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Fine ceramics (advanced ceramics, advanced technical ceramics) — Measurement of Seebeck coefficient and electrical conductivity of bulk-type thermoelectric materials at room and high temperatures

Céramiques techniques — Mesurage du coefficient de Seebeck et de la conductivité électrique de matériaux thermoélectriques de base à températures ambiante et élevée

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Foreword

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This document was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

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Fine ceramics (advanced ceramics, advanced technical ceramics) — Measurement of Seebeck coefficient and electrical conductivity of bulk-type thermoelectric materials at room and high temperatures

1 Scope

This document specifies the measurement methods for the electronic transport properties of bulk-type thermoelectric materials at room and elevated temperatures. The measurement methods cover the simultaneous determination of Seebeck coefficient and electrical conductivity of bulk-type thermoelectric materials in a temperature range from 300 K to 1 200 K. The measurement methods are applicable to bulk-type thermoelectric materials used for power generation, energy harvesting, cooling and heating, among other things.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO 23331, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for total electrical conductivity of conductive fine ceramics*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
thermoelectric figure of merit
zT
dimensionless factor representing the thermoelectric conversion efficiency of a given material

3.2
thermoelectric power factor
$S^2\sigma$
characteristic value of a thermoelectric material given by the product of the square of Seebeck coefficient (S) and electrical conductivity (σ)

Note 1 to entry: The units of the thermoelectric power factor are watts per metre per square kelvin (W/mK^2).

3.3
Seebeck coefficient
S
intrinsic property which describes the induced voltage (thermal electromotive force, *E*) from a given temperature difference (Δ*T*) in a material

Note 1 to entry: The units of the Seebeck coefficient are microvolts per kelvin (μV/K).

3.4
electrical conductivity
σ
ability of a material to allow the transport of electric charges

Note 1 to entry: The units of electrical conductivity are Siemens per centimetre (S/cm).

4 Principle

This document is for simultaneously measuring the Seebeck coefficient and the electrical conductivity of bulk-type thermoelectric materials using one measurement system. The off-axis four-terminal method can be used to simultaneously measure the Seebeck coefficient and the electrical conductivity of bulk-type thermoelectric material using one measurement system. As shown in Figure 1, the specimen is set between two metal blocks in the heating zone and two thermocouple probes separately contact the surface of the specimen. The measurement of the Seebeck coefficient of a bulk-type thermoelectric material is necessary to measure the temperature difference between two positions (point H and point C) on a specimen and the voltage across the two same positions (Figure 1). Seebeck coefficient can be calculated by following Formula (1):

$$S = E / \Delta T \quad (1)$$

where

E is the induced thermoelectric voltage (thermal electromotive force) between the point H and point C of the specimen;

ΔT is the temperature difference between the point H and point C (= T_H - T_C).

For Seebeck coefficient measurement, measured temperature is the average temperature of the hot- and cold-side thermocouple probes.

By using the measuring system illustrated in Figure 2, electrical conductivity is also measured based on the four-terminal method. This method is conducted by placing four probes. Constant current is applied through the two outmost probes, causing a measurable voltage drop, *V*, between the two inner probes. The electrical resistance, *R*, is calculated using Ohm's law following Formula (2):

$$R = V / I \quad (2)$$

where

V is the voltage;

I is the current.

The resistivity, *ρ*, is be calculated following Formula (3):

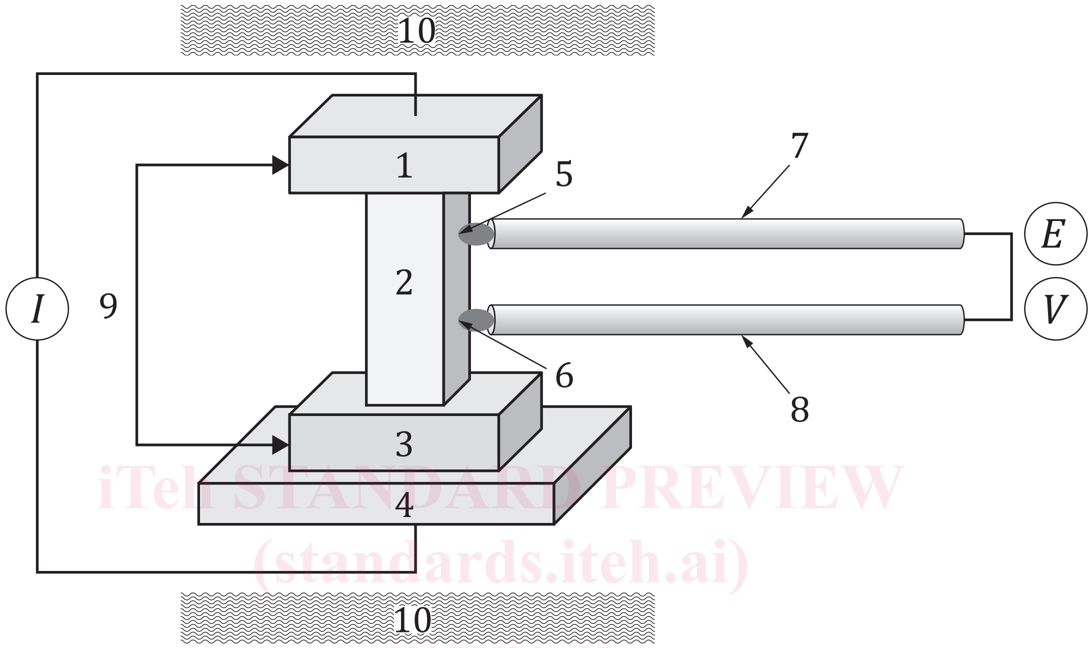
$$\rho = RA / l \quad (3)$$

where

A is the cross-sectional area of the specimen;

l is the separation between the two inner probes.

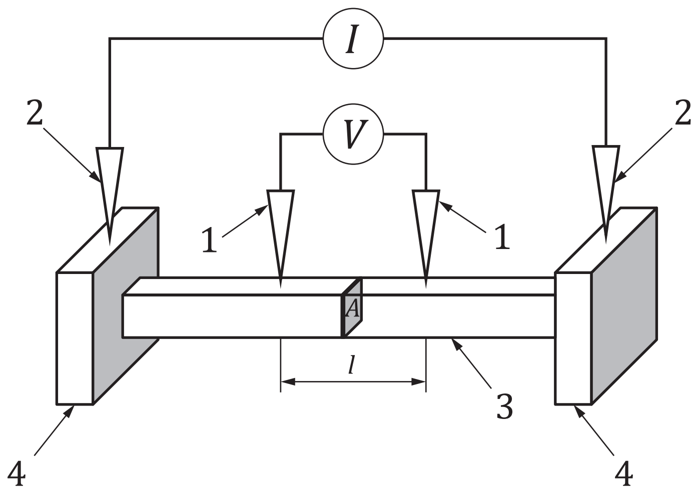
The electrical conductivity is the reciprocal of the resistivity. For electrical conductivity measurement, measured temperature is the actual temperature of the specimen, which generally can be measured by furnace temperature.



Key

1 upper metal block
2 specimen
3 lower metal block
4 heater
5 point C
6 point H
7 upper thermocouple probe (cold side)
8 lower thermocouple probe (hot side)
9 current electrode
10 heating furnace

Figure 1 — Schematic diagram of off-axis four-terminal method for simultaneous measurement of Seebeck coefficient and electrical conductivity



Key

1 inner probes
2 outer probes
3 specimen
4 electrodes

Figure 2 — Schematic diagram of four-terminal method to measure the electrical resistivity

The results of an interlaboratory test are given in Annex A.

5 Significance and use

This document gives guidance for simultaneously measuring the high-accuracy and low-error Seebeck coefficient and electrical conductivity of thermoelectric materials. Therefore, this standard is intended to be used for the development, characterization and quality control of thermoelectric materials, data acquisition for high-efficiency thermoelectric system design, etc.

Thermoelectric materials show Seebeck effect, Peltier effect and Thomson effect. The Seebeck effect is the direct conversion of heat into electricity. The conversion efficiency of a thermoelectric material is determined by the dimensionless thermoelectric figure of merit, zT, calculated following Formula (4):

$$zT = S^2 \sigma T / \kappa \tag{4}$$

where

- S is the Seebeck coefficient;
- σ is the electrical conductivity;
- κ is the thermal conductivity;
- T is the absolute temperature.

Thermoelectric materials show a trade-off relation between Seebeck coefficient and electrical conductivity according to carrier concentration. Therefore, the accuracy of the power factor, $S^2\sigma$, where S is the Seebeck coefficient and σ is the electrical conductivity, can be improved through simultaneous measurement of Seebeck coefficient and electrical conductivity in one run.

6 Apparatus

6.1 Current source, accurate to ±0,5 % on ranges of −1 A to +1 A used in the measurement.

6.2 Electronic voltmeter, at least capable of measuring potential differences from 10^{-7} V to 0,05 V with a resolution below 10^{-7} V.

6.3 Conducting metal blocks.

The contact surface of conducting metal blocks shall be sufficiently large compared to a measurement specimen. A specimen shall be placed between two conducting metal blocks, such as platinum or tungsten. One end of the specimen is heated while the other acts as a heat sink, dispersing heat, thus cooling that side. In addition, the conducting metal blocks play a role as the electrodes for applying the current when measuring the electrical conductivity.

NOTE Pt or Pt – Pd alloy is the best electrode material due to high measuring temperatures.

6.4 Thermocouple probes.

The diameter of thermocouple probes shall be 0,5 mm or less to obtain reproducible Seebeck coefficient value. Thermocouples should have a resolution of at least 0,01 K or better. Thermocouple probes integrating electrical probes for measuring the voltage and thermal probes for measuring the temperature should be designed for working from 300 K to 1 200 K. Thermocouple probes should be checked periodically as their output may drift with usage or contamination.

NOTE In some equipment, the voltage can be measured only with thermocouple wires without additional electrical probes.

6.5 Test chamber.

The test chamber shall be capable of heating both the specimen and the conducting metal blocks up to at least 1 200 K as well as maintaining the test temperature within ±1 K during the test, by which vacuum environment shall be available for test requirement. The test chamber should be evacuated below 3 Pa and can be backfilled with a variety of gases such as helium, argon, nitrogen and oxygen or a mixture of these. Low-pressure helium can be used to improve the thermal contact between the probe and the sample. However, low pressure may affect the measured Seebeck coefficient. Determination of optimum pressure of backfilled gas is required by Seebeck coefficient measurement according to gas pressure for the same sample to be measured. For the measurement of oxides, oxygen partial pressure should be controlled and monitored to avoid the reduction or oxidation of the samples.

6.6 Dimension-measuring device, such as a Vernier-calliper or other devices used for measuring the dimensions of the specimen, accurate to at least 0,01 mm in accordance with ISO 3611.

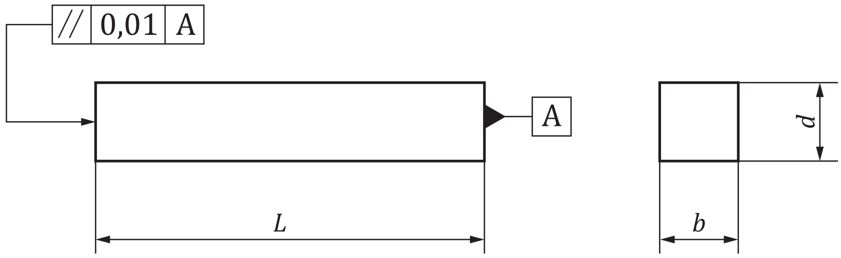
6.7 Apparatus and equipment, checked periodically through measuring a certified reference material or a reference material to ensure if they are working properly (see Annex B).

7 Sampling

7.1 Shape and dimension of specimen

The preferred shape of the specimen should be rectangular bar to ensure stable contacts with thermocouple probes. The area of contact between the specimen and electrode is important, especially to measure the Seebeck coefficient since this relates to heat transfer. The point of contact between the specimen and the electrode is difficult to ensure the reliability of Seebeck coefficient measurement. The two end sides of the specimen in contact with the metal blocks shall be parallel. The parallelism tolerance of two end sides should be 0,01 mm or less. To secure the contact area between the specimen and the electrode, surface roughness, R_a, of 10 µm or less is required. Figure 3 gives the recommended dimensions of a rectangular bar-type specimen.

Dimensions in millimetres



Width *b*	Depth *d*	Length *L*
1,5 to 5	1,5 to 5	5 to 25

Figure 3 — Recommended dimensions for a rectangular specimen

The cylindrical specimen can also be used. In this case, two thermocouple probes shall make stable contacts on the surface of the specimen.

7.2 Pre-treatment

The surfaces of the specimen shall be ground and polished to ensure they are flat and acquire stable contact with conducting metal blocks and thermocouple probes.

7.3 Storage

Specimens shall be stored separately and not allowed to impact or scratch each other.

7.4 Number of specimens

Three or more test pieces should be measured for the purpose of giving an overall estimation of Seebeck coefficient and electrical conductivity.

8 Procedure

8.1 Dimension measurement of specimen

Measure the width, depth and length of a specimen with a resolution of 0,01 mm. If the specimen is cylindrical, measure the diameter and length of the specimen.

8.2 Placement of specimen

Place the specimen between two conducting metal blocks so that the specimen does not rock or shift during the measurement. Thermocouple probes with lateral spring are then placed on the specimen, as shown in Figure 1.

When connecting the thermocouple probes to the surface of the specimen, measure the accurate distance between two thermocouple probes (*l* in Figure 1) to within 5 % of the distance.

NOTE 1 Thermocouple probes mounted in a spring assembly can be moved in and out to achieve the desired pressure.

NOTE 2 The spacing between two thermocouple probes can be adjustable, depending on the length of specimen.

8.3 Evacuating and purging the chamber

For measurement at high temperature in a vacuum environment, make the chamber reach a vacuum of at least 3 Pa.

For measurement at high temperature in an inert gas environment, the test chamber should be backfilled with a variety of inert gas such as helium, argon, nitrogen or oxygen, or a mixture of these, after purging the chamber several times.

8.4 Measurement of electrical conductivity

a) As shown in Figure 1, the specimen is placed between two conducting metal blocks.

b) Heat the specimen placed between metal blocks in the test chamber to the desired test temperature and maintain this temperature.

c) For measurement of electrical resistivity, the effect of Peltier-induced voltage should be excluded. Before measuring, the linearity of I-V plot should be checked. This confirms the steady-state to improve the accuracy of the electrical resistivity measurement.

d) Measure the electrical conductivity using the four-terminal method according to the provisions of ISO 23331. Constant current, I, is applied to the specimen through the conducting metal blocks and voltage drop, V, is measured on the thermocouple probes as shown in Figure 1. The voltage drop across the sample should be measured within a second after applying the dc current to remove a parasitic thermoelectric offset-voltage caused by the Peltier effect. When the electrical contact between the test specimen and the probes is stable, the voltage shall be proportional to changes in the applied current.

8.5 Measurement of Seebeck coefficient

a) After measurement of electrical conductivity, heat one metal block to create a temperature gradient in the specimen.

b) For measurement of Seebeck coefficient, thermal contact between the specimen and the thermocouple should be confirmed. Before measuring, the linearity of temperature-dependent voltage should be checked. This process enables the accuracy of the Seebeck coefficient measurement to be improved.

c) At each measuring temperature, generate at least five temperature gradients within the sample. These gradients are to be kept in the range of 0 K – 10 K.

d) For each gradient, measure the temperature difference ($\Delta T = T_H - T_C$) between the thermocouple probes and simultaneously measure the corresponding induced thermoelectric voltage, E.

e) Plot the measured values of E as a function of the measured values of ΔT and check for linearity.

9 Calculation

9.1 Seebeck coefficient

Relative Seebeck coefficient, S_M, can be calculated by following Formula (5):

$$S_M = \frac{E}{(T_H - T_C)} = \{S_C T_C - S_H T_H + S(T_H - T_C)\} / (T_H - T_C) \quad (5)$$

where

S_M is the relative Seebeck coefficient (μV/K);