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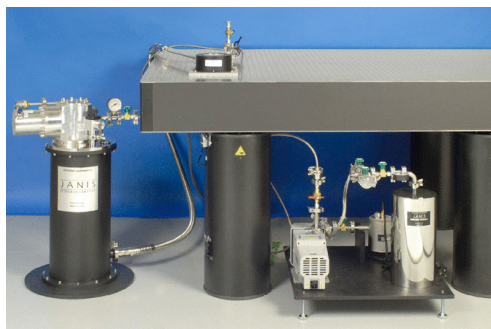
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# A rapid method to extract Seebeck coefficient under a large temperature difference

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The Seebeck coefficient is one of the three important properties in thermoelectric materials. Since thermoelectric materials usually work under large temperature difference in real applications, we propose a quasi-steady state method to accurately measure the Seebeck coefficient under large temperature gradient. Compared to other methods, this method is not only highly accurate but also less time consuming. It can measure the Seebeck coefficient in both the temperature heating up and cooling down processes. In this work, a Zintl material ( $\text{Mg}_{3.15}\text{Nb}_{0.05}\text{Sb}_{1.5}\text{Bi}_{0.49}\text{Te}_{0.01}$ ) was tested to extract the Seebeck coefficient from room temperature to 573 K. Compared with a commercialized Seebeck coefficient measurement device (ZEM-3), there is  $\pm 5\%$  difference between those from ZEM-3 and this method. Published by AIP Publishing. <https://doi.org/10.1063/1.4986965>

## I. INTRODUCTION

Thermoelectric (TE) materials, capable to convert waste heat into electricity without noise and pollution, have drawn much attention in recent years. TE efficiency is directly related to the material's figure of merit ( $ZT$ ),  $ZT = (S^2\sigma/\kappa)T$ , where  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity, and  $T$  is the absolute temperature.<sup>1–5</sup> For applications aiming at large electric power production, a high power factor ( $S^2\sigma$ ) is equally important,<sup>6</sup> while a high peak  $ZT$  is needed for high conversion efficiency. Compared with electrical conductivity and thermal conductivity, the Seebeck coefficient has more influence on efficiency and output power density.

The traditional Seebeck coefficient measurement device like ZEM-3 (ULVAC Riko) is conducted under small temperature differences ( $\Delta T$ ). By changing  $\Delta T$ , a series of small  $\Delta T$ 's (within 3 K) between two thermocouples and the corresponding open circuit voltages ( $\Delta V$ ) are measured.<sup>7–10</sup> The slope from the linear fitting of  $\Delta T$  and  $\Delta V$  can be obtained which is regarded as the Seebeck coefficient. However, the thermal contact, temperature variation, and chemical reaction between TE materials and thermocouples will not only lead to misreading of  $\Delta T$  but also generate offset voltage<sup>7,11</sup> in the Seebeck measurement.<sup>7</sup> Even though the offset voltage can be avoided in the slope method, the misreading of  $\Delta T$  will still bring large errors to the Seebeck coefficient. Measurement performed under large  $\Delta T$  was successful when minimizing the influence of offset voltage and reading errors on temperature and voltage.<sup>12</sup>

The large  $\Delta T$  method is preferred over the small  $\Delta T$  method if the sample is designed for high-temperature thermoelectric energy conversion.<sup>13</sup> It is important to accurately

measure the Seebeck coefficient under large thermal gradient. The reported method for the Seebeck measurement under large  $\Delta T$  is the integral method. The relation between the temperature-dependent Seebeck coefficient and open circuit voltage can be written as the following equation:

$$V(T_h, T_c) = \int_{T_c}^{T_h} S(T) dT. \quad (1)$$

In this case, while changing the hot side temperature ( $T_h$ ), the cold side temperature ( $T_c$ ) is fixed. A series of voltage can be recorded in different  $T_h$ 's. Then  $V(T_h, T_c)$  can be obtained as a function of  $T_h$ . Taking a derivation of  $V(T_h, T_c)$ , the function of  $S(T)$  can be achieved. In this method, a fitting curve is the major challenge for accurately determining the Seebeck coefficient. The fitting method must comprise the data set with minimal oscillations, as small random and biased errors will be amplified in the derivative.<sup>13</sup> And it is also difficult to maintain a fixed temperature of the cold side throughout measurement.

Besides, both of these two methods should be working under steady state to accurately measure temperature and voltage, which are time consuming due to the adjustment of different  $\Delta T$ 's. To enable rapid measurement of the Seebeck coefficient, the quasi-steady state method and dynamic method have been adopted to the small  $\Delta T$  method<sup>14,15</sup> in which temperature is not necessarily maintained steady. In this work, we propose a method to address the Seebeck coefficient under large  $\Delta T$  with temperature continuously changed. This method with less time consuming shows high accuracy, as the error is within 5% compared with ZEM-3.

## II. EXPERIMENTAL DETAILS

### A. Description of setup

A schematic measurement setup is shown in Fig. 1. There is a heater at the top and a cooling system at the bottom in

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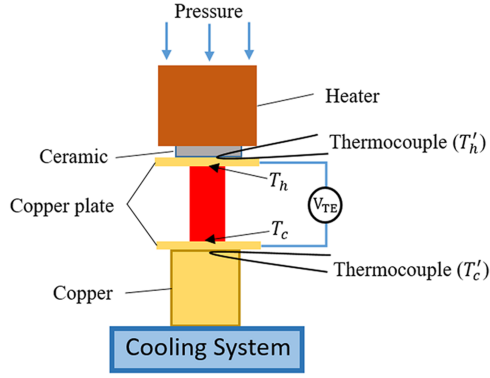


FIG. 1. Schematic of the Seebeck coefficient measurement setup.

order to generate large  $\Delta T$  in the TE material. According to Eq. (1), the open circuit voltage is only related to temperatures on the hot and cold sides of a sample, since the function of Seebeck  $[S(T)]$  is the intrinsic property that will not be affected by temperature distribution through the leg. Therefore, a radiation shield was not added to eliminate radiation loss in this experiment.<sup>16</sup> Considering the real applications, TE legs are brazed with copper plates in this experiment. The bottom copper plate was directly contacted with the cooling system to make a relatively steady cold side temperature. There is no need to insulate the bottom copper plate with a bottom copper block, since a piece of AlN ceramic has been inserted between the upper copper plate and heater to insulate the thermoelectric materials with surroundings for the sake of accurate voltage measurement. Thermocouples were embedded at the surface of copper plates, which can also avoid the reaction between thermocouples and TE materials.<sup>7</sup> K-type thermocouples in 0.127 mm diameter (Omega, Inc.) were used for temperature monitoring. Such a small diameter allows the thermocouples to draw less heat from the sample, thus reducing the deviation from the actual temperature.<sup>15</sup> Compressive pressure was applied to minimize the contact resistance at the interface.<sup>12</sup> Since voltage and temperature measurements are better to be separate for an ideal measurement,<sup>15</sup> copper wires were brazed with copper plates for voltage reading. Controlled by LabVIEW, the temperatures were read by NI-9203 and voltages were read by the nano-voltmeter Keithley 2182a with nV resolution. While the response of the thermocouple and voltmeter is less than 0.1 s, the recording time for one loop in LabVIEW is set to be 0.1 s. The interval of recording is so small that temperatures and voltages can be regarded as being recorded simultaneously.

## B. Preparation of sample

The sample in this work is a new n-type Zintl material ( $\text{Mg}_{3.15}\text{Nb}_{0.05}\text{Sb}_{1.5}\text{Bi}_{0.49}\text{Te}_{0.01}$ ),<sup>17</sup> which was cut and polished to size  $\sim 2.1 \times 2.1 \text{ mm}^2$  in cross section and  $\sim 12 \text{ mm}$  in height. Both sides of the TE leg were electroplated with copper, nickel, and gold in sequence and then soldered ( $\text{In}_{52}\text{Sn}_{48}$ , melting point 391 K;  $\text{Pb}_{97}\text{Sn}_{1.5}\text{Ag}_{1.5}$ , melting point 586 K to the cold and hot sides, respectively) to copper plates separately.<sup>18</sup> Instead of measuring voltage with thermocouples,

copper wires were soldered to both sides of copper plates which could eliminate the contact voltage.<sup>11</sup> Since we have not found a good high-temperature braze material and a contact layer for Zintl material, in this work, the sample was measured from room temperature to 573 K. The experiments were performed under high vacuum (below  $10^{-6}$  mbar) to eliminate the oxidation of the sample.

## C. Methodology

In this method, we gradually change  $T_h$  from room temperature to high temperature, while maintaining  $T_c$  steady. By tuning the input voltage of power supply, the heating rate can be maintained around a certain value. To make sure that the temperatures and open circuit voltages are measured at the same time, a small heating rate should be adopted in this method to reduce the error caused by temperature drift during data collection.<sup>14</sup>

As indicated in Fig. 1, for the upper copper plate, the temperature of one side of the copper plate in contact with the TE material can be noted as  $T_h$  and that of the opposite side can be noted as  $T'_h$ . Due to the small thickness and high thermal conductivity of the copper plates,  $T_h$  and  $T'_h$  can be considered equal. It also applies to the bottom copper plate that  $T_c$  equals to  $T'_c$ . Considering the Seebeck coefficient of copper  $[S_{Cu}(T)]$  and offset voltage ( $U_{off}$ ), the open circuit voltage generated by TE materials ( $V$ ) is a little different from the measured open circuit voltage ( $V'$ ). To obtain the Seebeck coefficient at  $T'_h$ , we define two temperatures  $T'_{h1}$  and  $T'_{h2}$ , which are close to  $T'_h$ .

Therefore, the following relation can be obtained:

$$T'_{h1} - T'_{h2} = T_{h1} - T_{h2}. \quad (2)$$

$T_{h1}$  and  $T_{h2}$  are the temperatures of TE corresponding to  $T'_{h1}$  and  $T'_{h2}$  separately. Based on Eq. (1), we can use the following equations to get the corresponding measured voltages  $V'_1$  and  $V'_2$  for n-type samples.<sup>15</sup> Since  $T'_{h1}$  and  $T'_{h2}$  are very close, the offset voltage<sup>9</sup> can be regarded as equal at these two temperatures,<sup>11</sup>

$$V'_1 = \int_{T_c}^{T_{h1}} (S(T) - S_{Cu}(T)) dT + U_{off}, \quad (3)$$

$$V'_2 = \int_{T_c}^{T_{h2}} (S(T) - S_{Cu}(T)) dT + U_{off}. \quad (4)$$

The Seebeck coefficient between  $T_{h1}$  and  $T_{h2}$  can be regarded as constant, which also equals to the value between  $T'_{h1}$  and  $T'_{h2}$ . From Eq. (2) to Eq. (4), we can get another equation,

$$\begin{aligned} V'_1 - V'_2 &= \int_{T_{h2}}^{T_{h1}} (S(T) - S_{Cu}(T)) dT \\ &= (S(T_h) - S_{Cu}(T_h)) (T_{h1} - T_{h2}) \\ &= (S(T'_h) - S_{Cu}(T'_h)) (T'_{h1} - T'_{h2}). \end{aligned} \quad (5)$$

From Eq. (5), we can measure two temperatures close to  $T'_h$  and the corresponding voltages to get the Seebeck coefficient of the sample at  $T'_h$ . This method allows  $U_{off}$  and temperature reading errors to be eliminated. Compared with the small

$\Delta T$  method that measures the temperature differences across a sample, the change of hot side temperature was measured here. Thermocouples measuring small absolute temperature differences across a sample have the tolerant errors even with high accuracy.<sup>19</sup> However, they are extremely accurate in measuring changes in temperature. The uncertainties from the thermocouples are largely eliminated due to the measurement of the change of hot side temperature. That is to say, even though the open circuit voltages and temperatures we measured are not completely the same as the open circuit voltages and temperatures of TE, the Seebeck coefficient can still be accurately obtained. To further reduce the error, more data measured around  $T'_h$  can be selected to extract the slope of the measured hot side temperature and open circuit voltage at  $T'_h$ . From the slope, the Seebeck coefficient can be obtained at  $T'_h$ . It should be noticed that  $T'_c$  will also increase with  $T'_h$  increased since heat flux is enlarged. For a certain temperature measurement, if the change of  $T'_c$  is very small compared to the increase of  $T'_h$ ,  $T'_c$  and  $T_c$  can still be deemed to be fixed. To ensure repeatability and confirm the stability of the sample during heating in the measurement environment, the Seebeck coefficient should be measured during both heating and cooling processes. After the heating up process, the power supply was turned off, and let the hot side cool down spontaneously by heat transfer to the surroundings. Same as the Seebeck measurement during heating up, voltages and temperatures were also recorded in the cooling down process to extract the Seebeck coefficient. It is acceptable that the deviation between data sets is within 5%. This method will be compared with ZEM-3 to see whether this method is reliable.

### III. RESULTS AND DISCUSSION

Figure 2(a) shows that there is a small increase of  $T'_c$  from 293.72 K to 293.80 K. For a small time interval in Fig. 2(a), the oscillation of  $T'_c$  is within  $\pm 0.02$  K, which may be caused by the potential reading error of LabVIEW. The recorded  $T'_h$  also has the same phenomenon. In Fig. 2(b), plenty of dots form a thin line, which shows the small oscillation in temperature reading. To eliminate the influence of temperature oscillation, a relatively large  $T'_h$  range ( $\pm 3$  K) was selected. While  $T'_h$  was increased from 320 K to 326 K, the temperature increased at the cold side was 0.08 K which is 1.3% of the temperature increased at the hot side. Therefore, the increase of  $T'_c$  can be ignored, and  $T'_c$  can be regarded as a constant. Since the data were recorded in every 0.1 s, there were more than 1000 recorded temperatures and voltages. To further lower the influence of reading error of the thermocouple and voltmeter, data points were selected with a 1 K interval. Totally, 7 data points were chosen to extract the Seebeck coefficient. The selected corresponding temperatures and voltage are marked in Fig. 3(a). The slope is  $-198 \mu\text{V/K}$  which is a negative value, since this TE material is an n-type material. Added by the Seebeck coefficient of copper that is about  $2 \mu\text{V/K}$  at 323 K from Ref. 20, the Seebeck coefficient measured at 323 K is  $-196 \mu\text{V/K}$  in this method. The Seebeck coefficient from ZEM-3 at 323 K is  $-205 \mu\text{V/K}$ . The error in this measurement is 4.4%, which is accurate enough. Applying the same method, we can conduct the Seebeck

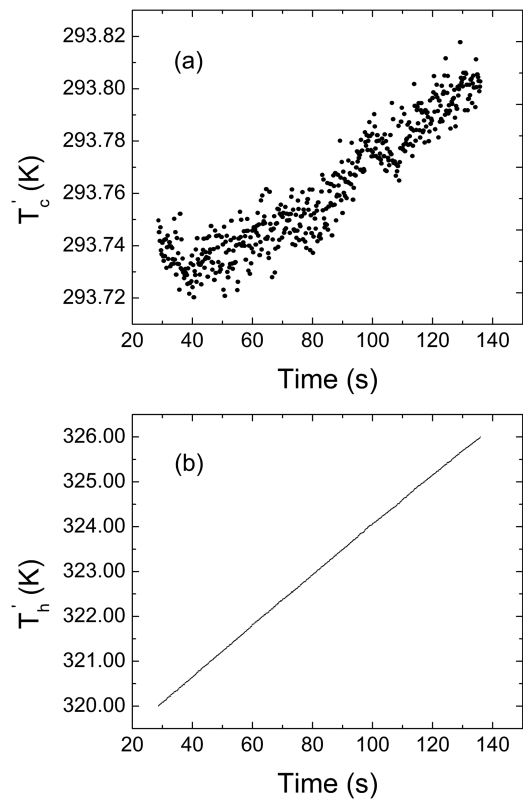


FIG. 2. (a)  $T'_c$  as a function of time with  $T'_h$  around 323 K; (b)  $T'_h$  around 323 K as a function of time.

coefficient measurement at different temperatures in the process of both heating up and cooling down. To show the elimination of offset voltage, a relation between  $\Delta V'$  and  $\Delta T'_h$  is plotted in Fig. 3(b).  $\Delta T'_h$  is the difference between 323 K and other temperatures, and  $\Delta V'$  is the difference between the measured voltage at 323 K and measured voltages at other temperatures. It should be pointed out that when  $\Delta T'_h$  is zero,  $\Delta V'$  is close to zero which means offset voltage has been eliminated. However, because of the intrinsic error of the thermocouple and nano-voltmeter, the interception may not be necessarily at zero but at a very small value that does not affect the measurement accuracy too much.

Figure 4(a) illustrates the temperature changing rate ( $\varepsilon$ ) of heating up and cooling down processes. The increasing rate was kept between 3 K/min and 5 K/min, not only to avoid temperature drift but also to maintain a relatively large rate. During the cooling down process, the cooling rate decreased from 11 K/min to 0.2 K/min.  $T'_h$  decreased quickly at the very beginning since the heat loss was heavily at high temperature. The temperature decreasing rate is small at nearly room temperature due to the small temperature difference between the hot side and cold side. Figure 4(b) shows the Seebeck coefficient extracted in different situations. We can find that the Seebeck coefficient extracted from the temperature increasing and cooling process highly matches the data from ZEM-3 with error around 5%, which demonstrates that this method is convincing and this material is stable. The largest deviation occurred at 573 K between heating up and cooling down, which may be explained by a significant temperature drift at the cooling rate about 11 K/min. Compared with the integral



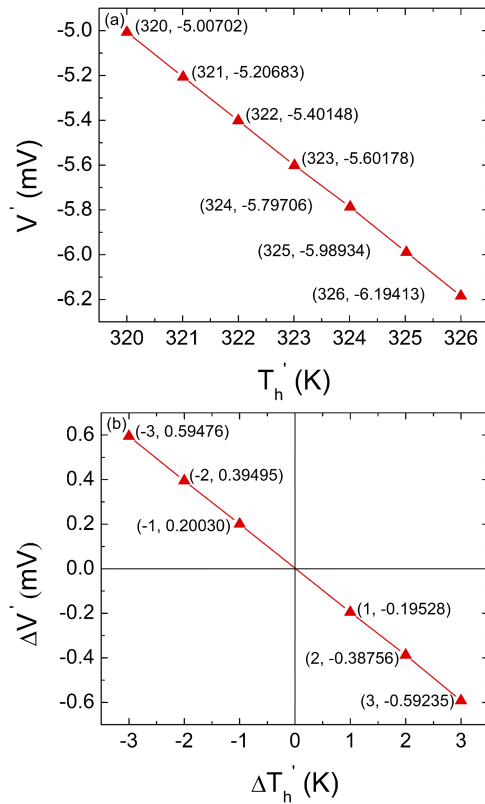


FIG. 3. (a) The measured open circuit voltage ( $V'$ ) as a function of  $T_h'$  with  $T_h'$  around 323 K; (b) the relation between  $\Delta T_h'$  and  $\Delta V'$ .

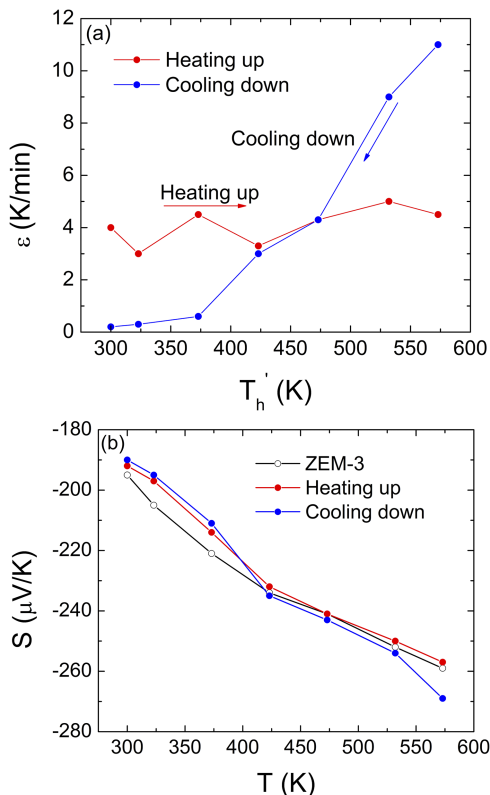


FIG. 4. (a) Temperature changing rates in heating up and cooling down processes; (b) the Seebeck coefficient extracted at different temperatures from different measurement methods.

method, this method overcomes the drawback of curve fitting. Usually, it takes 3 h for ZEM-3 to measure electrical properties from room temperature to 573 K in every 50 K. In this method, the measurement can be accomplished within 1 h.

#### IV. CONCLUSION

A setup is developed for accurate Seebeck coefficient measurement under large  $\Delta T$ . This method not only overcomes the shortage of integral method but also addresses the existing errors in small  $\Delta T$  measurement. The Seebeck coefficient measured in this method has an error within  $\pm 5\%$  compared with ZEM-3. The Seebeck measurement during the cooling down process proves the reliability of this method. This quasi-steady state method consuming less time, however, should be performed at the rate around 3~5 K/min during the heating process. To further improve the device, resistivity and thermal conductivity will be addressed under large  $\Delta T$  in the near future.

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