Proposal of time domain impedance spectroscopy to determine precise dimensionless figure of merit for thermoelectric modules within minutes

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Several techniques exist that use a thermoelectric element (TE) or module (TM) to measure precise dimensionless figure of merit \((zT)\), both qualitatively and quantitatively. The techniques can be applied using both alternating (AC) and direct current (DC). Herein, the transient Harman (TH) and impedance spectroscopy (IS) methods were investigated as direct \(zT\) measurement techniques using identical TM, which showed that \(zT\) at 300 K was 0.767 and 0.811 within several minutes and several hours, respectively. The \(zT\) values differed despite the use of the same TM, which revealed that measuring ohmic resistance using DC and pulse DC is potentially misleading owing to the influence of Peltier heat on current flow. In this study, time domain impedance spectroscopy (TDIS) was proposed as a new technique to measure \(zT\) using proper DC and AC. \(zT\) obtained using TDIS was 0.811 within several minutes using the time and frequency domains, and was perfectly consistent with the result of the IS method. In conclusion, the TDIS is highly appropriate in estimating \(zT\) directly using only proper electrometric measurements, and without any heat measurements.

List of symbols

| Symbol | Description |
|--------|-------------|
| TE     | Thermoelectric element |
| TM     | Thermoelectric module |
| AC     | Alternating current |
| DC     | Direct current |
| IS     | Impedance spectroscopy |
| TH     | Transient Harman method |
| PTH    | Pulse and transient Harman method |
| TDIS   | Time domain impedance spectroscopy |
| R2C model | A simple model of thermoelectric or thermo-module using two resistance and one capacitance |
| RC model | A simplified model of thermoelectric or thermo-module using two resistance and one capacitance |
| VM     | Voltmeter |
| DAQ system | Data acquisition system |
| SNR    | Signal-to-noise ratio |
| \(n\)  | Number of elements in a thermoelectric module (TM) (–) |
| \(T\)  | Absolute temperature (K) |
| \(\Delta T\) | Temperature difference (K) |
| \(\Delta T_f\) | Temperature fluctuation of sample stage anchoring (K) |
| \(S\)  | Seebeck coefficient (V/K) |
| \(\rho\) | Resistivity (Ωm) |
| \(\kappa\) | Thermal conductivity (W/mK) |
| \(\omega\) | Angular frequency (rad/s) |

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\( \omega_{TE} \) Characteristic frequency of thermoelectric or thermo-module using impedance spectroscopy (IS) \((\text{rad/s})\)

\( \omega_{R2C} \) Characteristic frequency of thermo-module using R2C approximation \((\text{rad/s})\)

\( Z(\omega) \) Impedance as a function of angular frequency \(\omega\) \((\Omega)\)

\( Z_{R2C}(\omega) \) Impedance as a function of angular frequency \(\omega\) applying R2C approximation \((\Omega)\)

\( Z_{\text{meas}}(\omega) \) Measured impedance as a function of angular frequency \(\omega\) \((\Omega)\)

\( R_{\text{ohm}} \) Ohmic resistance \((\Omega)\)

\( R_{AC} \) AC resistance with an alternating current by Harman method \((\Omega)\)

\( R_{DC} \) DC resistance with a direct current by Harman method \((\Omega)\)

\( R_{TE} \) Thermoelectric resistance \((\Omega)\)

\( R_{\text{ohm}} + R_{TE} \) Sum of ohmic \((R_{\text{ohm}})\) and thermoelectric \((R_{TE})\) resistances \((\Omega)\)

\( C_{\text{TE}} \) Thermoelectric capacity in system \((\text{F})\)

\( t \) Time \((\text{s})\)

\( \tau_{exp} \) Expected heat time constant in system \((\text{s})\)

\( \tau_{R2C} \) Estimated time constant using R2C approximation in Eq. (3) \((\text{s})\)

\( \tau_{RC} \) Estimated time constant using RC approximation in Eq. (4) \((\text{s})\)

\( T_p \) Pulse period of pulse and transient Harman (PTH) method \((\text{s})\)

\( t_p \) Pulse width of pulse and transient Harman (PTH) method \((\text{s})\)

\( R(t) \) Resistance as a function of time \(t\) \((\Omega)\)

\( R_{\text{meas}}(t) \) Measured resistance as a function of time \(t\) \((\Omega)\)

\( (R_{\text{ohm}})_{\text{IS}} \) Estimated ohmic resistance \((R_{\text{ohm}})\) by impedance spectroscopy (IS) method \((\Omega)\)

\( (R_{\text{ohm}})_{\text{TH,DAQ}} \) Estimated ohmic resistance \((R_{\text{ohm}})\) by transient Harman (TH) method using data acquisition (DAQ) system \((\Omega)\)

\( (R_{\text{ohm}})_{\text{TH,DAQ,R2C}} \) Estimated ohmic resistance \((R_{\text{ohm}})\) by transient Harman (TH) method using data acquisition (DAQ) system assuming R2C approximation in Eq. (3) \((\Omega)\)

\( (R_{\text{ohm}})_{\text{TH,DAQ,RC}} \) Estimated ohmic resistance \((R_{\text{ohm}})\) by transient Harman (TH) method using data acquisition (DAQ) system assuming RC approximation in Eq. (4) \((\Omega)\)

\( R_{\text{ohm}} \) Estimated ohmic resistance \((R_{\text{ohm}})\) by pulse DC using data acquisition (DAQ) system \((\Omega)\)

\( (R_{\text{ohm}})_{\text{delta}} \) Estimated ohmic resistance \((R_{\text{ohm}})\) using delta method, in which a current source is synchronized with an oscillating square wave at a frequency using a voltmeter \((\Omega)\)

\( (R_{\text{ohm}} + R_{TE})_{\text{IS}} \) Sum of estimated ohmic and thermoelectric resistances \((R_{\text{ohm}} + R_{TE})\) measured by impedance spectroscopy (IS) method \((\Omega)\)

\( (R_{\text{ohm}} + R_{TE})_{\text{TH,VM}} \) Sum of estimated ohmic and thermoelectric resistances \((R_{\text{ohm}} + R_{TE})\) measured by transient Harman (TH) method using voltmeter (VM) \((\Omega)\)

\( (R_{\text{ohm}} + R_{TE})_{\text{TH,DAQ}} \) Sum of estimated ohmic and thermoelectric resistances \((R_{\text{ohm}} + R_{TE})\) measured by transient Harman (TH) method using data acquisition (DAQ) system \((\Omega)\)

\( (R_{\text{ohm}} + R_{TE})_{\text{TH,DAQ,R2C}} \) Sum of estimated ohmic and thermoelectric resistances \((R_{\text{ohm}} + R_{TE})\) measured by transient Harman (TH) method using data acquisition (DAQ) system assuming R2C approximation in Eq. (3) \((\Omega)\)

\( (R_{\text{ohm}} + R_{TE})_{\text{TH,DAQ,RC}} \) Sum of estimated ohmic and thermoelectric resistances \((R_{\text{ohm}} + R_{TE})\) measured by transient Harman (TH) method using data acquisition (DAQ) system assuming RC approximation in Eq. (4) \((\Omega)\)

\( \rho \) Figure of merit \((=S^2/\rho\kappa)\) \((1/K)\)

\( zT \) Dimensionless figure of merit \((zT = S^2T/\rho\kappa = R_{TE}/R_{\text{ohm}} = (R_{\text{ohm}} + R_{TE})/R_{\text{ohm}} - 1)\) \((\Omega)\)

\( (zT)_{\text{IS}} \) Estimated dimensionless figure of merit \((zT)\) by impedance spectroscopy (IS) \((\Omega)\)

\( (zT)_{\text{TH,DAQ}} \) Estimated dimensionless figure of merit \((zT)\) by transient Harman (TH) method using data acquisition (DAQ) system \((\Omega)\)

\( (zT)_{\text{TH,DAQ,R2C}} \) Estimated dimensionless figure of merit \((zT)\) by transient Harman (TH) method using data acquisition (DAQ) system assuming R2C approximation \((\Omega)\)

\( (zT)_{\text{TH,DAQ,RC}} \) Estimated dimensionless figure of merit \((zT)\) by transient Harman (TH) method using data acquisition (DAQ) system assuming RC approximation \((\Omega)\)

\( (zT)_{\text{PTH}} \) Estimated dimensionless figure of merit \((zT)\) by pulse and transient Harman (PTH) method using data acquisition (DAQ) system \((\Omega)\)

\( (zT)_{\text{TDIS,VM}} \) Estimated dimensionless figure of merit \((zT)\) by time domain impedance spectroscopy (TDIS) method using voltmeter (VM) \((\Omega)\)

\( (zT)_{\text{TDIS,DAQ}} \) Estimated dimensionless figure of merit \((zT)\) by time domain impedance spectroscopy (TDIS) method using data acquisition (DAQ) system \((\Omega)\)

\( I(t) \) Passing current \([\text{A}]\) for DC or \([A_{\text{rms}}]\) for AC at time \(t\)

\( I_{\text{opt}} \) Optimum current for measurement \(<|S|/R_{\text{ohm}}\) [A] or \([A_{\text{rms}}]\)

\( I_{\text{max}} \) Maximum suitable current for time domain impedance spectroscopy (TDIS) [A] or \([A_{\text{rms}}]\)

\( q \) Joule heat \((=R_{\text{ohm}}I^2)\) \((\text{W})\)

\( Q_p \) Peltier heat \((|=S|T)\) \((\text{W})\)

\( \kappa \) Cross-sectional area of thermoelectric material \((\text{m}^2)\)

\( L \) Length of thermoelectric material \((\text{m})\)

\( \eta \) A proportional factor associated with heat flow of Peltier heat \((Q)\) to one side of the thermoelectric element \((-)\)

\( q_p \) Peltier heat flux through each thermoelectric element \((=Q_p/A)\) \((\text{W/m}^2)\)

\( \alpha \) Thermal diffusivity \((\text{m}^2/\text{s})\)

\( \phi \) Phase angle of impedance \((=\tan^{-1}(\text{Im}[Z_{\text{meas}}(\omega)]/\text{Re}[Z_{\text{meas}}(\omega)]))\) \((\text{rad})\)
Thermoelectric materials and elements (TEs) that can convert a temperature gradient into electricity (Seebeck effect) or electricity into a temperature gradient (Peltier effect) have drawn significant attention as a key technology for renewable energy\textsuperscript{1,2}. The performance and energy efficiency of TEs at the temperature $T$ have been described as a function of dimensionless figure of merit $zT$, where $z = \frac{S^2}{\rho \kappa}$ is the function of Seebeck coefficient ($S$), resistivity ($\rho$), and thermal conductivity ($\kappa$)\textsuperscript{1–3}. The $zT$ values are typically estimated using two different TEs such as a rectangular solid for the measurement of $S$ and $\rho$, and a thin disk for the measurement of $\kappa$; however, the ideal estimation of the $zT$ requires the use of the same TE or identical material. A direct $zT$ measurement technique using a rectangular solid of the TE was proposed by Harman et al. in 1958. The Harman method\textsuperscript{4–6} uses AC resistance $R_{AC}$ with an alternating current (AC) and DC resistance $R_{DC}$ with a direct current (DC), based on which $zT$ is expressed as $zT = \frac{R_{DC}}{R_{AC}} - 1$. However, the applicability of the method is limited owing to lack of information on the frequency of the AC and suitable magnitude of the AC and DC into the TEs.

Another approach to directly estimate $zT$ using the same TE is a technique called impedance spectroscopy (IS), which uses the frequency domain based on an one-dimensional heat conduction equation\textsuperscript{7–16}. Figure 1a,b show the schematic of Nyquist plot and the relation between its angular frequency ($\omega$) and impedance $Z(\omega)$, based on which the $zT$ is expressed as\textsuperscript{10,12,16}

$$zT = \frac{Z(\omega \rightarrow 0)|_{Q_p > > Q_l}}{Z(\omega \rightarrow \infty)|_{Q_p > > Q_l}} = 1 + \frac{R_{ohm} + R_{TE} \left(1 + \frac{Q_l}{Q_p}\right)}{R_{ohm} + R_{TE} \left|_{Q_p > > Q_l}\right| - 1} = \frac{R_{ohm} + R_{TE}}{R_{ohm}} - 1 = \frac{R_{TE}}{R_{ohm}} - 1 = \frac{\frac{\mathcal{S}^2 T}{\rho \kappa} - 1}{\frac{\mathcal{S}^2 T}{\rho \kappa} - 1 + \frac{Q_l}{Q_p}} = \frac{S^2}{\rho \kappa} T,$$

where $R_{ohm}$ and $R_{TE}$ are ohmic and thermoelectric resistance, $Q_p (=S|\Delta T|$) and $Q_l (= R_{ohm} \mathcal{F})$ are Peltier and Joule heat, $A$ and $L$ are cross-sectional area and length of the TE, respectively, and $\eta$ is a proportional factor associated with the heat flow of $Q_l$ to one side of the TE. In addition, $zT (= R_{TE}/R_{ohm})$ is denoted by the ratio of certain physical parameters such as resistance because $zT$ is dimensionless\textsuperscript{10,16}. Therefore, the physical meaning of the $zT$ implies a ratio of the ohmic resistance ($R_{ohm}$) to increasing resistance ($R_{TE}$) generated by the temperature difference ($\Delta T$) between the edges of the TE, which, in turn, is caused by the Peltier heat induced by DC. In particular, measuring the resistance, which is a macro physical quantity, is easy using recent electrometric instruments with a combination of a voltmeter for DC measurement and a lock-in amplifier for AC measurement by a precision
current source. Equation (1) also shows that the condition $Q_p > Q_t$ must be met to obtain the precise value of $zT$. Therefore, the optimum current $I_{opt}$ should be $I_{opt} < |S|/R_{\text{Rohm}}$. Moreover, the IS method is a suitable technique to determine the $zT$ for both TEs and thermoelectric modules (TMs), which are an assembly of thermoelectric elements. Hence, the measurement of $Z(\omega = 0)$ takes several minutes. A suitable characteristic frequency ($\omega_T$) is required at $\omega \rightarrow 0$ (or $\omega < \omega_T$). $\omega_T$ is denoted as a function of thermal diffusivity ($\alpha$) and $L$ of the TE, $\omega_T \propto \alpha/L$, and typically approaches 1 rad/s owing to the small value of $\alpha$ ($\alpha \alpha$) of the TEs. Therefore, the angular frequency satisfying $Z(\omega = 0)$ would approximately be of the order of 10^{-2} to 10^{-4} rad/s, depending on $L$[12,13]. The theory and model of the IS method clearly demonstrates that the Harman method is one of the results obtained using $Z(\omega = \infty) \rightarrow R_{\text{RC}}$ and $Z(\omega = 0) \rightarrow R_{\text{TE}}$ from Eq. (1) at $Q_p > Q_t$[14]. Furthermore, the R2C approximation was applied to roughly explain the angular frequency dependence $Z_{\text{R2C}}(\omega)$, as shown in Fig. 1a,b, using optimum current $I_{opt}$, which is expressed as[12,16]

$$Z_{\text{R2C}}(\omega) = R_{\text{ohm}} + R_{\text{TE}} \left(1 + \frac{\eta Q_t}{Q_p}\right)$$

$$\left|Q_p \rightarrow Q_t \right| \left(1 - \frac{(\omega Q_p / \omega_{\text{R2C}})}{1 + (\omega / \omega_{\text{R2C}})^2} \right) = R_{\text{ohm}} + R_{\text{TE}} \left(1 - \frac{\omega Q_p / \omega_{\text{R2C}}}{1 + (\omega / \omega_{\text{R2C}})^2} \right)$$

The transient Harman (TH) method, which is an alternative technique derived from the Harman method, is based on the transient response of resistance $R(t)$ of the TEs and TMs using time domain, as shown in Fig. 1c. The TH method is relatively simpler to apply in the determination of $zT$ using results of the $R(t)$; several researchers have also reported its applicability[17-22]. In this method, $R_{\text{ohm}}$ and $R_{\text{ohm}} + R_{\text{TE}}$ correspond to $R(t = 0)$ and $R(t \rightarrow \infty)$, respectively, and $zT$ is expressed as $zT = R(t \rightarrow \infty)/R(t = 0) - 1$ using Eq. (1). The IS and TH methods (or R2C approximation) show that an equivalent circuit of the TE and TM can be expressed using three components, namely, $R_{\text{ohm}}, R_{\text{TE}}$, and $C_{\text{TE}}$ (called thermoelectric capacity), as shown in Fig. 1d. $C_{\text{TE}}$ is related to heat capacity of not only the TE(s) but also other components constituting the TE(s) like electrodes, especially for the TM[10,12].

In this study, we comprehensively investigate several techniques of direct $zT$ estimation based on the IS and TH methods. We employ a commercial base I-shaped TM composed of bismuth-telluride (BiTe) (inset in Fig. 1c) to avoid influences of heat leakages through lead-wires attached for measurement and their contact resistance[23,24]. Furthermore, we highlight the disadvantages of both methods and suggest new techniques to overcome the drawbacks of the conventional methods. Finally, we propose a suitable technique to determine the value of $zT$ precisely and directly within several minutes using a combination of AC and DC electrometric instruments, called time domain impedance spectroscopy (TDIS), and discuss the important factors required to obtain the value of $zT$ precisely through measurements.

Results

Figure 2 shows the frequency dependence of the measured impedance $Z_{\text{meas}}(\omega)$ in the case of the IS method for a TM prepared at 300 K with various AC from $I = 100 \mu A_{\text{rms}}$ to $1000 \mu A_{\text{rms}}$[16], and the inset shows its Nyquist plot using 1 mA$_{\text{rms}}$. The characteristic angular frequency ($\omega_{\text{R2C}}$) using the R2C approximation given by Eq. (2) was 0.255 rad/s ($= 40.6$ MHz) owing to $L = 1.4$ mm ($\omega_{\text{R2C}} \propto 1/L^2$). ($R_{\text{ohm}})_{\text{IS}} = Z_{\text{meas}}(\omega \rightarrow \infty) = \text{Re}[Z_{\text{meas}}(\omega = 513 \text{ Hz})]$ at $\omega \omega_{\text{R2C}} \rightarrow 10^3$ (or phase angle $\psi < 0.1^\circ$) was 480.0 mΩ, and ($R_{\text{ohm}} + R_{\text{TE}})_{\text{IS}} = Z_{\text{meas}}(\omega = 0) = \text{Re}[Z_{\text{meas}}(\omega = 0.5 \text{ MHz})]$ at $\omega \omega_{\text{R2C}} \rightarrow 10^{-2}$ (or $\psi < 0.1^\circ$) was 869.5 mΩ at a current less than 10 mA$_{\text{rms}}$, satisfying $Q_p > Q_t$. At 100 mA$_{\text{rms}}$, the contribution of $Q_t$ affected $\text{Re}[Z_{\text{meas}}(\omega)]$ and $\text{Im}[Z_{\text{meas}}(\omega)]$ in the lower frequency region. Therefore, $\text{Re}[Z_{\text{meas}}(\omega)]$ ($\propto \omega$) increased marginally at $10^{-2} \text{ Hz}$ owing to $Q_p = 6.9$ mW. $Q_{p}(\omega = 4.8$ mW) using the representative magnitude of $S = -121 \mu W/K \text{ at } 300 \text{ K}$, corresponding to BiTe standard material[14]. In addition, $\phi = \tan^{-1}(\text{Im}[Z_{\text{meas}}]/\text{Re}[Z_{\text{meas}}])$ helps identify the suitable frequency for determining $Z_{\text{meas}}(\omega \rightarrow \infty)$ and $Z_{\text{meas}}(\omega \rightarrow 0)$ because $\omega_{\text{R2C}}$ is unknown[15]. Finally, using the IS method, the value of $zT$ was clearly estimated as $(zT)_{\text{IS}} = 0.811 = (R_{\text{ohm}} + R_{\text{TE}})_{\text{IS}}/(R_{\text{ohm}})_{\text{IS}} - 1 = 869.5 / 480.0 - 1$.

Figure 3 shows the results of the TH method for the same TM used in the IS method at 300 K for transient current $I(t)$. $R_{\text{meas}}(t)$ was measured using a voltmeter (VM) and the remaining voltages were made using a data acquisition (DAQ) system. The inset in Fig. 3a shows the time dependence of $R_{\text{meas}}(t)$ for different values of current ranging from −500 mA to +500 mA. In addition, the current dependencies of $R_{\text{meas}}(t \rightarrow \infty)$ at higher magnitudes of current due to the influence of $Q_t$ are clearly observable. $I(t)$ using 1.447 mA at $t \geq 0$ that is shown in Fig. 2a was selected from the essential condition of $Q_p = 100 \mu W > Q_t = 1 \mu W$ using $(R_{\text{ohm}})_{\text{VM}}$. Figure 2b shows that the value of $R_{\text{meas}}(t \rightarrow \infty)$ = $(R_{\text{ohm}} + R_{\text{TE}})_{\text{THVM}}$ = 869.3 mΩ measured by the voltmeter was specifically determined owing to the large signal-to-noise ratio (SNR). $R_{\text{meas}}(t \rightarrow \infty)$ was also measured at a range of current as shown in an inset in Fig. 3b, because $R_{\text{TE}}$ was replaced with $R_{\text{TE}}(1 + \eta Q_t/Q_p)$ in the higher current region in Eq. (1). It shows that $R_{\text{meas}}(t \rightarrow \infty)$ is proportional to $I(\propto Q_t/Q_p)$ in the higher current region, as expected[16]. To avoid aliasing of the signals measured by the voltmeter, the sampling rate was set as 2.3 Hz; consequently, $R_{\text{meas}}(t \rightarrow 0)$ = $(R_{\text{ohm}})_{\text{THVM}}$ was ambiguous. Therefore, data acquisition had to be performed at a higher sampling rate to detect the variation of $R_{\text{meas}}(t \rightarrow 0)$. The characteristic frequency $\omega_{\text{R2C}} = 0.255$ rad/s can be used as an approximate standard to derive the heat time constant $\tau_{\text{exp}}$ of the system ($\sim 4 s$ = $1/\omega_{\text{R2C}}$). Figure 3c also shows $R_{\text{meas}}(t)$ obtained using a DAQ system at a sampling rate of 100 kHz, which would be sufficient to detect the transient response of $R_{\text{meas}}(t)$. Owing to the small SNR in the surroundings (or higher sampling rate), the data was averaged for a period ranging from 10 kHz to 1 Hz. However, detecting $R_{\text{meas}}(t = 0)$ from the results of the TH method is difficult despite the use of the DAQ. As the expected value of $R_{\text{meas}}(t = 0)$ was 480.0 mΩ from $(R_{\text{ohm})_{\text{VM}}}$, the first data for $R_{\text{meas}}(t = 0)$ was 471.27, 477.57, and 483.32 mΩ at 10 kHz, 1 kHz, and 100 Hz averaging, respectively. At a sampling rate of 100 kHz, the raw data of $R_{\text{meas}}(t = 0)$ was distributed from 23.94 to 554.62 mΩ during 10 µs. This result shows that detecting $R_{\text{meas}}$ using the raw data of the TH method is difficult despite using the higher DAQ system.
Figure 2. Frequency dependence of impedance of real $\text{Re}[Z_{\text{mea}}(\omega)]$ and imaginary part $\text{Im}[Z_{\text{mea}}(\omega)]$, respectively and phase angle $\phi$ at each AC (100 $\mu$A$_{\text{rms}}$ to 100 mA$_{\text{rms}}$) for the TM prepared. The upper axis shows normalized angular frequency $\omega/\omega_{\text{R2C}}$. A lock-in amplifier and Quasi-AC method (implemented using a high-precision AC source and digital multimeter using real-time data acquisition for the low-frequency region) were applied to measure the impedances at frequencies more than and less than 10 mHz, respectively. An inset shows its Nyquist plot of $Z_{\text{R2C}}(\omega)$ and fitting plot by R2C approximation given in Eq. (2).

Figure 3. Time dependence of transient response for (a) direct current $I(t)$, measured resistance $R_{\text{mea}}(t)$ and voltage $V_{\text{mea}}(t)$ by (b) a voltmeter, and (c) a DAQ system at a sampling rate of using 100 kHz and its averaging results without error bar for each averaging period, respectively. The insets of (a) and (b) show the time dependence of $R_{\text{mea}}(t)$ at each current and current dependence of $R_{\text{mea}}(t \to \infty)$, respectively.
Another method was developed to determine $R_{dhm}$ and $R_{dhm} + R_{TE}$ by fitting the formula into the data obtained by the DAQ system. This proposal was based on the fact that $R_{dhm}(t)$ is almost stabilized at 100 Hz averaging. Therefore, we used the value of $R_{max}(t)$ measured by the DAQ using 100 Hz averaging in the TH method. This approach was adopted based on our hypothesis that the average frequency enables us to represent the transient response with $\tau_{exp}$. To estimate $R_{max}(t \to 0) = (R_{dhm})_{TH,DAQ}$ and $R_{max}(t \to \infty) = (R_{dhm} + R_{TE})_{TH,DAQ}$, as shown in Fig. 3c, two fitting equations for period $\Delta t$ were applied from the equivalent circuit in Fig. 1d\textsuperscript{16}.

$$R_{R2C}(t) = \frac{R_{dhm} + R_{TE}}{1 + \frac{R_{dhm} + R_{TE}}{Q_p} \exp \left(-\frac{t}{\tau_{R2C}}\right)} = \frac{R_{dhm} + R_{TE}}{1 + \frac{R_{dhm} + R_{TE}}{Q_p} \exp \left(-\frac{t}{\tau_{R2C}}\right)} \tag{3}$$

$$R_{RC}(t) = R_{dhm} + R_{TE} \left(1 + \frac{\eta \tau_{R2C}}{Q_p}\right) \exp \left(-\frac{t}{\tau_{RC}}\right) = \frac{R_{dhm} + R_{TE}}{1 + \frac{R_{dhm} + R_{TE}}{Q_p} \exp \left(-\frac{t}{\tau_{RC}}\right)} \tag{4}$$

where $\tau_{R2C}$ and $\tau_{RC}$ are the estimated time constants using each equation, respectively. Figure 4 shows the calculation results from the period $\Delta t$. Figure 4a,b show $R_{max}(t \to 0)$ using the R2C ($= (R_{dhm})_{TH,DAQ,R2C}$) and RC ($= (R_{dhm})_{TH,DAQ,RC}$) approximations expressed in Eqs. (3) and (4), respectively. Near $\Delta t \to 0$, both $R_{dhm}$ and $R_{dhm}(t \to \infty)$ were approximately 494 mΩ, and increased with increasing $\Delta t$ owing to the excessive data available for $R_{dhm}(t)$. Finally, $(R_{dhm})_{TH,DAQ,RC}$ and $(R_{dhm})_{TH,DAQ,R2C}$ were asymptotically close to 524.6 mΩ in Fig. 4a and 504.5 mΩ in Fig. 4b, respectively, which are approximately 1.09 and 1.05 times higher compared with $(R_{shhm})_{TH} = 480.0$ mΩ. The difference between $(R_{dhm})_{TH,DAQ}$ and $(R_{dhm})_{TH}$ obstructs the determination of $(R_{dhm})_{TH,DAQ}$ when estimating $zT$. In other words, the value of $zT$ is underestimated because $(R_{dhm})_{TH,DAQ} > (R_{dhm})_{TH}$. Therefore, estimating $(R_{dhm})_{TH,DAQ}$ from $R_{max}(t \to 0)$ obtained using the TH method is unsuitable even if the DAQ was used for measurement. Furthermore, Fig. 4c,d show that $(R_{dhm} + R_{TE})_{TH,DAQ}$ converged at certain values, i.e., $(R_{dhm} + R_{TE})_{TH,DAQ,R2C} = (R_{dhm} + R_{TE})_{TH,DAQ,RC} = 871.6$ mΩ in Fig. 4c,d, which are consistent with $(R_{dhm} + R_{TE})_{TH} = 869.5$ mΩ. The difference is acceptable because the difference is approximately 2.1 mΩ, which corresponds to the approximate 3 μV difference during the DC measurement. Moreover, the estimated time constants $\tau_{R2C}$ and $\tau_{RC}$ were 3.27 and 4.06 s, respectively, which matched the estimated value. However, in the RC approximation using Eq. (4), $\tau_{RC} = 4.06$ s is not only close to $\tau_{RC} = 1/\omega RC = 4$ s as a representative heat transport time in this system, but also simpler to apply. Figure 4f quantitatively shows that the required period using the normalized time $\Delta t/\tau_{RC}$ is more than 10 for each parameter. Furthermore, $(zT)_{TH,DAQ}$ was estimated to be 0.767 $\pm$ 0.014 ($= (R_{shhm} + R_{TE})_{TH,DAQ}/(R_{dhm})_{TH,DAQ,RC} = 871.6/504.5 \approx 1$), which is marginally smaller than that of the IS method because it is likely to overestimate $(R_{dhm})_{TH,DAQ}$ compared with $(R_{dhm})_{TH}$. We also attempted to precisely measure $R_{shhm}$ using the pulse DC with an identical DAQ system because the $R_{shhm}$ term adds the contribution of the temperature difference generated for the DC. Figure 5 shows the results of measuring $R_{max}(t \to 0)$ as a function of $t/T_p$, where $T_p$ is the pulse period. From Eqs. (1) and (4), the expression for $R_{max}(t \to 0)$ at $Q_p > Q_s$ can be derived as

$$R_{max}(t \to 0) \simeq R_{RC}(t \to 0) = R_{dhm} + R_{TE} \left(1 - \exp \left(-\frac{t}{\tau_{RC}}\right)\right) \simeq R_{dhm} + R_{TE} \frac{t}{\tau_{RC}} = R_{dhm} \left(1 + zT \frac{t}{\tau_{RC}}\right). \tag{5}$$
Figure 5. Normalized time dependence of (a) pulse current $I(t/T_p)$, measured resistance $R_{\text{mea}}(t/T_p)$ at (b) $t_p = 100$ ms and $T_p = 1000$ ms, (c) $t_p = 10$ ms and $T_p = 100$ ms, (d) $t_p = 1$ ms and $T_p = 10$ ms for each pulse DC (1–10 mA) by a DAQ system (100 kHz sampling rate), respectively. 10%, 40%, and 50% of the entire pulse period $T_p$ in (a) correspond to the pulse DC width $t_p$, relaxation period to remove the temperature gradient (or difference) on the TEs of the TM, and offset period to determine the zero voltage for the next measurement, respectively. The inset in (d) shows how $(R_{\text{ohm}})_{\text{pulse}}$ can be estimated from obtained data.
Although the values of $R_{\text{mea}}(t/T_p = 0)$ were approximately 480.0 mΩ ($=(R_{\text{ohm}})_{\text{IS}}$) within the scattered data, it increased linearly at $t_p = 100$ ms due to $t_p/\tau_{RC} = 2.46 \times 10^{-2}$, as expected from Eq. (5). Moreover, if the value of $zT$ is large, typically 1, the term $zT^2t_p/\tau_{RC}$ in Eq. (5) should be less than $10^{-3}$ to ensure precise $R_{\text{ohm}}$ measurement. The increase in $R_{\text{mea}}(t/T_p \sim 0)$ was suppressed at shorter $t_p$, and the variation of $R_{\text{mea}}(t)$ during $t_p$ was considered negligible owing to the considerably lower $t_p/\tau_{RC}$ as shown in Fig. 5d for $t_p/\tau_{RC} = 2.46 \times 10^{-4}$. Furthermore, current dependence was absent owing to a shorter $t_p$, which possibly satisfies $Q_J > Q_P$ during the $t_p/T_p$ cycle. Finally, although the use of pulse DC was expected to be suitable for measuring $(R_{\text{ohm}})_{\text{IS}}$, the measurement error within the scattered data near $t_p/T_p \sim 0$ was also considered.

Figure 6 shows the $t_p$ dependence of $(R_{\text{ohm}})_{\text{IS}}$ and fell within the accepted error margin. It quantitatively shows that $(R_{\text{ohm}})_{\text{IS}}$ approached $(R_{\text{ohm}})_{\text{IS}} = 480.0$ mΩ at $t_p/\tau_{RC} < 10^{-3}$, as expected from Eq. (5). However, the measurement error of $(R_{\text{ohm}})_{\text{IS}}$ was predominant at all $t_p$ owing to the low SNR. Moreover, $(R_{\text{ohm}})_{\text{IS}}$ measured at a larger current, i.e., 10 mA, resulted in a smaller error compared with that measured at a smaller current; however, the error in the measurement of $(R_{\text{ohm}})_{\text{IS}}$ was still large. Based on this evaluation, pulse and transient Harman (PTH) method was proposed for determining $(zT)_{\text{PTH}}$ using $(R_{\text{ohm}})_{\text{IS}}$. $(zT)_{\text{PTH}}$ was estimated to be $0.804 \pm 0.043 (= (R_{\text{ohm}})_{\text{IS}} + 2.46 \times 10^{-2} \times 10^{-3})$ using $(R_{\text{mea}})_{\text{TH,DAQ}} = 483.2 \text{ mΩ}$ at $I = 1 \text{ mA}$ and $t_p = 5 \text{ ms}$ ($t_p/\tau_{RC} = 10^{-3}$), which is close to that of the IS method. Additionally, we attempted to measure $(R_{\text{mea}})_{\text{IS}}$ using the delta method, in which a current source is synchronized with an oscillating square wave at a frequency (a kind of pulse current) using a voltmeter. Subsequently, the resistance can be measured after eliminating offset voltage and removing the influences of the thermoelectric-motive force in the circuit. The details are summarized in Supplementary Information. Furthermore, an important conclusion was drawn from the measurements that were used to determine $(R_{\text{mea}})_{\text{IS}}$. Using pulse DC in Figs. 5 and 6, $(R_{\text{ohm}})_{\text{IS}}$ in Fig. S1, and $R_{\text{ohm}} + R_{\text{TE}}$ using DC in Fig. 3c by the PTH method. The precise measurement of $R_{\text{ohm}}$ from $R_{\text{mea}}(t \rightarrow 0)$ using only continuous DC is unsuitable for the TMs and TEs possessing large $zT$ values despite the use of the DAQ system. This unsuitability can be attributed to the fact that large $zT$ values affect the measurement noise (depending on the surroundings in the measurement system) even if the normalized pulse width $t_p/\tau_{RC}$ is less than $10^{-3}$. Although the transported Peltier heat $Q_P$ at $I = 1 \text{ mA}$, shown Figs. 5 and 6 appeared small near $|T| = 69.3 \mu W$ ($=|S|T = 231 \times 10^{-6} \times 300 \times 1 \times 10^{-5}$) at $300 \text{ K}$, the Peltier heat flux $q_P$ across the TE was not negligible, i.e., $q_P = 164 \text{ W/m}^2$ ($=Q_{\text{JP}}/A = 69.3 \times 10^{-6} \times (0.65 \times 10^{-3})^{-2}$) for $A = 0.65 \times 0.65 \text{ mm}^2$ owing to the generation of $\Delta T \sim q_P/L/k$.

**Discussion**

Based on the above-mentioned results and considerations, we proposed a combined measurement technique, namely, time domain impedance spectroscopy (TDIS), which attempts to measure $Z_{\text{meas}}(0 \rightarrow \infty)$ using a lock-in amplifier and AC at $\omega/\tau_{RC} > 10^4$ (or $|\phi| < 0.1^\circ$) and $R_{\text{ohm}} + R_{\text{TE}} = R_{\text{mea}}(t \rightarrow \infty)$ using a voltmeter. Alternatively, it employs a DAQ system using DC at $t_p/\tau_{RC} > 10$ based on the TH method and partially derives the optimum current from the knowledge of the IS theory and models. Consequently, $(zT)_{\text{TDIS,VM}} = 0.811 \pm 2.4 \times 10^{-4} (= (R_{\text{ohm}} + R_{\text{TE}})_{\text{TH,VM}}/(R_{\text{ohm}})_{\text{IS}} - 1 = 869.3/480 - 1)$ using the voltmeter or $(zT)_{\text{TDIS,DAQ}} = 0.816 \pm 3.6$.
\[ \frac{R_{\text{ohm}}}{R_{\text{TE}}} + Z_{\text{in}}/R_{\text{ohm}} \]

| Technique | Condition | Impedance spectroscopy (IS) | Transient Harman method (TH) | Pulse and Transient Harman method (PTH) | Time domain impedance spectroscopy (TDIS) | Time domain impedance spectroscopy (TDIS) |
|-----------|-----------|----------------------------|-----------------------------|---------------------------------|---------------------------------|---------------------------------|
| DC        | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (DAQ) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (DAQ) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (Voltmeter) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (Voltmeter) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (Voltmeter) |
| DC        | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (DAQ) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (DAQ) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (Voltmeter) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (Voltmeter) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (Voltmeter) |
| DC        | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (DAQ) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (DAQ) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (Voltmeter) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (Voltmeter) | \[ R_{\text{ohm}}(t \rightarrow 100 \text{ s}) \] (Voltmeter) |

**Figure 7.** A summary of \( zT \) of the prepared TM estimated by various techniques, devices used, and conditions for \( R_{\text{ohm}} \) and \( R_{\text{ohm}} + R_{\text{TE}} \) at 300.000 K.
Table 1. A summary of techniques for direct \( zT \) estimation and its notes.

| Technique for \( zT \) estimation | Impedance spectroscopy (IS) | Transient Harman method (TH) | Pulse and transient Harman method (PTH) | Time domain impedance spectroscopy (TDIS) |
|----------------------------------|-----------------------------|------------------------------|----------------------------------------|----------------------------------------|
| (notation) \( zT \)              | \( zT \)                    | \( zT \)                     | \( zT \)                               | \( zT \)                               |
| Object domain(s)                 |                             |                             |                                        |                                        |
| Required device(s)               |                             |                             |                                        |                                        |
| \( R_{\text{Rohm}} \) \( Z_{\text{Rohm}}(\omega \to \infty) \) or \( R_{\text{Rohm}}(t \to 0) \) | \( Z_{\text{Rohm}}(\omega \to \infty) \) for lock-in amplifier | \( R_{\text{Rohm}}(t \to 0) = (R_{\text{Rohm}})_{\text{TH}} \) by DAQ or voltmeter | \( R_{\text{Rohm}}(t \to 0) = (R_{\text{Rohm}})_{\text{TH}} \) by DAQ using pulse current | \( Z_{\text{Rohm}}(\omega \to \infty) \) for lock-in amplifier |
| Requirement(s)                   |                             |                             |                                        |                                        |
| \( \omega/\nu_{\text{DAC}} > 10^3 \) or \( |\phi| < 0.1^\circ \) | \( R_{\text{Rohm}}(t \to 0) \) by high frequency data acquisition | \( R_{\text{Rohm}}(t \to 0) = (R_{\text{Rohm}})_{\text{TH}} \) at \( f/\nu_{\text{DAC}} < 10^{-3} \) | \( \omega/\nu_{\text{DAC}} > 10^4 \) or \( |\phi| < 0.1^\circ \) | \( \omega/\nu_{\text{DAC}} > 10^4 \) or \( |\phi| < 0.1^\circ \) |
| Required device(s)               |                             |                             |                                        |                                        |
| \( R_{\text{Rohm}} + R_{\text{T}} \) \( Z_{\text{Rohm}}(\omega \to \infty) \) or \( R_{\text{T}}(t \to \infty) \) | \( Z_{\text{Rohm}}(\omega \to 0) \) for lock-in amplifier or quasi-AC method | \( R_{\text{T}}(t \to 0) = (R_{\text{T}})_{\text{TH}} \) by DAQ or voltmeter | \( R_{\text{T}}(t \to 0) = (R_{\text{T}})_{\text{TH}} \) by DAQ | \( R_{\text{T}}(t \to 0) = (R_{\text{T}})_{\text{TH}} \) by DAQ or voltmeter |
| Requirement(s)                   |                             |                             |                                        |                                        |
| \( \omega/\nu_{\text{DAC}} < 10^{-2} \) or \( |\phi| < 0.1^\circ \) | \( R_{\text{T}}(t \to 0) \) by high frequency data acquisition | \( R_{\text{T}}(t \to 0) = (R_{\text{T}})_{\text{TH}} \) by DAQ | \( R_{\text{T}}(t \to 0) = (R_{\text{T}})_{\text{TH}} \) by DAQ | \( \omega/\nu_{\text{DAC}} > 10^4 \) or \( |\phi| < 0.1^\circ \) |
| Notation of \( zT \)             | \( zT \)                     | \( zT \)                     | \( zT \)                               | \( zT \)                               |
| \( (zT)_{\text{TH}} = \frac{Z_{\text{T}}(\omega \to \infty)}{Z_{\text{T}}(\omega \to 0)} - 1 \) | \( (zT)_{\text{TH}} = \frac{R_{\text{Rohm}}(t \to \infty)}{R_{\text{Rohm}}(t \to 0)} - 1 \) | \( (zT)_{\text{TH}} = \frac{R_{\text{T}}(t \to \infty)}{R_{\text{T}}(t \to 0)} - 1 \) | \( (zT)_{\text{TH}} = \frac{R_{\text{T}}(t \to \infty)}{R_{\text{T}}(t \to 0)} - 1 \) | \( (zT)_{\text{TH}} = \frac{R_{\text{T}}(t \to \infty)}{R_{\text{T}}(t \to 0)} - 1 \) |
| Additional requirements           |                             |                             |                                        |                                        |
| Optimum current \( I_{\text{opt}}(t>0) \) \( < R_{\text{T}}(\omega \to \infty) \) \( \frac{Z_{\text{Rohm}}(\omega \to \infty)}{Z_{\text{Rohm}}(\omega \to 0)} \) due to \( Q_{P} > Q_{T} \) | Precise temperature control \( \Delta T \) \( < \Delta T = zT \frac{R_{\text{Rohm}}(t \to 0)}{|S|} \) | high vacuum \( (\sim 10^{-4} \text{ Pa}) \) to ensure adiabatic condition | \( \omega/\nu_{\text{DAC}} > 10^4 \) or \( |\phi| < 0.1^\circ \) | \( \omega/\nu_{\text{DAC}} > 10^4 \) or \( |\phi| < 0.1^\circ \) |
| Measurement period               |                             |                             |                                        |                                        |
| More than several hours          | Several minutes             | Several minutes             | Several minutes                        | Several minutes                        |
| Advantage(s)                     |                             |                             |                                        |                                        |
| Exact                           | Simple and easy to perform  | Simple                      | Exact, easy, and fast                  |                                        |
| Disadvantage(s)                  |                             |                             |                                        |                                        |
| Long time required for estimation at \( Z_{\text{Rohm}}(\omega \to 0) \) | Not exact due to misinterpretation \( R_{\text{Rohm}}(t \to 0) \) | ...                                | ...                                    | ...                                    |

Several minutes. Precise measurements were obtained directly using a combination of AC and DC electrometric measurements without any heat measurements.

In this study, we reported the \( zT \) estimation using the TM owing to its higher resistance (~1Ω) compared with a TE (~1 to 10 mΩ). In the future, the measurement technique of the TDIS method will be applied to determine \( zT \) using any TE with a definite geometry, such as a rectangular solid TE. Furthermore, we plan to establish the accuracy of the TDIS method using the temperature dependence of the \( zT \) of BiTe, which decreases with temperature in the lower temperature region.

Conclusions

In this study, we developed a new method to directly estimate \( zT \). The proposed method is based on the theory and model of the IS method using frequency domain with a Π-shaped TM for a BiTe system. However, the IS method possesses several drawbacks, such as the long time required to determine \( zT \). The reason behind this drawback is that the information about both \( Z_{\text{Rohm}}(\omega \to \infty) \) and \( Z_{\text{Rohm}}(\omega \to 0) \) using frequency domain with AC is required. In addition, we used the TH method using the TM with high frequency data acquisition which is based on the time dependence of the resistance \( R_{\text{Rohm}}(t) \) to measure the resistance \( R_{\text{Rohm}}(t \to \infty) \) and \( R_{\text{Rohm}}(t) \). However, the results showed that determining \( R_{\text{Rohm}}(t \to 0) \) using the TH method is difficult. Furthermore, we attempted to estimate \( R_{\text{T}}(t \to 0) \) using the PTH method with pulse DC. However, we found that continuous DC was unsuitable for determining \( R_{\text{T}}(t \to 0) \) because determining the resistance derived from the electronic and Peltier heat at \( R_{\text{T}}(t \to 0) \) is difficult. To overcome these drawbacks, we proposed the TDIS method by combining the frequency and time domains to determine \( R_{\text{Rohm}} = Z_{\text{Rohm}}(\omega \to \infty) \) using the lock-in amplifier with AC and \( R_{\text{T}} = Z_{\text{T}}(\omega \to \infty) \) using the voltmeter with DC. Finally, \( zT \) was estimated as \( zT = \frac{R_{\text{T}}(t \to \infty)}{Z_{\text{T}}(\omega \to \infty) - 1} \) using optimum current \( I_{\text{opt}} \) that satisfies the condition \( Q_{P} \) (Peltier heat) \( > Q_{T} \) (Joule heat), given that \( I_{\text{opt}} < \frac{|S|}{T_{\text{Rohm}}}. \) Furthermore, the estimated \( zT \) values of the TM using the IS and the TDIS methods were in perfect agreement, i.e., 0.811 at 300 K. Moreover, the TDIS method helped in qualitatively and quantitatively describing \( zT \) obtained from the IS method. We expect that this study will aid in developing more effective methods to determine \( zT \) precisely within several minutes for not only TMs but also any given TE.

Methods

A commercial-base Π-shaped thermoelectric module composed of BiTe was prepared (KSML007F, KELK). The total number \( n \) of the TE for n- and p-types was \( n = 14 \). The impedance \( Z_{\text{Rohm}}(\omega) \) and resistance \( R_{\text{T}}(t) \) were measured by four-probe method after attaching lead-wires to apply current and measure the voltage. One side of the module was tightly fixed by a spring plate to a sample stage capable of controlling the temperature using a precise temperature control system (336, Lakeshore) at 300.000 ± 0.3 mK by calibrated Cernox thermo-sensor (Lakeshore) and two PID feedback heaters chilled by a cryo cooler (RDK-101D, Sumitomo Heavy Industry) under \( 10^{-4} \) Pa by vacuum pumps. The frequency dependence of \( Z_{\text{Rohm}}(\omega) \) was measured by a lock-in amplifier (SR830, Stanford Research Systems) using an AC source (6221, Keithley) for frequencies higher than 10 mHz. Conversely, the quasi-AC method was employed using a DC source and a voltmeter (2182A, Keithley) for...
frequencies less than 10 mHz, implemented using a high-precision AC source and digital multimeter using real-time data acquisition for the low-frequency region\(^{12,28}\). The time dependence of the resistance \(R_{\text{mea}}(t)\) was measured using a DC and pulse current source (6221, Keithley) for currents less than 100 mA, and a DC source (2400, Keithley), voltmeter (2182A, Keithley), and DAQ system (USB-6281, NI) for currents higher than 100 mA. All the instruments were connected through GPIB and USB cables and controlled appropriately by the LabVIEW (NI) program.

Data availability
Data is available upon reasonable request to the corresponding author.

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Author contributions
Y.H. designed this work. M.T. performed the experiments. Y.H. and M.T. carried out the calculations for analysis. Y.H. arranged and supervised all experiments. All authors discussed the results and the manuscript.

Competing interests
The authors declare no competing interests.

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