Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Electronic Supplementary Information (ESI)**

# Significant effect of Mg-pressure-controlled annealing: non-stoichiometry and thermoelectric properties of $Mg_{2-\delta}Si_{1-x}Sb_x$

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## Experimental set up for Mg-pressure-controlled annealing

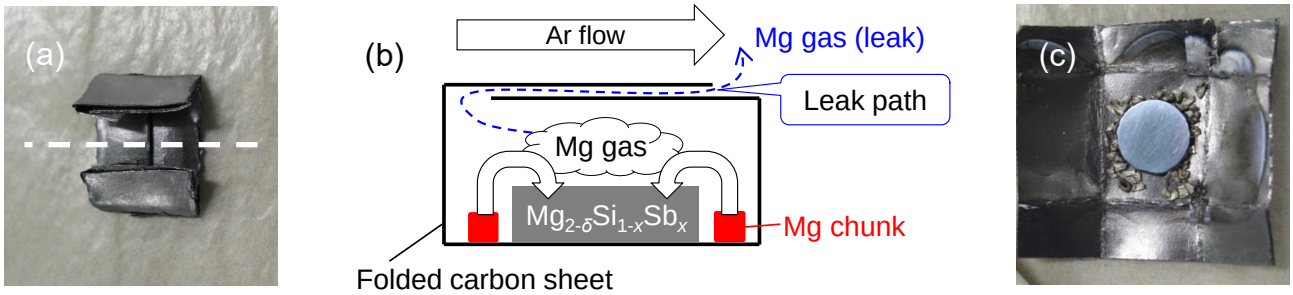


Figure S1. Experimental set up for Mg-pressure-controlled annealing. (a) A picture of $Mg_{2-\delta}Si_{1-x}Sb_x$ and Mg chunk wrapped with a carbon sheet. (b) Schematic illustration of cross section of the dashed line in Fig. S1 (a) during annealing. The inside of the folded carbon sheet corresponds to a semi-closed system which has narrow leak path for Ar and Mg gases. (c) A picture of $Mg_{2-\delta}Si_{1-x}Sb_x$ after annealing with Mg chunk (under high Mg partial pressure, $P_{Mg} = 1\times10^{1}$).

**XRD and EDS analysis**

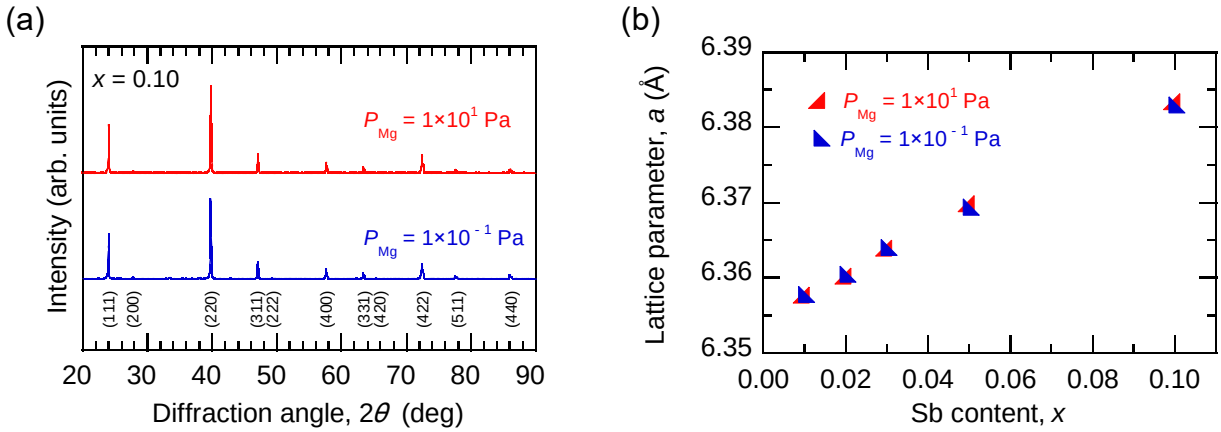


Figure S2. (a) XRD pattern of $Mg_{2-\delta}Si_{0.90}Sb_{0.10}$ and (b) lattice parameters of $Mg_{2-\delta}Si_{1-x}Sb_x$ ($0.01 \leq x \leq 0.10$) after annealing under $P_{Mg} = 1\times10^{1}$ Pa and $P_{Mg} \leq 1\times10^{-1}$ Pa.

Table S1. Sample composition determined by a semi-quantitative EDS analysis for $Mg_{2-\delta}Si_{0.90}Sb_{0.10}$ annealing under $P_{Mg} = 1\times10^{1}$ Pa and $P_{Mg} \leq 1\times10^{-1}$ Pa.

| $P_{Mg}$ (Pa) | Mg (at%) | Si (at%) | Sb (at%) |
|---|---|---|---|
| $1\times10^{1}$ | 64.3 | 32.0 | 3.7 |
| $1\times10^{-1}$ | 63.6 | 32.8 | 3.6 |

**Equilibrium carrier concentration with vacancy-dopant association**

To estimate the effect of the vacancy-dopant association, we assume that Mg vacancies neighboring Sb dopant atoms are stabilized and thus do not react with the Mg gas and that only Mg vacancies neighboring four Si atoms can react with the Mg gas. The total concentration of Mg sites neighboring four Si atoms can be expressed as:

$$\left[\mathrm{Mg}^{\times}_{\mathrm{Mg:4Si}}\right] = 2(1-x)^4 \qquad \text{(S1)}$$

Mg vacancies are also divided into two categories: (i) those neighboring at least one Sb dopant atom, and (ii) those neighboring four Si atoms. Here, the distributions of Sb dopant atoms and Mg vacancies are regarded to be random.

$$\left[\mathrm{V}''_{\mathrm{Mg}}\right] = \frac{1}{2}\left[\mathrm{Sb}^{\cdot}_{\mathrm{Si}}\right] \times \{1-(1-x)^4\} + \left[\mathrm{V}''_{\mathrm{Mg:4Si}}\right] \qquad \text{(S2)}$$

Thus, the equilibrium reaction between the sample and the gas phase can be written as:

$$\mathrm{V}''_{\mathrm{Mg:4Si}} + \mathrm{Mg(g)} \rightleftarrows \mathrm{Mg}^{\times}_{\mathrm{Mg:4Si}} + 2\mathrm{e}'$$

$$K'_{\mathrm{V}} = \left[\mathrm{Mg}^{\times}_{\mathrm{Mg:4Si}}\right]^{1} \cdot [\mathrm{e}']^{2} \cdot \left[\mathrm{V}''_{\mathrm{Mg:4Si}}\right]^{-1} \cdot {P'_{\mathrm{Mg}}}^{-1} \qquad \text{(S3)}$$

From eqs. (2), (4), and (S1)-(S3), the relationship between $n_{\mathrm{eq}}$ and $x$ with defect association is obtained:

$$n_{\mathrm{eq}} = \frac{K'_{\mathrm{V}}P'_{\mathrm{Mg}}}{8(1-x)^4}\left(\sqrt{1+\frac{16x(1-x)^8}{K'_{\mathrm{V}}P'_{\mathrm{Mg}}}}-1\right) \qquad \text{(S4)}$$

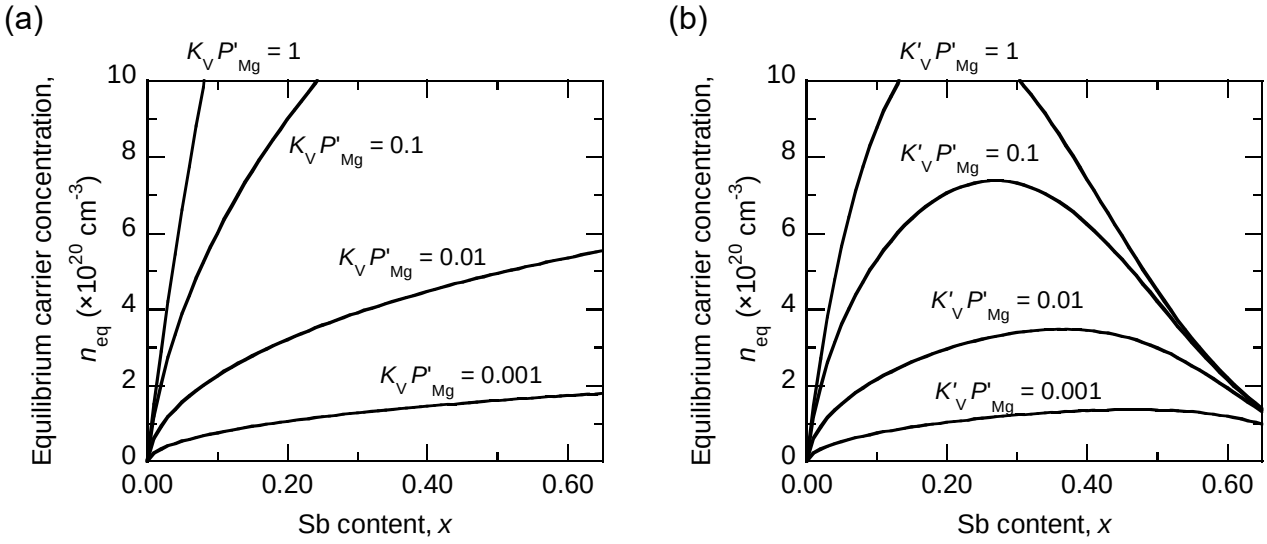


Figure S3. The equilibrium carrier concentration of $Mg_{2-\delta}Si_{1-x}Sb_x$ for various $K_{\mathrm{V}}P'_{\mathrm{Mg}}$ values.

The vacancy-dopant association is not considered in (a) and is considered in (b).

**Band structure of $Mg_2Si$**

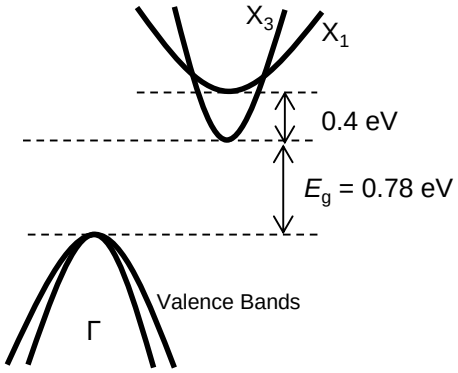


Figure S4. Schematic of band structure of $Mg_2Si$.

**Lattice thermal conductivity**

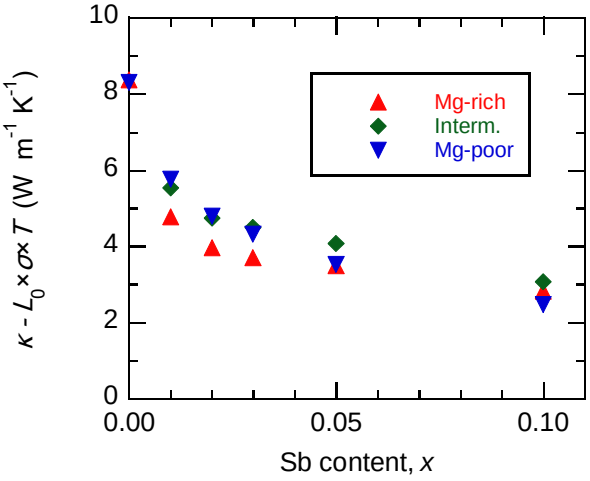


Figure S5. Room-temperature lattice thermal conductivity of $Mg_{2-\delta}Si_{1-x}Sb_x$ estimated using the Wiedemann-Franz relation.

**Compatibility factor *s*, relative current density *u*, and reduced efficiency**

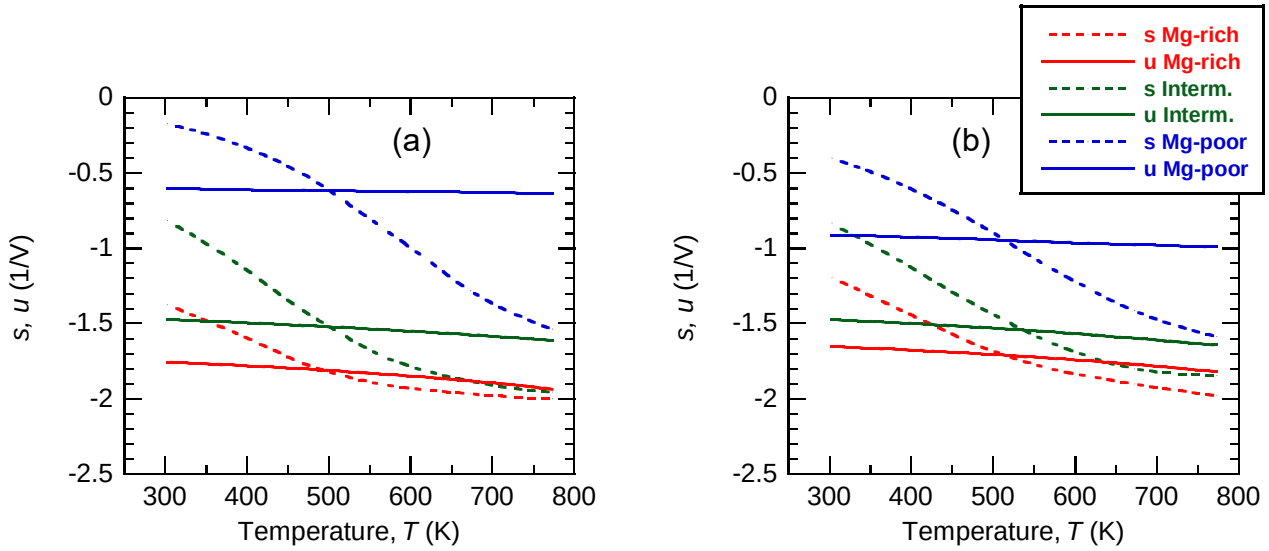


Figure S6. The compatibility factor *s* and the relative current density *u* for (a) $Mg_{2-\delta}Si_{0.95}Sb_{0.05}$ and (b) $Mg_{2-\delta}Si_{0.80}Sb_{0.20}$ with different levels of Mg non-stoichiometry.

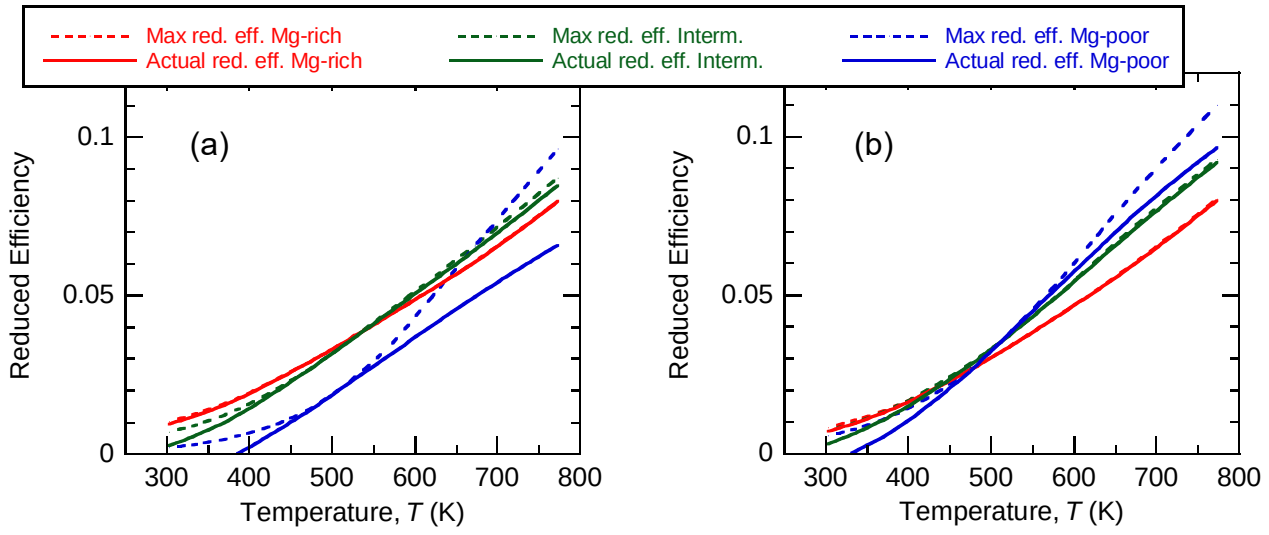


Figure S7. The maximum and actual reduced efficiencies for (a) $Mg_{2-\delta}Si_{0.95}Sb_{0.05}$ and (b) $Mg_{2-\delta}Si_{0.80}Sb_{0.20}$ samples with different levels of Mg non-stoichiometry.