Measurement of the Seebeck coefficient under high pressure by dual heating

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Abstract

This study presents a new method for measuring the Seebeck coefficient under high pressure in a multi-anvil apparatus. The application of a dual-heating system enables precise control of the temperature difference between both ends of the sample in a high-pressure environment. Two pairs of W-Re thermocouples were employed at both ends of the sample to monitor and control the temperature difference, and independent probes were arranged to monitor the electronic motivate force (emf) produced by temperature oscillation at a given target temperature. The temperature difference was controlled within 1 K during the resistivity measurements to eliminate the influence of emf owing to a sample temperature gradient. The Seebeck measurement was successfully measured from room temperature to 1400 K and obtained by averaging two measured values with opposite thermal gradient directions (~20 K). Thermoelectric properties were measured on disk-shaped p-type Si wafers with two different carrier concentrations as a reference for high Seebeck coefficients. This method is effective to determine the thermoelectric power of materials under pressure.

I. INTRODUCTION

The application of pressure to thermoelectric materials produces interesting property changes.\textsuperscript{1-5} Knowledge of thermoelectric properties at high pressures is therefore important for understanding not only pressure tuning of thermoelectric conversion materials to improve transport properties, but also the electromagnetic behavior of materials in the Earth’s interior. The Seebeck coefficient describes the
voltage ($\Delta V$) that develops from a given temperature difference ($\Delta T$) in a material ($S = \Delta V/\Delta T$). The Seebeck coefficient ($S$) is an integral part of the heat-to-electricity conversion in thermoelectric devices, given by $zT = S^2\sigma T/\kappa$, where $\sigma$ is electrical conductivity, $\kappa$ is thermal conductivity, $T$ is temperature, and $z$ is thermoelectric figure of merit. Previous theoretical and experimental studies have suggested that particularly high $zT$ magnitudes can be obtained in existing thermoelectric materials (e.g., PbTe, PbSe, Bi$_2$Te$_3$) at high pressure.$^{6-9}$

The Seebeck coefficient is an important parameter to identify the type of electric charge carrier in a semiconductor. Although a good thermoelectric material should have only one dominant type of charge carrier type, the Earth’s constituent minerals have thermoelectric contributions from both n- and p-type carriers. For example, the thermopower of olivine, the dominant mineral in the upper mantle, shows a gradual change across zero with increasing temperature, suggesting a transition from polaron dominance in conduction to magnesium vacancy dominance around 1573K.$^{10,11}$ Some thermal boundary layers are known to exist in the Earth’s interior (e.g., core-mantle boundary). Large temperature gradients may affect the redox state of the Earth’s deep interior by the Seebeck effect, which makes knowledge of the electrical charge polarity in constituent minerals required for understanding the redox evolution of the mantle. However, Seebeck coefficient measurements at pressures relevant to the Earth’s mantle remains unreported.

Seebeck coefficient measurements under pressure have progressed using a Bridgman-type high-pressure apparatus at room temperature, but most recent studies
have involved a diamond anvil cell (DAC).\textsuperscript{4,5,12–14} However, DAC studies may involve uncertainties in the determined properties of bulk materials owing to the small sample size and unstable heating at high temperature. In contrast, thermoelectric measurements in a multi-anvil apparatus allow substantially larger samples and more stable heating. Several studies have therefore determined the electrical conductivity of mantle minerals up to 25 GPa and 2000 K using in situ complex impedance spectroscopy in a Kawai-type multi-anvil high pressure apparatus.\textsuperscript{15} Thermal conductivity or diffusivity under simultaneously high temperatures and pressures have also been measured using impulse heating methods in a Kawai-type multi-anvil press.\textsuperscript{16} However, measurements of the Seebeck coefficient in a multi-anvil apparatus at high pressure remain scarce. A high-pressure setup for performing the simultaneous determination of diffusivity and Seebeck coefficient in a multi-anvil apparatus at room temperature was first reported by Jacobsen et al.\textsuperscript{17} Yuan et al.\textsuperscript{18} developed a method for simultaneously measuring electrical resistivity and the Seebeck coefficient at high pressure (5 GPa) and temperatures up to 750 K in a cubic multi-anvil apparatus. This method uses the inherent temperature gradient in samples along the axial direction of the cylindrical heater, which is essential for measuring the Seebeck coefficient. The $\Delta T$ between both sample ends in a high-pressure cell tends to increase with increasing average sample temperature. Large uncertainties are often unavoidable at high temperature because the thermoelectromotive force (emf) of the semi-conducting materials themselves is typically non-linear with $\Delta T$. Alternatively, installation of an additional heater can be useful to control small $\Delta T$ between sample ends during thermoelectric power.
measurements to allow accurate determination of the Seebeck coefficient near the target temperature.

For this purpose, we have developed a dual-heating system for accurate $\Delta T$ control between both ends of the sample in the 6-axis press installed at Institute for Planetary Materials, Okayama University. Because a Kawai-type (6-8) multi-anvil press can generate much higher pressures than a cubic multi-anvil press, we developed an octahedron cell including dual heaters. We introduce the system specifications and performance with technical and analytical protocols to determine the Seebeck coefficient under high temperature and pressure conditions. This method is useful to determine the thermoelectric properties of conductive materials as a function of temperature at high pressure.

II. EXPERIMENTAL METHOD

A. Principle of Seebeck coefficient measurement by dual heating

Measurement of the Seebeck coefficient in materials only requires knowledge of the temperature difference and voltage across two locations on the sample. The $\Delta T$ and electric potential are measured from probes in direct contact with the sample ends, and the Seebeck coefficient can be determined from the slope of $\Delta V$ vs. $\Delta T$ following the differential method. Figure 1 shows a schematic design of the Seebeck coefficient measurement used in our laboratory. The probes serve as both two sets of thermocouples and voltage leads from both ends of the sample. The thermocouples are not involved in the emf measurement. Each thermocouple is connected to each side of a
disk-shaped sample through a metal electrode. Each of the dual-heating systems is configured as a separate circuit from the thermopower measurement circuit. An AC power supply was used for heating. Proportional-integral-differential (PID) temperature control was used to generate $\Delta T$ between both ends of the sample. Each heater controls the temperature at the position of the thermocouple to which it is closer located. The $\Delta V$ is measured at fixed pressure and variable $\Delta T$. The $\Delta V$ values are measured and plotted to eliminate any voltage offset. The Seebeck coefficient ($S$) is calculated from the slope of the temperature difference ($\Delta T = T_1 - T_2$) and emf ($\Delta V$) assuming linearity in $S$ for the bulk sample. The absolute Seebeck coefficient is corrected for contributions of voltage from the contact wires by subtracting the Seebeck voltage produced by the probe wires. In the case of the semiconductor samples with particularly larger Seebeck coefficients (> 100 $\mu$V/K), however, the small emf produced by the metal leads and WC anvils (~1 $\mu$V/K) can be ignored.

B. Electrical resistivity measurement

A four-wire resistance measurement design was used to measure the temperature-dependence of sample electrical resistivity. In the resistivity measurement, the temperature is controlled to be the same at both ends of the sample to avoid the thermopower derived from the sample itself. The obtained resistance data were processed to compute sample resistivity using Ohm’s law, $R = \frac{V}{I}$, where $R$ is resistance, $V$ is the voltage drop, and $I$ is current. The sample resistivity was calculated on the basis
of the sample dimension $\rho = \frac{RA}{L}$ where $L$ and $A$ are the sample length and cross-
sectional area, respectively.

C. Sample and Cell Assembly

The samples used for testing are p-type Si wafers with relatively higher $S$ than n-
type Si.\textsuperscript{21} One reason for choosing Si-based materials is that the band structure of Si is
well known. Si-based devices are considered as an important thermoelectric materials,
and often applied to a refrigeration systems, such as central processing units (CPUs) or
field emission displays (FEDs).\textsuperscript{22} We measured two p-type Si wafers manufactured by
Sinyo Co.Ltd. and Shin-Etsu Chemical Co. with low and high carrier concentrations,
respectively, although the exact concentration is unknown. Si wafers with a thickness of
0.52 mm were cored into a disk shape with 2-mm diameter using an ultrasonic drilling
machine.

A Kawai cell (6-8 type) was used for thermoelectric measurements under high
pressure. The cell assembly is shown in Fig. 2. A Cr$_2$O$_3$-doped MgO octahedron with an
dge-length of 14 mm was used as a pressure medium in second stage tungsten carbide
 anvils with a truncation edge length of 8 mm. The outer assemblage consisted of a
Cr$_2$O$_3$-bearing MgO pressure medium, ZrO$_2$ thermal insulator, and a cylindrical MgO
 polycrystalline sleeve. Two TiB$_2$-doped BN + AlN composite disk heaters with 4-mm
diameter and 0.3-mm thickness were set at both sides of the sample using an MgO
 spacer. The electrodes of the sheet heater with two independent circuits were each
connected to the truncated WC anvil surface in the orthogonal direction. The disk-shaped sample was sandwiched by Mo electrodes. One sample face was covered by a Mo electrode, a $W_{97}Re_{3}-W_{75}Re_{25}$ thermocouple (0.1 mm in diameter) for temperature reading, and one end of the W wire for probing the voltage difference placed at the center of the sample. The junction of the other $W_{97}Re_{3}-W_{75}Re_{25}$ thermocouple and W wire were set on the opposite sample face. The other end of the W wires was connected to the truncation surface of the WC anvils located perpendicular to the sample surface. Outside the Kawai cell, six of the eight second-stage WC anvils were used as electrodes for monitoring the thermopower between both ends of the sample and dual heaters. These six second-stage anvils were connected to all six first-stage anvils, each of which was electrically insulated using Cu foil across the insulation plate. The two sets of $W_{97}Re_{3}-W_{75}Re_{25}$ thermocouples were electrically insulated from the sheet heater by MgO and exited the cell through the pyrophyllite gaskets. The wires for monitoring $T_1$, $T_2$, and $\Delta V$ were connected to a Keysight 34970A data logger.

High-pressure and high-temperature experiments were performed in a 6-axis multi-anvil apparatus. The 6-axis press has no guide blocks, which allows sufficient space to handle the set of lead wires and minimize short circuits during compression. Each anvil of the 6-axis press is electrically insulated, which implies that even if four of the six surfaces are used for dual heating, the remaining two anvils can be used as electrodes for measuring emf. Reducing the numbers of probes through the gaskets is of great merit in multi-anvil experiments because wire breakage frequently occurs during compression.
III. RESULTS AND DISCUSSION

A. Dual heating

To ensure accurate control of $\Delta T$ between both ends of the sample, we tested the dual heating performance at 5 GPa by two approaches. In case (1), the temperature on one side of the sample ($T_1$) was held fixed while the temperature on the other side ($T_2$) oscillated. In case (2), when $T_1$ deviated from the target $T$, $T_2$ was simultaneously controlled in the opposite direction. The average $T$ oscillates in the former case, whereas a constant average $T$ can be maintained in the latter case. In this oscillation mode, $\Delta T$ values across the sample can be continuously adjusted from positive to negative. In both cases, a maximum peak-to-peak $\Delta T$ of ±20 K was applied.

Examples of temperature oscillations (± 20 K) in high-temperature runs are shown in Fig. 3. The temperature fluctuation was controlled within 1 K of the set value at the two thermocouple junctions on both ends of the sample. For measurements at each temperature, $\Delta T$ was produced around a given target temperature. The $\Delta T$ could not be precisely controlled at $T$ close to room temperature because the power required to generate $\Delta T$ on both sides of the sample was too small compared with the original $\Delta T$ created by a single heater. However, a control of $\Delta T$ was possible when the target $T$ was $> 373$ K. Accurate control of the temperature becomes impossible at $T > 1473$ K and the heater electrode frequently broke at $T > 1500$ K. When both ends of the sample are held at the same temperature by dual heating, the power ($W$) generated by each heater is equivalent. In case (1) where $T_1$ is held fixed, $W_2$ increases when $T_2$ increases and $W_1$
correspondingly decreases. In case (2), \(W_1\) and \(W_2\) showed the opposite behavior. In both cases, the total applied power remains nearly constant.

**B. Seebeck Coefficient measurement**

The Seebeck coefficient measurements of p-type Si wafers were performed over a temperature range of 473–1473 K at 100-K intervals at 3 and 5 GPa. The temperature dependence of the Seebeck coefficient of the bulk material was determined during both the heating and the cooling cycles. The sample environment in the cell assembly usually changes during heating, and electrical conductivity measurements of hydrous samples in a multi-anvil press have shown different paths along heating and cooling cycles owing to sample dehydration. The reliability of obtained data can therefore be confirmed by overlapping the Seebeck coefficient measured during both heating and cooling.

Our results show a linear response of voltage to changes in \(\Delta T\) with the slope yielding the Seebeck coefficient (Fig. 4). \(\Delta V\) should ideally be zero, when \(\Delta T = 0\).

Although a small degree of voltage offset is observed, the extent is substantially smaller than \(\Delta V\) produced by small changes of \(\Delta T\). The measured voltage includes not only the sample but also both electrical and thermal contacts to the sample and the instrumentation.

The Seebeck coefficient of heavily B-doped Si obtained under variable temperature and constant pressure is shown in Fig. 5. The thermopower measurements were carried out by maintaining a constant press load and varying the temperature. At fixed pressure (5 GPa), the Seebeck coefficient decreases slightly with increasing temperature between
473 and 873 K, and then abruptly decreases to zero with increasing temperature above 973 K. Although the carrier concentration of this sample is unknown, the absolute $S$ value and $T$-dependence of Si are in excellent agreement with those of p-type Si with carrier densities on the order of $10^{18}$–$10^{19}$ cm$^{-3}$ measured at room pressure.$^{25-27}$ The sign of $S$ changes from positive to negative at ~1273 K, which is close to the melting temperature of Si at 5 GPa. Previous experimental studies on the melting curve of Si I (diamond structure) yield the following relation $T$ (K) = $-62.3 \times 1.4$P (GPa) + 1683.$^{28-33}$ At 5 GPa, the melting temperature of Si is calculated to be 1372 K. The temperature of the Seebeck coefficient polarity change is lower than the Si I melting temperature, and is therefore not considered to be caused by melting.

Figure 6 shows the Seebeck coefficients of B-doped Si with low carrier concentrations at 3 GPa and variable temperature up to 1273 K. The thermopowers were measured at two different press loads and variable temperature up to 1000 K. The Seebeck coefficient slightly decreases with increasing temperature, and then abruptly decreases to negative values over the temperature range of 473–573 K. Above 573 K, the Seebeck coefficient slightly decreases with increasing temperature. Electrical resistivity also decreases abruptly in the same temperature range (Fig. 7). This behavior is consistent with that of p-type Si with low carrier concentrations on the order of $10^{14}$ cm$^{-3}$ measured at room pressure,$^{34}$ which is consistent with the dopant carrier concentration (4.6×$10^{14}$ cm$^{-3}$) estimated from the measured electrical resistivity of this sample (29 Ω·cm) at room temperature and 3 GPa.$^{35}$

The results of measurements of Si with different levels of donor doping demonstrate
a negligible pressure effect on the thermoelectric properties of Si, and that carrier concentration influences the $T$-dependent Seebeck coefficient. The temperatures at which the Seebeck coefficient rapidly decreases, increases from 500 to 900 K with increasing carrier concentration from $10^{14}$ to $10^{19}$ cm$^{-3}$. This trend agrees qualitatively with results from an ab initio calculations that show the thermopower reaches a maximum at an electron carrier concentration of $\sim 10^{15}$ cm$^{-3}$ at 500 K, while the maximum at 900 K shifts to a higher dopant level of $10^{18}$ cm$^{-3}$.

The Seebeck coefficient is the sum of the diffusive part and phonon drag part with the former dominating thermopower in heavily doped samples and the latter dominating that of pure Si. However, the phonon drag effect only dominates at temperatures below 300 K. For low dopant level Si, the thermopower rapidly vanishes at a distinct temperature of $\sim 500$ K. The drop off of the Seebeck coefficient appears at the approximate temperature range between extrinsic and intrinsic electrical resistivity. At this temperature, the electronic transport enters the bipolar intrinsic regime (Fig. 6). At high charge carrier concentrations of about $10^{18}$ cm$^{-3}$, the intrinsic regime likely becomes dominant near the melting temperature. The thermopower for Si wafers in the intrinsic transport regime converges to small negative values for electrons at higher temperature. Because the band gap of semiconductors generally decreases with increasing temperature, the chemical potential moves toward the band edge with increasing temperature in the “extrinsic” region and enters the band gap in the “intrinsic” temperature region. The observed drop off of the Seebeck coefficient over the investigated temperature range therefore indicates that the carrier concentration
increases at certain temperatures, from the doping concentrations to the intrinsic values.

IV. CONCLUSIONS

We report a new technique to measure the Seebeck coefficient under high pressure and high temperature in a Kawai-type mutil-anvil apparatus. We have developed a dual-heating system in the 6-axis press installed at the Institute for Planetary Materials of Okayama University. The dual-heating system can precisely control the temperature difference between the two ends of a sample up to 1473 K and at least 5 GPa. The resistivity and Seebeck coefficient of Si have been measured to evaluate the effectiveness of this method. The results are in good agreement with the previous results measured at ambient pressure, suggesting that the applied pressure effect does not greatly affect the thermoelectric properties of Si. This approach is reliable and simple with a high success rate and good reproducibility. This technique can be widely applied for investigating the thermoelectrical properties of not only thermoelectric materials and but also mantle and core materials in the Earth’s interior.

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References

FIG. 1. Schematic drawing of the Seebeck coefficient and resistivity measurement setup by dual heating in a Kawai-type multi-anvil apparatus. Temperatures at two ends of the sample are monitored by two sets of thermocouples, and two resistive heaters are separately computer-controlled. A data logger (Keysight 34970A) collects $T_1$, $T_2$ and $\Delta V$ data as a function of time.
FIG. 2. Schematic illustration of the octahedron cell assembly used for the Seebeck coefficient and resistivity measurements.
FIG. 3. Variations of temperature and heating power during the Seebeck coefficient measurement at 673 K by dual heating for case 1 with the fixed $T_1$ and case (2) where the temperatures of $T_1$ and $T_2$ oscillate in opposite directions. The top, bottom, and average temperature of the sample are shown as a function of time for (a) case 1 and (c) case 2. Red, blue, and gray circles denote $T_1$, $T_2$, and average temperature, respectively. The applied power for heating at the top and bottom heaters is shown as a function of time for (b) case 1 and (d) case 2. Red and blue circles denote applied powers $W_1$ and $W_2$ for heaters 1 and 2, respectively.
FIG. 4. Voltage response to the temperature difference ($\Delta T$) for (a) the heavily B-doped Si at 473, 673, 873, 1073, and 1273 K and (b) Si with low carrier concentration at 473, 673, 873, and 1073 K.
FIG 5. Temperature dependence of the Seebeck coefficient of p-type Si with high carrier concentration at 5 GPa. Also shown are previously reported Seebeck coefficients of Si with high carrier concentrations ($10^{18-19}$ cm$^{-3}$).
FIG. 6. Seebeck coefficient of p-type Si with low carrier concentration at 3 GPa as a function of temperature. Solid and gray lines indicate calculated values\textsuperscript{31} for p- and n-type Si, respectively. The dashed line represents the calculated Seebeck coefficients for the intrinsic regime\textsuperscript{31}.
FIG. 7. Electrical resistivity of p-type Si with low carrier concentration at 3 GPa as a function of reciprocal temperature.
2nd cooling
3rd heating

Temperature (K)

Seebeck coefficient (µV/K)

-200 -100 0 200 300 400 500 600 700 800 1200 1400 1600

1 atm P-type (B-doped) Si
Theory
- $6.3 \times 10^{18}$ cm$^{-3}$ (ref. 25)
- $10^{19}$ cm$^{-3}$ (ref. 26)

Experiment
- $6.3 \times 10^{18}$ cm$^{-3}$ (ref. 25)
- $5 \times 10^{18}$ cm$^{-3}$ (ref. 27)
- $8.1 \times 10^{19}$ cm$^{-3}$ (ref. 27)

5 GPa highly B-doped Si
- 2nd cooling
- 3rd heating
Log[R (ohm cm)]

1000/T (K⁻¹)

3 GPa
Low B-doped Si