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LOW-DIMENSIONAL ORGANIC CONDUCTORS AS THERMOELECTRIC MATERIALS

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We have developed a system to measure electrical resistivity, thermopower and thermal conductivity of tiny fragile organic conductors simultaneously. Figure of merit Z has been successfully determined from these transport coefficients for a two-dimensional organic conductor τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, (y≤0.875), where EDO-*S,S*-DMEDT-TTF is ethylenedioxy-*S,S*-dimethylethylenedithio-tetrathiafulvalene, for the first time.

Keywords: *electrical resistivity, figure of merit, organic conductor, thermal conductivity, thermoelectric material, thermopower*

Introduction

Organic conductors have attracted much attention because of their variety of electronic ground states from insulating to superconducting. Kinds of mechanisms have been proposed to explain insulating states observed for the organic conductors. Some of them are charge-density-wave, spin-density-wave (SDW), field-induced SDW, Mott insulating and charge-ordered states. These electronic states are closely related to the anisotropic crystal structure composed of planer donor/acceptor organic molecules and inorganic counter anions. Anisotropic and weak interaction between frontier molecular orbitals results in low-dimensional, narrow-band electronic systems. The ratio of electrical conductivities along the most conducting and resistive directions sometimes amounts to in the order of 10^5. A typical bandwidth of the organic conductors is about 0.5 eV even in the most conducting direction, while it is 2–3 eV in conventional metallic or semiconducting elements.

Understanding of the unconventional electronic states of the organic conductors has been developed for more than 30 years. Its application to, for example, solid-state devices is very limited mainly because the crystals are small (~1 mm or less in length) as well as mechanically and thermally fragile. Another reason to limit their application is probably difficulty to control carrier concentrations to tune their physical properties, while it is usually done in conventional *p*- and *n*-type semiconductors. Most of the organic conductors have stoichiometric composition of organic molecules and inorganic counter anions such as 2:1 or 1:1 and it is difficult to modify the composition chemically. Recently, however, the present authors have shown an evidence of band-filling control [1, 2] in a nonstoichiometric organic conductor, τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, (y≤0.875), where EDO-*S,S*-DMEDT-TTF is an organic donor molecule, ethylenedioxy-*S,S*-dimethylethylenedithio-tetrathiafulvalene. Clear change in a frequency of Shubnikov-de Haas oscillations was observed after heating a crystal up to 420 K. This shows that the band-filling or concentration of charge carriers was changed as a result of anion decomposition by heat treatment [1, 2].

τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, (y≤0.875) has a crystal structure made of alternative stacking of conducting and insulating layers along the *c*-axis. The conducting layer is made of 2:1 composition of the donor molecules and the inorganic anions AuBr_2^- [3]. Packing pattern of the donor molecules within the conducting *ab* plane is called 'τ-type' and results in a four-fold symmetry of band structure and metallic electrical conduction below room temperature. The insulating layer is composed of AuBr_2^- corresponding to the composition y and has different periodicity from that of the conducting layer [3]. Since y probably changes from sample to sample [4], the τ-type conductor shows sample dependence of physical properties. This material also shows other interesting physical properties such as large negative magnetoresistance [5] and a weak ferromagnetic behavior below 30 K [6], and large thermopower S as a metallic organic conductor. Electrical conductivity and thermopower along the *ab* plane of this material are 200 S cm^{-1} [1] and –90 μV K^{-1} at 300 K, respectively. Furthermore,

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S amounts to about $-150\ \mu V\ K^{-1}$ at lower temperature. This is very large as a metallic organic conductor and implies its application as a thermoelectric material. In this study we developed a simple system to evaluate ability of thermoelectric efficiency of fragile organic conductors. One of measures of such ability is known as figure of merit Z that is defined as

$$Z = \frac{S^2}{\rho\kappa} \qquad (1)$$

where ρ and κ are electrical resistivity and thermal conductivity, respectively. We needed to develop a system to measure these transport coefficients simultaneously for the same sample due to the sample dependence noted above. We will show the first result of estimating Z by the simultaneous measurement of the three transport coefficients of an organic conductor below.

Experimental

A plate-like single crystal of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, ($y \leq 0.875$) was synthesized electrochemical oxidation reported elsewhere [1]. The crystal was cut into a long rectangle piece ($0.800\times0.150\times0.050$ mm^3) by a razor blade. Figure 1 shows a schematic top view of the sample holder used in this study. Each end of the rectangle sample (a) was attached to current electrodes (b1 and b2) of Manganin wire (50 μm in diameter) with carbon paste. The electrodes were supported by thin golden wires (c1 and c2) each of which was connected to copper blocks (d1 and d2), respectively. There are four pairs of Chromel–Constantan thermocouples (e1–e4) in the sample holder. The diameter of the thermocouple wires is 13 μm (5 m inch). They were connected to copper wires using silver paste on the biggest copper block (d5) whose temperature was monitored by a platinum thermometer (f). The contact points between the thermocouples and the copper wires were insulated by a piece of cigarette paper (g) glued by vanish to the copper block. Two of the thermocouples were attached to the sample and the other two to the current electrode b2. DC electrical current through d1–c1–b1–a–b2–c2–d2 was of the order of 10 μA and generated by a current generator. Then voltage drop across the sample was measured between Chromel wires of e1 and e2 to determine ρ.

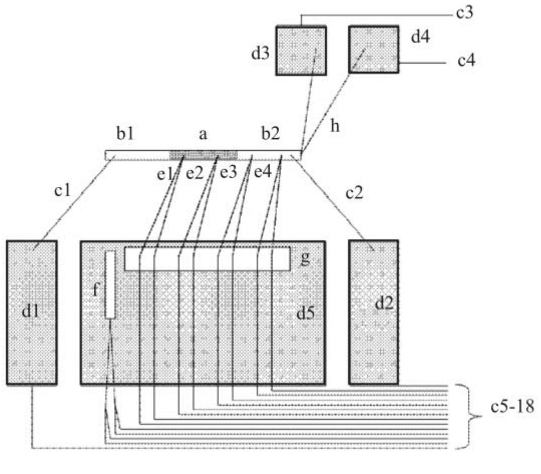

Fig. 1 A schematic diagram of the sample holder to measure electrical resistance, thermopower and thermal conductivity simultaneously. a – sample, b1, b2 – Manganin current electrodes, c1–c4 – lead wires, d1–d5 – copper blocks, e1–e4 – Chromel-Constantan thermocouples, f – platinum thermometer, g – cigarette paper, h – heater

Once ρ was determined at a temperature, the electrical current was set to zero and the circuit between d1 and d2 was made open. Next electrical current was applied to the heater h connected to copper blocks d3 and d4 electrically, and thermally to the end of b2. Heater power was set so as to generate thermal gradient of the order of 1 K between e1 and e2 as well as between e3 and e4 in vacuum. Temperature difference across the sample, ΔT_s was determined by e1 and e2, while that across b2, ΔT_m was done by e3 and e4. Thermopower of the sample was determined as $\Delta E_s/\Delta T_s$, where ΔE_s is the absolute thermoelectric power of the sample deduced from the voltage between Chromel wires of e1 and e2 and between Constantan wires of e1 and e2, respectively.

Finally thermal conductivity of the sample κ_s was calculated by using ΔT_s, ΔE_s and a reported thermal conductivity of manganin κ_m [7]. The present way is one of variations of the steady method with a reference material.

Results and discussion

We have succeeded to determine simultaneously ρ, S and κ of a small crystal of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, ($y \leq 0.875$) as shown in Fig. 2. The magnitude of ρ is about three times larger than that in the previous report [1], but this is within an error due to uncertainty of measuring size of the small crystal with a rather distorted shape. Temperature dependence of ρ (Fig. 2a) is metallic below room temperature as was reported before, but it turns to non-metallic below 150 K, while the reported resistivity along the conducting *ab* plane is metallic down to 4.2 K [1]. The reason of the discrepancy is unclear. A possibility of the sample dependence and/or less quality of electrical contacts should be examined with other samples.

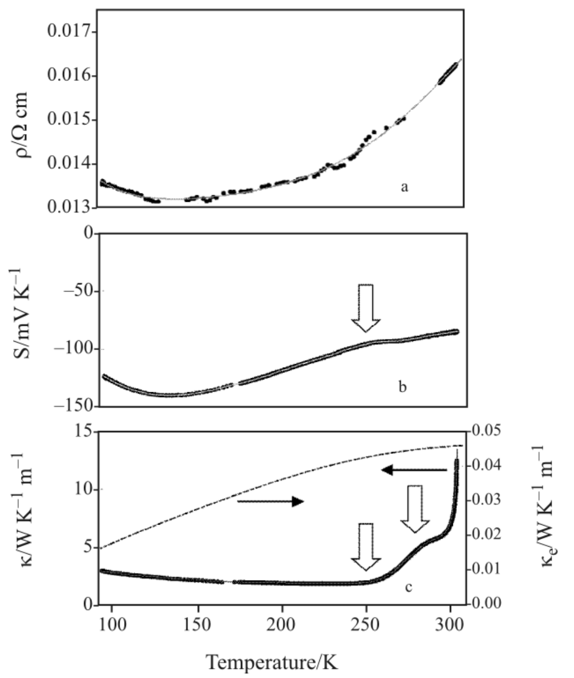

Fig. 2 Temperature dependence of a – electrical resistivity ρ, b – thermopower *S* and c – thermal conductivity κ of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, ($y \le 0.875$). Solid curves are polynomial fits to data plotted by solid circles. The white arrows in b and c indicate anomalies described in the text. The broken curve in c is contribution of electrical carriers to thermal conductivity κ_e calculated from the data in a

Thermopower *S* is negative and –85 μV K^{-1} at 300 K. The absolute value of *S* shows maximum of about –140 μV K^{-1} between 120 and 140 K as in Fig. 2b. The present result is consistent with a previous one with another method where thermocouples were not contacted to the sample directly [8]. The negative *S* suggests that dominant carriers are electrons, while a possibility of semimetallic band structure was pointed out [1]. An anomaly of temperature dependence of *S* was observed at about 260 K (a white arrow in Fig. 2b). Development of a superstructure closely related to the difference in periods of the conducting and insulating layers of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, ($y \le 0.875$) has been observed by diffuse X-ray scattering measurement below 245 K [9]. The anomaly in Fig. 2b is probably related to the growing of the superstructure. Since the temperature resolution and signal-to-noise ratio are low in the previous result, no clear anomaly was reported in [8].

Temperature dependence of κ of the present material is unexpectedly large as compared with that of ρ and *S* below 305 K. The magnitude of κ is 7 W K^{-1} m^{-1} at 300 K. This is within the distribution of κ values, which are typically between 1 and 10 W K^{-1} m^{-1}, reported for other organic conductors [10–14]. It has been pointed out the contribution of charge carriers to thermal conductivity κ_e is very small (~5%) in another organic conductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [11]. This is also the case with the present result. The broken curve in Fig. 2c is the calculated κ_e from ρ in Fig. 2a by assuming Wiedemann–Franz law $\kappa/\sigma T = L_0$, where $L_0 = 2.45\times10^{-8}$ W Ω K^{-2}. Between 90 and 310 K the ratio of κ_e to the total κ has the smallest value of about 0.5% at 100 and 300 K and the largest one (~2%) at 240 K, respectively.

A rapid decrease in κ on lowering temperature from 305 to 250 K was observed as in Fig. 2c. There seem to be two anomalies in the temperature dependence at about 260 and 290 K shown by white arrows. The former is probably related to the development of the superstructure, while no anomaly has not been reported around 290 K in other physical properties. The lowest value of κ is about 2 W K^{-1} m^{-1} between 200 and 250 K and negative but small temperature dependence was observed below 200 K. We can conclude that the heat conduction in the present material is dominated by the lattice contribution from these observations.

To determine the figure of merit *Z*, polynomial curves were fitted to the data of ρ, *S* and κ as in Fig. 2. Temperature dependence of *Z* and dimensionless figure of merit *ZT* was calculated from those data

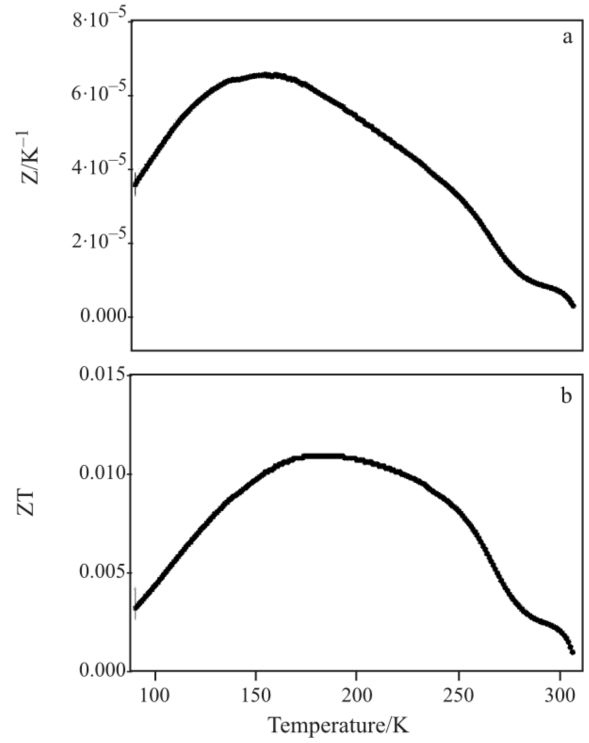

Fig. 3 Temperature dependence of a – figure of merit *Z* and b – dimensionless figure of merit *ZT* of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, ($y \le 0.875$)

(Fig. 3). The figure of merit is 6.1×10^{-6} K^{-1} at 300 K. It was found that *Z* rapidly increases on lowering temperature and reaches 6.5×10^{-5} K^{-1} around 150 K as in Fig. 3a. The dimensionless figure of merit *ZT* is 2.0×10^{-3} and its maximum is 1.1×10^{-2} around 160 K. Since the present work is the first report on *Z* of an organic conductor, there is no direct report of *Z* on the other organic conductors. By combining the transport coefficients reported in literatures, we can estimate *Z* and *ZT* of another organic conductor. For $(TMTSF)_2PF_6$ that is the first organic superconductor, σ and κ from [13] and *S* from [15] give $Z=1.0\times10^{-5}$, 8.2×10^{-6} and 3.4×10^{-6} K^{-1}; $ZT=1.0\times10^{-3}$, 1.6×10^{-3} and 1.0×10^{-3} at 100, 200 and 300 K, respectively. So the maximum value of *ZT* of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, ($y\leq0.875$) is probably about 7 times larger than that of $(TMTSF)_2PF_6$. The large *ZT* is mainly due to large *S* of the τ-type salt.

Conclusions

We have developed a system to measure σ, *S* and κ simultaneously for a tiny crystal of fragile organic conductors. The system was successfully utilized to determine temperature dependence of *Z* and *ZT* of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, ($y\leq0.875$). It was found that the dimensionless figure of merit *ZT* of τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, ($y\leq0.875$) has a maximum around 160 K and it is about 7 times bigger than that of a well-known organic superconductor $(TMTSF)_2PF_6$. Even if *ZT* of the τ-type salt might be much bigger than that of other organic conductors, it is still so small that we cannot use the τ-type salt as a thermoelectric material to generate power. Since materials in practical use must have *ZT* bigger than 1, further tuning of physical properties by heat treatment on τ-(EDO-*S,S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, ($y\leq\leq0.875$) and/or exploring other materials using the present system will be needed for the application of organic conductors to thermoelectric conversion.

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