Electronic Supplementary Information

High Thermoelectric Conversion Efficiency of MgAgSb-based Material with Hot-Pressed Contacts

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Single leg device efficiency model

The single leg device efficiency model takes into account the temperature-dependent properties of the thermoelectric material and the radiative heat transfer between the thermoelectric leg and the surrounding heated radiation shield which is assumed to be a blackbody at hot junction temperature (Fig. S1).



Fig. S1 Discretized thermoelectric leg with energy balance. In the iterative method the thermoelectric leg is mathematically subdivided in a large number of increments (dx) permitting the assumption of constant material properties (Seebeck coefficient, S(x), electrical resistivity, $\rho(x)$, thermal conductivity, k(x)) in each increment. The energy flow Q_{x+dx} at location x+dx with temperature T_{x+dx} must balance the energy flow Q_x at location x with temperature T_x and the incremental radiative heat flow dQ_{rad} between the surface at mid temperature, $(T_{x+dx}+T_x)/2$ of the leg increment and the heated radiation shield (blackbody) at hot junction temperature ($T_{RS} \approx T_{HJ}$). The energy flows within the leg include the heat conducted due to the materials thermal conductivity and the heat flow accompanied by the charge transport due to the applied electrical current. Thus, the iterative method can most

accurately calculate the temperature profile within the thermoelectric leg for each applied electrical current. From that the energy flow at the hot junction, the created thermoelectric voltage, the thermoelectric power output, and conversion efficiency at every given electrical current can be obtained.

In the iterative method²⁹ the thermoelectric leg is mathematically subdivided in a large number of increments (dx) permitting the assumption of constant material properties (Seebeck coefficient, S(x), electrical resistivity, $\rho(x)$, thermal conductivity, k(x)) in each segment for the energy balance. The energy flow Q_{x+dx} at location x+dx with temperature T_{x+dx} must balance the energy flow Q_x at location x with temperature T_x and the incremental radiative heat flow dQ_{rad} between the surface at mid temperature, $(T_{x+dx}+T_x)/2$ of the leg increment and the heated radiation shield (blackbody) at hot junction temperature ($T_{RS} \approx T_{HJ}$). The energy flows within the leg include the heat conducted due to the imposed temperature different and the heat flow (from thermoelectric effects and electrical energy) accompanied by the charge transport due to the applied electrical current. The energy balance leads to two coupled differential equations, known as the discretized Domenicali's equations³⁰, with a modification to account for the incremental radiative heat transfer, $dQ_{rad} = P \cdot dx \cdot \varepsilon \cdot \sigma \cdot (T(x)^4 - T_{HJ}^4)$, depending on the Stefan-Boltzmann constant, σ , the local leg temperature, T(x), the temperature of the surroundings assumed to be at hot junction temperature, T_{HJ} , the incremental surface area, P·dx, with leg perimeter P and with ε being the total hemispherical IR emittance of the thermoelectric leg surface which is assumed to be gray and temperature independent³⁵. The emittance is obtained with the method described in the Experimental Setup and Measurement Methods section.

$$\frac{dT(x)}{dx} = \frac{1}{k(x)} [JT(x)S(x) - q(x)]$$
(S1)

$$\frac{dq(x)}{dx} = \rho(x)J^2 \left[1 + \frac{S(x)^2 T(x)}{\rho(x)k(x)} \right] - \frac{JS(x)q(x)}{k(x)} - \frac{\varepsilon P\sigma \left[T(x)^4 - T_{HJ}^4 \right]}{A_{TE}}$$
(S2)

The first equation correlates the local temperature gradient dT(x)/dx to the local heat flow density, q(x), the current density $J = I/A_{TE}$ with I and A_{TE} being the applied current and the crosssectional area of the thermoelectric leg, respectively, the local thermal conductivity, k(x), temperature, T(x) and Seebeck coefficient, S(x). The second correlation equates the local change in the heat flow density, dq(x)/dx with $\rho(x)$ being the local electrical resistivity. The last term on the right hand side appears due to the above introduced radiative heat transfer between the thermoelectric leg and the heat radiation shield at hot junction temperature which is assumed to be a blackbody (in experiments gray diffuse graphite spray surface) and the viewfactor is conservatively assumed as 1. For dx \rightarrow 0 the equations S1 and S2 can be written for the ith segment as:

$$T_{i+1} = T_i + \frac{dx}{k_i} [JT_i S_i - q_i], \ (i = 0, 1, 2, ..., n-1)$$
(S3)

$$q_{i+1} = q_i + \left[q_i J^2 \left(1 + \frac{S_i^2 T_i}{\rho_i k_i}\right) - \frac{J S_i q_i}{k_i} - \frac{\varepsilon P \sigma \left[T_i^4 - T_{HJ}^4\right]}{A_{TE}}\right] dx, \quad (i = 0, 1, 2, ..., n-1)$$
(S4)

The output from one segment of the leg becomes the input for the adjacent segment, such that the iterative method can be used to accurately determine the temperature and heat flow profile of the thermoelectric leg for each applied electrical current with T_{CJ} and T_{HJ} as the specified cold and hot junction temperature boundary conditions. From that the heat flow at the hot junction,

$$Q_{HJ} = q_n \cdot A_{TE}$$
, the created thermoelectric voltage, $V_{TE} = \sum_{0}^{n-1} S_i (T_{i+1} - T_i) + J \sum_{0}^{n-1} \rho_i dx$, the thermoelectric power output, $P_{TE} = V_{TE}I$, and conversion efficiency, $\eta_{TE} = \frac{P_{TE}}{Q_{HJ}}$ at every given electrical current is determined. It shall be noted that for the defined x direction the current and

heat flow densities are negative for a p-type thermoelectric leg.



Current and power densities of demonstrated single thermoelectric leg

Fig. S2 Power density of the demonstrated MgAgSb-based single thermoelectric leg as a function of conversion efficiency measured at various steady-state set temperature differences. The corresponding current densities are also indicated.

Determination of maximum single leg thermoelectric efficiency from experimental results It is rather time consuming to experimentally determine the maximum thermoelectric conversion efficiency because it would require very small current set point increments. For that reason we measure the thermoelectric I-V curve for the steady-state set temperature differences for reasonably large set current increments and calculate the thermoelectric power output for each current set point. The measured raw data and thermoelectric efficiencies are illustrated in figure S3 for the steady-state set temperature difference of 125 °C. Using equation (2) and the measured electrical heater power input (Fig. S3(b)) we calculate the measured thermoelectric efficiency for each current set point and obtain the maximum efficiency from the 4th order polynomial which fits the data well as indicated in figure S3(c). Then the above introduced model together with the *extracted* material properties is used to correct the experimentally obtained efficiency results for the radiative heat transfer between the thermoelectric leg and the radiation shield.



Fig S3 Experimental raw data (open markers) of MgAgSb-based single leg for the constant set temperature difference of 125 °C ($T_{CJ} = 20$ °C, $T_{HJ} = 145$ °C) with 4th order polynomial fits (solid lines) and extraction of maximum single leg thermoelectric conversion efficiency. (a) Thermoelectric (TE)-leg current (I_{TE}) – voltage (V_{TE}) curve and thermoelectric power output, P_{TE} , as a function of TE-leg current with 4th order polynomial fit. (b) Electrical heat input power, P_{H} , as a function of TE-leg current with 4th order polynomial fit. (c) Single leg thermoelectric conversion efficiency as a function of TE-leg current with 4th order polynomial fit indicating the maximum efficiency point at a TE-leg current of 0.67 A (TE-leg current density 7.47 A/cm²) and power output of 12.76 mW (power density of 1.42 kW/m²).



Comparison of temperature-dependent material properties

Fig. S4 Comparison of extracted material properties using the presented method and previously published temperature-dependent material properties²⁸. (a) Seebeck coefficient, (b) electrical resistivity, (c) thermal conductivity, and (d) figure of merit.

SEM pictures of sample contact pad region after single thermoelectric leg experiments



Fig. S5 SEM picture of sample-contact pad interface region after operating the single thermoelectric leg for over 36 hours. The interface is still well-defined, however some inter-diffusion of elements is observable. (a) shows the MgAgSb-based compound, the Ag-contact pad and the applied $Pb_{90}Sb_{10}$ solder at a magnification of 150X. SEM images of MgAgSb-based compound and the Ag-contact region at a magnification of 300X (b), 500X (c) and 1000X (d).