Quantitative nanoscale mapping of three-phase thermal conductivities in filled skutterudites via scanning thermal microscopy

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ABSTRACT

In the last two decades, a nanostructuring paradigm has been successfully applied in a wide range of thermoelectric materials, resulting in significant reduction in thermal conductivity and superior thermoelectric performance. These advances, however, have been accomplished without directly investigating the local thermoelectric properties, even though local electric current can be mapped with high spatial resolution. In fact, there still lacks an effective method that links the macroscopic thermoelectric performance to the local microstructures and properties. Here, we show that local thermal conductivity can be mapped quantitatively with good accuracy, nanometer resolution and one-to-one correspondence to the microstructure using a three-phase skutterudite as a model system. Scanning thermal microscopy combined with finite element simulations demonstrate close correlation between sample conductivity and probe resistance, enabling us to distinguish thermal conductivities spanning orders of magnitude, yet resolving thermal variation across a phase interface with small contrast. The technique thus provides a powerful tool to correlate local thermal conductivities, microstructures and macroscopic properties for nanostructured materials in general and nanostructured thermoelectrics in particular.

Keywords: thermal conductivity, scanning thermal microscopy, thermoelectric materials, nanoscale heat transfer, thermal imaging

INTRODUCTION

Solid-state thermoelectric conversion is promising for recovering tremendous waste heat produced by human society and for enabling more effective thermal management. However, the high thermoelectric conversion efficiency, governed by the dimensionless figure of merit \( ZT \), requires simultaneously high electrical conductivity and Seebeck coefficient, yet low thermal conductivity, which are rather difficult to obtain in a single-phase material [1–5]. One of the primary mechanisms for improving thermoelectric performance in a material is to reduce lattice thermal conductivity through scattering of phonons by structural heterogeneity such as defects, interfaces and impurities. In the last two decades, the nanostructuring paradigm has been successfully applied to a wide range of thermoelectric materials, resulting in significant reduction in thermal conductivity and superior thermoelectric performance [6–12]. For example, nanocrystalline (Bi,Sb)\(_2\)Te\(_3\) with maximum \( ZT \) values of 1.4–1.6 were reported [7,13–15] and the improvement was largely attributed to the low lattice thermal conductivity resulting from intensified phonon scattering by nanostructures and defects [16]. In addition, by combining all-scale hierarchical architectural microstructures, including atomic defects, endotaxial nanoprecipitates and mesoscale grains [17], a wide range of heat-carrying phonons can be strongly scattered [9], resulting in record high \( ZT \)s in PbTe [17]. Similar reduction in thermal conductivity has also been reported in many nanocomposites, such as systems consisting of...
These advances in thermoelectric materials highlight the importance of nanostructuring in enhancing thermoelectric properties, yet, quite surprisingly, such improvements have been largely accomplished with no direct investigation of the local thermoelectric properties in nanostructured materials, even though local electric current can be mapped with high spatial resolution. Indeed, there still lacks an effective method that directly links the macroscopic thermoelectric performance to the local microstructures and properties. While the microstructural heterogeneity can be mapped with atomic resolution in terms of chemical and phase compositions, it reveals little about local transport behavior. Traditionally, the thermoelectric properties are only measured at the macroscopic scale, averaged over various microstructural features, and it is rather difficult to know exactly and directly which material constituent contributes to what in the local thermal transport processes. Therefore, high spatial resolution is critically needed in the thermal analysis of nanostructured materials in general, and nanostructured thermoelectrics in particular.

In the last decade, time domain thermoreflectance (TDTR) has emerged as a powerful tool for thermal transport property measurements [19,20], though its spatial resolution is limited to hundreds of nanometers [21–24], making the detailed mapping of thermal transport properties in nanostructured materials challenging. Various scanning thermal microscopy (SThM) techniques have been developed based on temperature-sensitive phenomena in the sample, promising potentially higher spatial resolutions [25–36], though they have rarely provided even a qualitative thermal mapping that correlates with the microstructures in a heterogeneous material, and strong crosstalk between thermal imaging and surface topography is often observed. Such direct correlation, especially in a quantitative manner, is highly desirable for understanding as well as further designing and optimization of high-performance thermoelectric materials, which we seek to accomplish via tightly coupled SThM experiments and finite element simulations utilizing a resistive heating thermal probe.

In this work, we show that local thermal conductivity can be mapped quantitatively with good accuracy, nanometer resolution and one-to-one correspondence to the microstructure, using filled skutterudite as a model system. Yb-filled CoSb$_3$, with its maximum $ZT$ up to 1.5, is one of the most promising thermoelectric materials for applications in the intermediate temperature range, since guest filling in the structural nanovoids acts to control the carrier concentration, while significantly suppressing the propagation of heat-carrying phonons [37–39]. However, impurity phases such as YbSb$_2$, Yb$_2$O$_3$ and CoSb$_2$ are commonly observed due to the filling fraction limit of approximately 0.3 in Yb$_x$Co$_4$Sb$_{12}$, low formation energy of Yb oxide and complexity in the Yb-Co-Sb phase diagram, and these impurity phases could exert significant influence on thermoelectric properties [40]. It thus provides us with an ideal model system to study its local thermal and electric conductivities.

**RESULTS**

**Three-phase microstructure**

The sample with a stoichiometry of Yb$_{0.7}$Co$_4$Sb$_{12}$ was prepared by a conventional induction melting-vacuum melting-quenching-annealing-sintering method, resulting in a three-phase microstructure as shown in Fig. 1. A back-scattered electron (BSE) image of the sample clearly reveals three phases as marked (Fig. 1a), with impurity phases 2 and 3 embedded in the matrix phase 1. It is anticipated that the excessively added Yb reacts with Sb to form the YbSb$_2$ phase, and the resultant Sb-deficiency leads to the formation of CoSb$_2$. Such scenarios are indeed confirmed by the elemental mappings of Yb, Co, Sb and O (Fig. 1b–e) as well as elemental ratios in each phases determined from the energy-dispersive X-ray spectroscopy (EDS) (Fig. 1f and Supplementary Fig. 1, available as Supplementary Data at NSR online), suggesting that the matrix phase 1 is filled skutterudite Yb$_{0.3}$Co$_4$Sb$_{12}$, while the impurity phases 2 and 3 are CoSb$_2$ and surface-oxidized YbSb$_2$, respectively. This analysis of phase composition is also confirmed by X-ray diffraction shown in Supplementary Fig. 2 (available as Supplementary Data at NSR online).

**Scanning thermal microscopy**

The microstructural analysis in Fig. 1 is powerful in mapping local chemical composition and phase structure of a material, yet it reveals nothing about the local thermoelectric properties. Traditionally, such properties are measured at the macroscopic scale, and their local variations, if any, can only be deduced indirectly from the macroscopic measurement or from computational analyses. If one can correlate local thermal properties directly with the microstructural features, then the effect of structural heterogeneity on the macroscopic thermoelectric conversion can be better understood and optimized. We seek to accomplish this via a scanning thermal probe [29,41,42], as shown in Fig. 2a. It has a
micro-fabricated solid-state resistive heater at the end of the cantilever \([31,43–46]\), which forms one branch of the Wheatstone bridge circuit that allows precise measurement of its electrical resistance. When the probe scan phases with lower (Fig. 2b) and higher (Fig. 2c) thermal conductivities, it will have lower and higher temperature drops, respectively, resulting in different probe resistances that can be measured accurately from the imbalanced Wheatstone bridge voltage. This enables us to image local thermal response quantitatively. Indeed, as shown in Fig. 2d, there is a linear relationship between probe resistance and temperature around the SThM operation temperature, calibrated by passively probing a hot-plate stage with well-defined temperatures:

\[
R(T) = R_0(1 + \alpha(T - T_0)),
\]

where \(R_0\) is the resistance of the thermal probe at room-temperature reference \(T_0 = 293.15\) K and \(\alpha\) is the temperature coefficient of resistance (TCR).

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**Figure 1.** Composition analyses of three-phase microstructure in a Yb\(_{0.7}\)Co\(_4\)Sb\(_{12}\); (a) a typical BSE image, wherein the three phases are labeled as 1, 2 and 3; (b)–(e) corresponding elemental mappings of Yb, Co, Sb and O for the area shown in (a); (f) a typical EDS spectrum of phase 1, and elemental ratios of three different phases labeled in (a).

**Figure 2.** The schematics of SThM setup; (a) resistive heating thermal probe in a balanced Wheatstone bridge circuit \((V_A - V_B = 0)\) before touching the sample; the thermal probe scans phases with (b) lower and (c) higher thermal conductivities, resulting in different probe temperatures that can be measured via imbalanced Wheatstone bridge for imaging; (d) linear correlation between temperature and resistance of the thermal probe calibrated by a hot plate with known temperatures.
measured to be 0.8/K between 350 and 450 K (Fig. 2d)—the temperature range relevant to our subsequent experiments. As such, the thermal probe functions not only as a heater, but also as a local temperature sensor via the resistance measurement, making it possible to measure the local thermal properties of the sample quantitatively [25,47].

In order to precisely measure the change in resistance induced by heat transfer to areas with different thermal conductivities, the Wheatstone bridge is balanced by adjusting the variable resistor before contacting the sample, and the bridge voltage is amplified with a 10× gain using a differential amplifier for enhanced sensitivity. After it touches the sample, heat transfers from the probe to the sample, resulting in drops in its temperature and resistance, and thus a voltage drop between nodes A and B of the Wheatstone bridge. Lower sample thermal conductivity has lower heat loss and thus a lower drop in resistance, corresponding to lower bridge voltage difference (Fig. 2b). Hence higher voltage difference indicates a higher sample thermal conductivity (Fig. 2c), making it possible to image local thermal conductivity variation based on the bridge voltage.

With a marker made near the area of the BSE image (Supplementary Fig. 3, available as Supplementary Data at NR online), we were able to locate the same area in our SThM studies. The topography mapping in Fig. 3a obtained from the contact mode reveals relatively flat surface without any correlation with the microstructure shown in BSE image of Fig. 1. However, simultaneously to the topography scan, the mapping of Wheatstone bridge voltage difference in Fig. 3b clearly reveals three different contrasts that correlate well with the BSE microstructure, repeated here in Fig. 3c for a direct comparison. Due to the drop in the probe temperature, and thus the resistance, the Wheatstone bridge voltage drops to negative. The matrix phase 1 has the smallest voltage drop, while the impurity phase 2 has the largest. Such contrast is induced by the difference in thermal conductivity, not from the topography variation, as evident by the line scan comparison in Fig. 3d. When a phase interface is crossed, sharp change in voltage difference is observed, while topography is relatively flat. On the other hand, within an individual phase, voltage difference is roughly constant, while topography variation is observed. The voltage difference mapped thus reflects the variation in thermal conductivity with no crosstalk to topography, wherein the matrix phase has the lowest thermal conductivity, while the impurity phase 2 has the highest. Thus, this is a direct characterization of local thermal conductivity that illustrates the role of impurity phases in thermal transport. Higher-resolution scans of two boxes marked in Fig. 3b are shown in Fig. 3e and f, demonstrating even higher sensitivity and spatial resolution. It is worth noting that, although YbSb2 (phase 3) is supposed to have the highest thermal conductivity, it appears that the significant surface oxidation reduces its thermal conductivity, resulting in intermediate voltage drops as mapped.

Figure 3. SThM mapping of Yb0.7Co4Sb12: (a) topography; (b) distribution of Wheatstone bridge voltage with 10× amplification; (c) BSE image; (d) comparison of line scans in topography and voltage mappings; (e) and (f) higher-resolution voltage mapping in smaller areas.
Figure 4. FEM simulation of the SThM experiment: (a)–(c) when the probe is held in air: (a) 3D and (b) cross-sectional temperature distribution of thermal probe under 3.5 V; (c) measured probe resistance as a function of DC drive voltage in comparison with simulation; (d)–(g) when the probe is in contact with a homogeneous sample having $\kappa = 5\text{W/(m.K)}$, and the contact resistance is taken to be $1 \times 10^8 \text{K/W}$; cross-sectional distribution of (d) heat flux density and (e) temperature on the tip-sample junction; and overlaid contour on the distribution of (f) heat flux distribution and (g) temperature in the sample underneath the probe.

Finite element simulation

In order to interpret and analyse the SThM data quantitatively, a finite element model (FEM) implemented in the COMSOL Multiphysics package was developed to study heat transfer among the thermal probe, the sample and surrounding air, as shown in Supplementary Fig. 4 (available as Supplementary Data at NSR online). Two dominant physical processes were considered: one is Joule heating in the resistive heater of thermal probe, and the other is heat conduction in the thermal probe, sample and surrounding air. The quasi-steady problem was solved using a stationary solver based on the conduction equation

$$-\nabla \cdot (\kappa \nabla T) = Q,$$  

(2)

where $\kappa$ is the thermal properties of each domain listed in Supplementary Table 1 (available as Supplementary Data at NSR online) and $Q$ is the heat source, set to be zero in all domains except in the resistive heater part of the thermal probe under an input voltage $V_0$,

$$Q = \frac{V_0^2}{R(T)}.$$  

(3)

It is important to recognize that the temperatures of the thermal probe and its resistance are intimately coupled, resulting in a nonlinear governing equation to solve. In the simulations, the initial value of temperature is set as $T_0 = 293.15 \text{K}$ for all domains, and the external boundaries of air-box and the sample (far from the thermal probe) are set to have ambient temperature $T = T_0$ as well. Across interfaces between different domains, temperature and heat flux density are assumed to be continuous, except on the tip-sample contact wherein a thermal contact resistance of $1 \times 10^8 \text{K/W}$ was defined, which was measured using similar type of SThM probe as in a previous study [48]. The presence of the contact resistance results in significant temperature drop at the tip-sample junction but rather small temperature increase in the resistive heater that is more relevant for the measurement (Supplementary Fig. 5, available as Supplementary Data at NSR online). More importantly, the temperature of the resistive heater is sensitive to the change in thermal conductivity of the sample, but insensitive to the contact resistance (Supplementary Fig. 6, available as Supplementary Data at NSR online), as the total heat loss due to the contact resistance is less than $1 \mu\text{W}$ while the total heat conductance through tip-sample junction is in the order of $100 \mu\text{W}$. We also point out that the radiative and convective heat losses, as shown in Supplementary Figs 7 and 8 (available as Supplementary Data at NSR online), are negligible in comparison to the heat conduction, and thus are not considered. More detailed analysis can be found in the Supplementary Data available at NSR online.

We first examine the thermal probe in air, far away from the sample. Under an input voltage of
Figure 5. Quantitative mapping of thermal conductivities; (a) changes in the probe resistance induced by samples with different thermal conductivities; and mappings of (b) resistance change and (c) corresponding thermal conductivities in Yb$_7$Co$_4$Sb$_{12}$; (d) line scan of resistance change across an interface between phase 1 and phase 3.

3.5 V, the temperature distribution is shown in Fig. 4a and b, indicating a substantial temperature rise in the thermal probe up to 683 K. The resistance of the probe is expected to rise with the increased input voltage in a nonlinear manner, caused by the higher temperature induced by the heating voltage. This is confirmed in Fig. 4c, wherein good agreement between the experimental measurement and FEM simulation is observed, giving us confidence that the simulation does capture the physical processes in SThM experiments accurately. We then in our simulation bring the thermal probe into contact with a sample having a thermal conductivity of $\kappa = 5W/(m.K)$, and the increased heat conduction through probe-sample junction results in a drop in the probe temperature, and thus a drop in its resistance. Analysis on the overall heat flux and temperature distributions suggests that only a few percentage of the generated heat passes to the sample through the contact via heat conduction. Nevertheless, due to the small contact area of the probe-sample junction, the heat flux density is substantial, and the resulting temperature drop in the thermal probe is significant, at around 190 K. These are evident in the distributions of heat flux density and temperature in the probe-sample junction shown in Fig. 4d and e. Note the significant temperature drop observed at the contact, yet the problem can be treated as quasi-static, and thus the temperature drop does not significantly influence the temperature of the resistive heater, as compared in Supplementary Fig. 5 (available as Supplementary Data at NSR online). Further zoom-in on the sample in Fig. 4f and g shows that the radius of the sample thermal volume affected by the probe is less than 100 nm, within which around 90% of the temperature variation in the sample occurs. This confirms the nanoscale resolution of our SThM technique.

Quantitative mappings of local properties

Are we capable of experimentally distinguishing materials with different thermal conductivities then? To answer this question, both FEM simulations and SThM experiments were carried out on a dozen or so samples with nominal thermal conductivities ranging from 0.66 to 80.8 W/mK, spanning two orders of magnitude, as listed in Supplementary Table 2 (available as Supplementary Data at NSR online). Under a constant 3.5-V input to the thermal probe,
Table 1. Comparison of thermal conductivities measured from SThM experiment and reported in the literature at 300 K.

| κ [W/(m.K)] | Yb$_{0.3}$Co$_4$Sb$_{12}$ | CoSb$_2$ | YbSb$_2$ | Yb$_2$O$_3$ |
|-------------|--------------------------|----------|-----------|-------------|
| Phase       | Measured                 | Reported  | Remarks   |             |
| 1           | 4.63                     | 3.2      | Polycrystal| Surface-oxidized|
| 2           | 11.71                    | 11.8     | Single-crystal|             |
| 3           | 9.52                     | 15.0     | Polycrystal|             |

*Ref. [39]; Ref. [49]; Ref. [50].

Figure 6. Mapping of local electric conductivity; (a) BSE image; (b) mapping of current; (c) IV curves measured in three phases using cAFM.

the drop in the resistances when the probe contacts the samples was predicted by FEM simulations and measured by SThM experiments, as shown in Fig. 5a. The point-wise experiments were repeated five times on each calibration sample in different areas, and the mean and standard deviations were obtained with the SThM contact force kept constant throughout all the experiments. In the simulation, a constant contact resistance of $1.0 \times 10^8$ K/W is assumed, as explained earlier, and the results suggest that the thermal contact resistance is only significant for samples with higher thermal conductivity, consistent with what we observed in Supplementary Fig. 6 (available as Supplementary Data at NSR online). The good agreement between simulations and experiments observed in Fig. 5a suggests that the thermal conductivity of the sample and the resistance drop can be quantitatively correlated. Indeed, for the three-phase microstructure mapped in Fig. 3, the distribution of resistance change, shown here in Fig. 5b, can be directly converted into a mapping of thermal conductivity shown in Fig. 5c based on this correlation. The resulting thermal conductivities in the three phases are summarized in Table 1, and good agreements with nominal values reported in literature are observed [39,49,50], validating quantitative SThM mapping. Of particular interests is the variation in thermal response at an interface between two phases, for which we investigated an interface marked by the dashed line in the box in Fig. 3f, passing from phase 3 to phase 1. The variation of expected resistance change when the probe scans across the interface is simulated by FEM and compared with experiments, and again good agreement is observed, as shown in Fig. 5d, with quantitative difference much less than 1%. FEM simulations were carried out under nominal thermal conductivity distributions with a sharp interface, as indicated by the blue line in Fig. 5d, while the transition length of thermal response variation is in the order of 100 nm for both experiment and simulation. Note that we have not considered the interfacial resistance in our analysis.

We also examined the electrical conductivity of the sample in the same area using a conductive AFM (cAFM), as shown in Fig. 6, where good correlation between current mapping and phase distribution is again evident. The current mapping in Fig. 6b suggests that the electrical conductivity in the matrix phase 1 and secondary phase 2 is relatively high, while that of phase 3 is relatively low due to the surface oxidation that we discussed earlier. As shown in Supplementary Table 3 (available as Supplementary Data at NSR online), phases 1 and 2 have comparable electrical conductivities of $2.3 \times 10^5$ S/m and $3.0 \times 10^5$ S/m, respectively, consistently with the slight contrast in Fig. 6b. For phase 3, the oxidation of YbSb$_2$ introduces an insulating layer on the surface, resulting in very low electrical conductivity. The I-V curves measured in each phase shown in Fig. 6c also confirm this observation. Obviously, these impurity phases with higher thermal conductivity but lower electrical conductivity exert detrimental influence on the thermoelectric properties of skutterudites, and thus are not desirable. Indeed, the thermoelectric properties measured at the macroscopic
scale, as shown in Supplementary Fig. 9 (available as Supplementary Data at NSR online), confirmed this analysis that its figure of merit $ZT$ is not optimal due to these impurity phases. As such, in order to exert significant scattering on phonons while negligible influence on electrons, it is critical to control precisely the stoichiometry and phase composition, as well as the size and morphology of impurity phases in filled skutterudites. In fact, this is important for nanostructured thermoelectrics in general.

**DISCUSSIONS**

It is rather remarkable that small contrasts in local thermal conductivity can be accurately mapped with nanoscale resolution via SThM as demonstrated. To help us understand this better, we compare the FEM-simulated heat-transfer processes involving three representative phases: matrix skutterudite $Yb_{0.3}Co_4Sb_{12}$ (phase 1), impurity phase $CoSb_2$ (phase 2) and surface-oxidized phase $Yb_2O_3$ (phase 3), using as the input their nominal thermal conductivities of 4.5, 11 and 9.5 W/(m.K), respectively. The relevant thermal transport parameters computed are summarized in Table 2. It is interesting to note that, although less than 2% of the total heat generated transfers through the tip-sample junction for each of the phases considered, the process, i.e. the change in heat transfer, is still dominated by the conductivity of the sample, and thus the heat flux at the tip-sample junction changes significantly for samples with different thermal conductivities, resulting in different temperatures of the contact and thus different probe temperatures and resistance that can be precisely measured using a Wheatstone bridge. This confirms the feasibility of the proposed technique and validates the experimental data. Further improvement can be achieved by carrying out SThM in a vacuum [51], which would enhance the sensitivity and resolution, though our study shows that it is not absolutely necessary.

It is also important to examine the transient behavior of heat transfer during SThM scanning, which is shown in Supplementary Fig. 10 (available as Supplementary Data at NSR online) obtained from FEM simulations. It takes less than 1.2 mSec for the probe temperature to reach its steady-state value, and this is much less than the pixel time of SThM (3.1 mSec for 0.5-Hz line scan), ensuring a quasi-steady-state condition during the SThM scanning. This also imposes an upper limit on scanning rate at 1.3 Hz per line. Finally, we note that the spatial resolution of this technique can be further improved using a dynamic approach. Under a quasi-steady-state condition, the affected thermal volume in the sample is substantial, with a radius on the order of 100 nm. This has been confirmed by the temperature distribution in the sample underneath of the probe (Fig. 4g), as well as the line scan of resistance change across an interface (Fig. 5d). If a dynamic probing is adopted instead, wherein the heating voltage of the probe is frequency-modulated and the corresponding harmonic response is probed, much higher spatial resolution in the order of 10 nm is expected. This will provide us with a powerful tool to study the effect of structural heterogeneity such as defects, interfaces and impurities on thermoelectric materials, which can be used to guide the design and optimization of thermoelectric materials with enhanced performance, especially when the thermoelectric coefficient can also be mapped in addition to thermal conductivity and electric current.

**CONCLUSION**

In this work, local thermal conductivities of a three-phase filled skutterudite were mapped quantitatively with good accuracy, nanometer resolution and one-to-one correspondence with microstructure. Quantitative mapping was accomplished via a SThM using a resistive heating thermal probe complemented by FEM simulations, enabling us to distinguish thermal conductivities spanning two orders of magnitude, yet resolving thermal variation across a phase interface with small thermal conductivity contrast. The technique developed thus provides a powerful tool to correlate local thermal conductivities, microstructures and macroscopic properties for nanostructured materials in general and thermoelectric materials in particular, which can be used to guide the design and optimization of thermoelectric materials with enhanced performance.
METHODS

Sample preparation

The sample with a stoichiometry of Yb$_{0.7}$Co$_4$Sb$_{12}$ was prepared by a conventional induction melting-vacuum melting-quenching-annealing-sintering method. High-purity Co powders (99.995%, Alfa Aesar), Sb shots (99.9999%, Alfa Aesar) and Yb chunks (99.95%, Alfa Aesar) were used as the starting materials. Co powders were first purified and melted into small shots with sizes of 1–5 mm by arc melting (SA-200, MRF Inc., USA), then loaded into a BN crucible together with Sb shots for induction melting (at 2000°C for 30 s under an Ar atmosphere, EQ-SP-25VIM, MTI Corporation, USA). The obtained ingot was subsequently crushed and loaded into a carbon-coated quartz tube with appropriate amounts of Yb and Sb in an argon-filled glove-box (Lab Star, Mbraun, Germany) and vacuum-sealed (10$^{-3}$ torr). Subsequently, the tube with raw materials was placed into a box furnace, heated to 1000°C in 5 h, soaked for 24 h and then rapidly quenched in ice water. The obtained ingot was ultrasonically cleaned and loaded into a carbon-coated quartz tube with appropriate amounts of Yb and Sb in an argon-filled glove-box (Lab Star, Mbraun, Germany) and vacuum-sealed (10$^{-3}$ torr). Subsequently, the tube with raw materials was placed into a box furnace, heated to 1000°C in 5 h, soaked for 24 h and then rapidly quenched in ice water. The obtained ingot was ultrasonically cleaned and vacuum-sealed in a quartz tube, then annealed in a box furnace at 750°C for 168 h. After annealing, the ingot was crushed, hand-grounded into fine powders and sintered into a bulk material using the spark plasma sintering (SPS-211Lx, Dr. Sinter, Japan) at 680°C and 50 MPa for 5 min.

Structure and property characterization

The phase composition was determined by the powder X-ray diffraction (XRD, Bruker D8 Focus X-ray diffraction, Germany) using the Cu Kα radiation (λ = 1.5406 Å). The BSE images were obtained in a TM3000 electron microscope (Hitachi, Japan). The chemical composition and elemental mapping were determined by a field emission scanning electron microscope equipped with EDS (FESEM/EDS, FEI Sirion, Japan). The electrical conductivity and Seebeck coefficient were simultaneously measured via commercial equipment (ZEM-3, Ulvac Riko, Inc., Japan) under a low-pressure helium atmosphere. Thermal conductivity was calculated from the product of the measured thermal diffusivity, specific heat and density. Thermal diffusivity was measured by a laser flash method (Netzsch LFA-457, Germany) and specific heat was measured by a differential scanning calorimetry method (DSC) using sapphire as the reference (Netzsch 404F1, Germany). The measurement temperature ranges from 300 K to 850 K.

Scanning thermal microscopy

The SThM was performed using an Asylum Research MFP-3D atomic force microscope (AFM) using a thermal probe with a spring constant of 0.2–0.5 N/m (AN2-300, Anasys Instruments) in contact mode with contact force around 110 nN and a scan rate of 0.5 Hz per line. The thermal probe is similar to any silicon AFM probe in geometry with an integrated heater at the end. A small region (7.5 µm × 15 µm) close to the cantilever tip with light phosphorus doping acts as a solid-state heater. The heater region connects through two heavily doped branches acting as the electrical leads. The electrical resistivity of the probe varies between 600 Ω and 2 kΩ for different probes and different drive voltages.

Conductive AFM

The variations of electrical conductivity of the sample were characterized using ORCA, a conductive AFM (cAFM) module developed by Asylum Research. All measurements and images were obtained using AFM contact mode with a metallic Pt/Ir-coated probe having a force constant of 2.8 N/m (PPP-EFM, Nanosensors). Two different modes were used: imaging mode to map the variation of electrical conductivity, and spectroscopic mode to measure the I-V characteristics at points of interest. In the imaging mode, 2-V DC bias was applied to the sample substrate and the necessary current for virtually keeping the tip grounded was used to image the electrical conductivity. In the spectroscopic mode under the stationary probe, a sweeping DC bias (–0.6 V to 0.6 V) was applied to the sample while measuring the current that kept the conductive tip grounded.

SUPPLEMENTARY DATA

Supplementary data are available at NSR online.

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