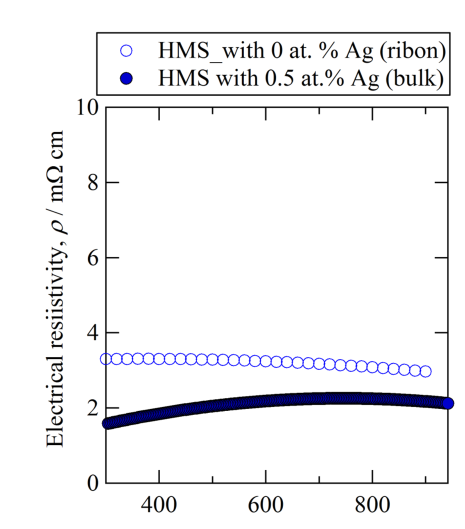
Thermoelectric property measurements

(a) Electrical resistivity: Four-probe method at 300 K < T < 900 K.
(b) Seebeck coefficient: Steady state method at 300 K < T < 900 K.
(c) Thermal conductivity: Laser flash method at 300 K < T < 900 K.

Results

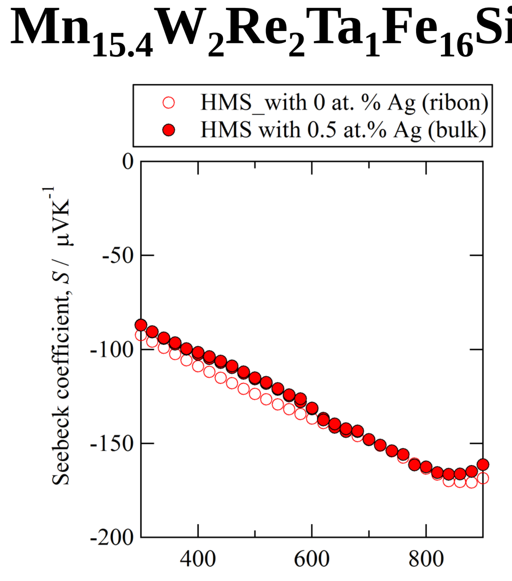
$Mn_{31.4}W_2Re_2Ta_1Si_{63.6}$ HMS phase (p-type)

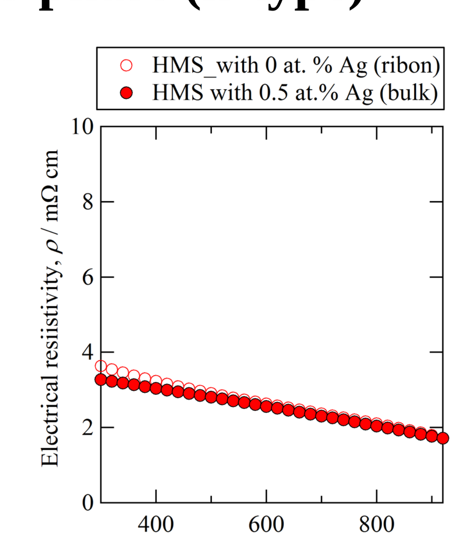




The electrical resistivity of p-type HMS was reduced a lot while the Seebeck coefficient was almost unchanged, both caused by the distributed small Ag.

$Mn_{15.4}W_2Re_2Ta_1Fe_{16}Si_{63.6}$ HMS phase (n-type)

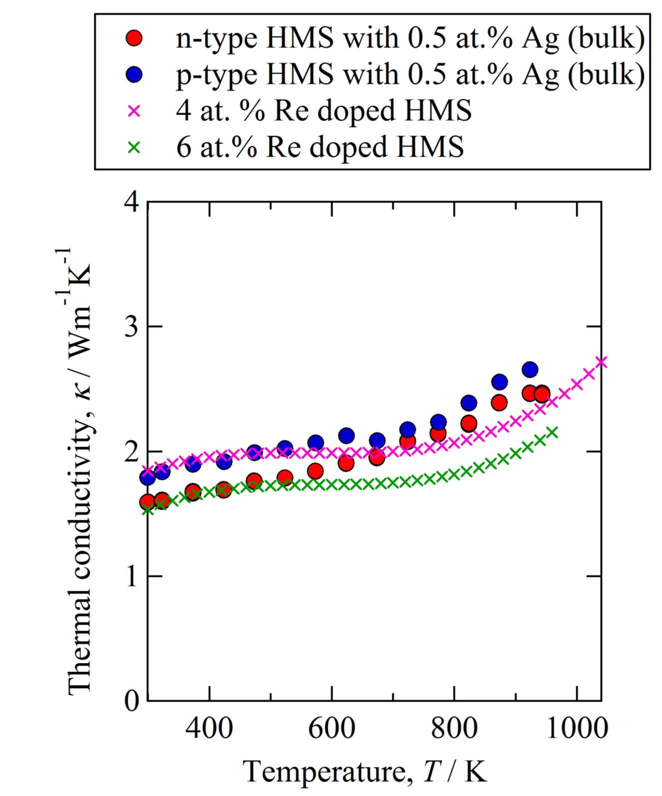




Surprisingly, the electrical resistivity and Seebeck coefficient of n-type HMS were not affected by adding 0.5 at. % Ag.

Thermal conductivity of HMS

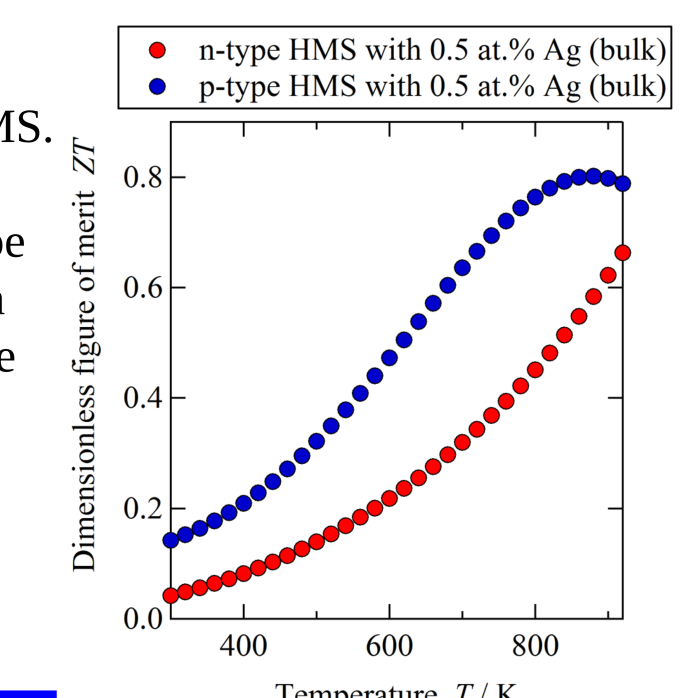
The thermal conductivity of bulk HMS containing 2 at.% Re, 2 at.% W, 1 at.% Ta and 0.5 at.% Ag is comparable with that of bulk HMS containing 4 ~ 6 at.% Re. Reduction in Re concentration leads to a great reduction in material cost.



ZT of HMS's containing a small amount of Ag

The *ZT* > 0.6 is the largest observed for n-type bulk HMS.

ZT = 0.8 of the present p-type HMS is slightly smaller than *ZT* = 1.04 reported for p-type HMS containing 6 at.% Re, but the material cost of present sample is less than half of 6 at.% Re HMS.



Conclusion & Future Impact

- Adding a bit of Ag to n-type and p-type compounds helps reduce the electrical resistivity and allows for creation of bulk samples.
- The p-type sample appears to have a lower Seebeck Coefficient after adding Ag, but the graphs are so close that one can't determine if the Seebeck Coefficient has changed.
- **This is useful for applications in motor vehicle efficiency as well as electrical refrigeration and power generation.**

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