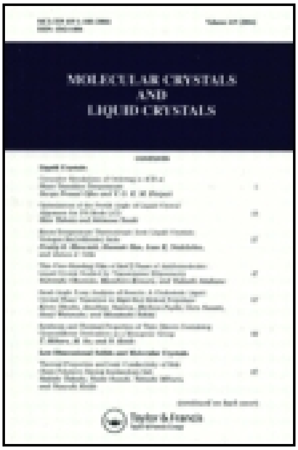

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ELECTRICAL PROPERTIES OF ORGANIC CONDUCTORS AT HIGH TEMPERATURE

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Physical properties up to 600 K are studied for $(TMTSF)_2PF_6$, $(TMTTF)_2PF_6$, $(DMET)_2I_3$, $(DMET)_2AuI_2$, $(DIMET)_2I_3$, $(DIMET)_2AuI_2$ and κ-$(ET)_2Cu(NCS)_2$. It has been found that all the compounds decompose between 450 and 500 K by TG-DTA measurement. Electric resistivity and thermopower of the TMTSF and DMET salts are metallic as were expected from their temperature dependence below 300 K. The TMTTF and DIMET salts show constant thermopower,

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though their resistivity is metallic. This suggests that the TMTTF and DIMET salts are intrinsically non-metallic even above room temperature. Rapid decrease in resistivity found for many of the Q1D salts before their decomposition suggests the partial escape of anions and change in the carrier concentration. κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ shows hysteretic temperature dependence of the resistivity above 300 K.

Keywords: TMTSF; DMET; κ-(BEDT-TTF)$_2$Cu(NCS)$_2$; high temperature; electrical properties; thermal analysis

INTRODUCTION

In contrast to the variety of ground states at the lowest temperature in the so-called ‘unified’ temperature-pressure phase diagram [1] for quasi-one-dimensional (Q1D) (TMTSF)$_2$PF$_6$ ($T_{\mathrm{SDW}} = 12\,\mathrm{K}$), and its analogs, room temperature region seems to be dominated by an identical metallic phase. This means that (TMTTF)$_2$PF$_6$, whose electric resistivity has broad minimum at $T_{\mathrm{min}} = 230\,\mathrm{K}$, transitions from the charge localized state to metallic one on increasing temperature and/or pressure. If it is the case, metallic behavior of physical properties of (TMTTF)$_2$PF$_6$ should be observed above room temperature as has already done under pressure [2].

In this paper, electric resistivity (ρ) and thermopower (S) of (TMTSF)$_2$PF$_6$ and (TMTTF)$_2$PF$_6$ were measured up to 450 K to understand their electronic state at and above room temperature as well as for other groups of Q1D conductors, (DMET)$_2$I$_3$ ($T_{\mathrm{c}} = 0.47\,\mathrm{K}$), (DMET)$_2AuI_2$ ($T_{\mathrm{SDW}} = 16\,\mathrm{K}$), (DIMET)$_2I_3$ ($T_{\mathrm{SDW}} = 41\,\mathrm{K}$) and (DIMET)$_2AuI_2$ ($T_{\mathrm{min}} \sim 300\,\mathrm{K}$), where DMET and DIMET are abbreviations of dimethyl(ethylenedithio)diselenadithiafulvalene and dimethyl(ethylenedithio)-tetrathiafulvalene, and Q2D κ-(BEDT-TTF)$_2$-Cu(NCS)$_2$ for comparison. Thermogravimetry and differential thermal analysis (TG-DTA) measurement was also carried out for the compounds to study their thermal stability at high temperature.

EXPERIMENTAL

The sample materials were obtained by usual electrochemical oxidation method. TG-DTA was carried out using a commercial system (TAS 100 with a TG unit (THERMOFLEX TG8110), Rigaku Co.) at Center for New Materials at Japan Advanced Institute of Science and Technology. Powdered sample was exposed in the flow of N$_2$ gas (50 ml/min) and heated up to 570 or 670 K with the sweep rate of 5 K/min.

Electric resistivity and thermopower were measured at Osaka City University. Each crystal was attached to electrodes, which are made of Au (Cu) for the ρ (S) measurement, by using carbon paste (XC-12, Fujikura-kasei Co.). Temperature was increased with the rate of 10–20 K/hour and both the measurements were carried out for different single crystals in vacuum until the electrical contacts were deteriorated by heat. It must be noted that the carbon paste itself survives well above 500 K as was checked by using chromel wire as a sample.

RESULTS AND DISCUSSION

Figure 1 shows the TG-DTA curves for $(TMTSF)_2PF_6$ with sample mass of (a) 7.11 and (b) 0.13 mg, respectively. Rapid decrease of the mass was observed above 450 K. A sharp exothermic peak around 500 K in the DTA curve corresponds to the mass decrease and shows that $(TMTSF)_2PF_6$ decomposes below 500 K. Mass spectrometry detected neither TMTSF nor PF_6^- in the residue after heating up to 580 K. Figure 1(b) shows that the initial mass of about 0.1 mg enables us to determine decomposition temperature with minor error. The apparent increase in mass in Figure 1(b) is due to the lack of the blank correction to avoid introducing external error. (Note that the sample mass in Figure 1(b) is less than 1/50 of that in 1(a).) Figure 2 shows the numerical temperature derivative of the TG (DTG) curve with the definition of characteristic temperatures. The extrapolated onset ($T_{\mathrm{e.o.}}$) and peak (T_{p}) temperatures seem to have good reproducibility as compared with the onset temperature (T_{o}). These temperatures and the position of exothermic peak in the DTA curve are plotted in Figure 3 for all the compounds studied.

As in Figure 4(a) the Q1D conductors show metallic resistivity above 300 K, and that is consistent with the extrapolation from the lower temperature as was reported previously. It has been found for the first time that most of the Q1D conductors show relatively large decrease in ρ at a

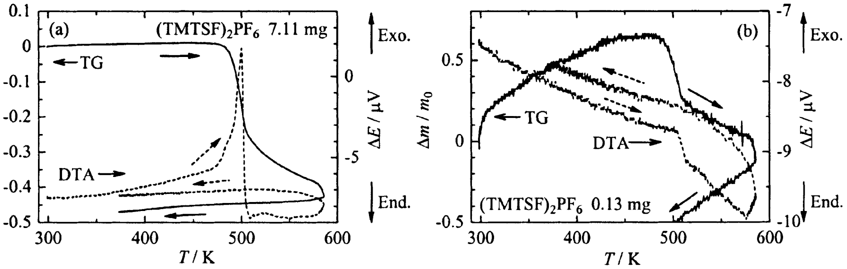

FIGURE 1 TG-DTA curves of $(TMTSF)_2PF_6$ up to 580 K for the sample mass of (a) 7.11 and (b) 0.13 mg.

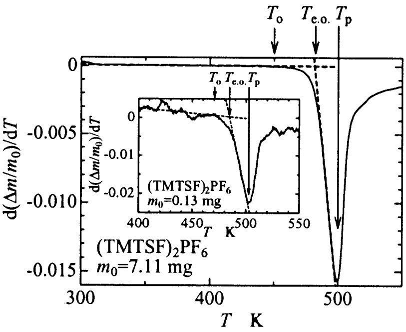

FIGURE 2 DTG curves for $(TMTSF)_2PF_6$ of 7.11 and 0.13 (inset) mg with the definition of characteristic temperatures, T_o, $T_{e.o.}$ and T_p.

temperature before the rapid increase at T_ρ due to the deterioration of electrical contacts and partial decomposition. Around 400 K, where purification of the component molecules by sublimation is usually carried out before the chemical oxidation synthesis of organic conductors, since i) the molecules do not decompose, ii) the mass starts to decrease and iii) the conducting property is still held, it is probable that the initial decomposition is associated with partial escape of the anions from the crystals and this is related to the decrease in ρ in Figure 4(a) except for $(DMET)_2AuI_2$. Thus, the appropriate thermal treatment probably gives a way to control the carrier concentration of the electronic system.

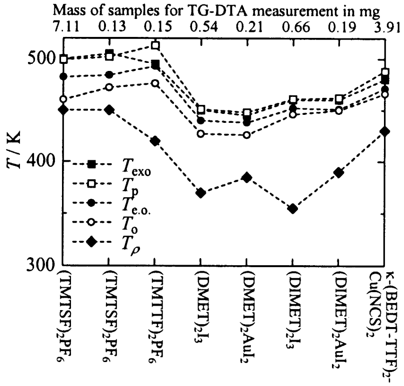

FIGURE 3 Temperatures of onset (T_o), extrapolated onset ($T_{e.o.}$) and top (T_p) of the peak of the DTG curve (see Figure 4), the exothermic peak of DTA curve (T_{exo}), and onset of the rapid increase in resistivity (T_ρ). The broken lines are guides to the eye.

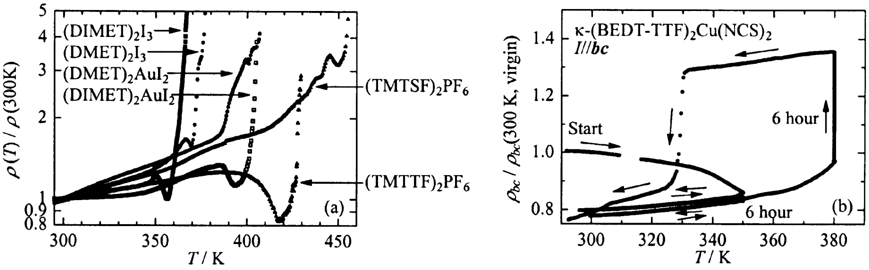

FIGURE 4 Temperature dependence of the normalized electric resistivity of (a) Q1D conductors and (b) κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

Apparently complicated hysteresis of in-plane resistivity was observed for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ above 300 K as in Figure 4(b). It was found that ρ decreases by anneal at and below 350 K, while ρ gradually increases in time at 380 K. The thermal treatment at 350 K did not change the superconducting transition temperature within the experimental error in the ρ measurement at least for one sample. Rapid increase in ρ of the Cu(NCS)$_2$ salt was observed above 420 K by using another crystal (not shown).

Thermopower was measured for the Q1D conductors to elucidate whether they are in a metallic state or not. Above 300 K, S of (TMTSF)$_2$PF$_6$, (DMET)$_2$I$_3$ and (DMET)$_2$AuI$_2$ is metallic and has almost the same slope as that below 300 K (Figure 5(a)), while (TMTTF)$_2$PF$_6$, (DIMET)$_2$I$_3$ and (DIMET)$_2$AuI$_2$ show almost constant S (Figure 5(b)). This suggests that the salts of TMTTF and DIMET, that contain no Se atoms, are

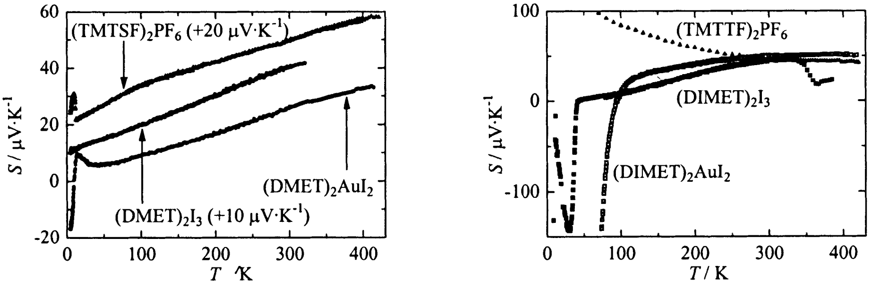

FIGURE 5 Thermopower of (a) (TMTSF)$_2$PF$_6$, (DMET)$_2$I$_3$, (DMET)$_2$AuI$_2$, (b) (TMTTF)$_2$PF$_6$, (DIMET)$_2$I$_3$ and (DIMET)$_2$AuI$_2$. The data are shifted by 10 μV·K^{-1} from sample in (a). The data for (DMET)$_2$AuI$_2$, (DIMET)$_2$I$_3$ and (TMTTF)$_2$PF$_6$ below 300 K are taken from [3–5]. Low temperature data for (TMTSF)$_2$PF$_6$ is consistent with the previous report [6].

in a non-metallic phase even above room temperature in spite of the apparent metallic resistivity. It is interesting that (DIMET)$_2$I$_3$, that undergoes the spin-density-wave transition at 41 K [7], seems non-metallic above room temperature. This suggests that (DIMET)$_2$I$_3$ is at the boundary between the metal and the non-metal around 300 K. The rapid decrease in S of (DIMET)$_2$I$_3$ between 340 and 360 K is probably due to the partial anion loss. The main reason that S becomes unmeasurable at much lower temperature than for ρ is the restriction of the technique for measuring thermopower where the sample crystal is easily broken by thermal stress.

SUMMARY

In spite of the apparent metallic behavior of ρ, the constant S above 300 K shows that (TMTTF)$_2$PF$_6$, (DIMET)$_2$I$_3$ and (DIMET)$_2$AuI$_2$ are non-metallic even above 300 K. This suggests the existence of the boundary between the non-metal and metal in an improved unified $T - p$ phase diagram. It was found for the first time that ρ of the present Q1D conductors decreases rapidly before the decomposition except for (DMET)$_2$AuI$_2$. This is probably related to the partial escape of anions and change in the carrier concentration. The annealing at 350 K results in the gradual decrease in ρ of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, while the superconducting transition temperature is not affected.

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