In-Situ Measurement of Electrical Character of PbTe at High Pressure and High Temperature *

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There is a widespread interest in lead telluride (PbTe) as a good thermoelectric material. We report the temperature dependence of thermopower $S(T)$ and resistance $R(T)$ for PbTe at the different pressures of from 1.8 GPa to 5 GPa obtained by using the cubic anvil high pressure apparatus. With increasing pressure, $R(T)$ and $S(T)$ decrease. The effect of pressure on $R(T)$ is larger than that on $S(T)$. The power factor that is determined by thermopower and resistivity increases with increasing pressure. This method is an efficient tool for synthesizing good thermoelectric materials at high pressure and high temperature.

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Thermoelectric materials can be used both as generators that convert heat into electricity and as refrigerators that utilize electricity for cooling. Thermoelectric devices are lightweight, small, and without any moving parts or bulk fluids.[1,2] Presently, the application of thermoelectric devices is limited by their low efficiencies which are determined by the thermoelectric dimensionless figure of merit, ZT, where T is the temperature and $Z = S^2\sigma/\kappa$ (S is the thermopower, σ is electrical conductivity, and κ is the thermal conductivity). The best materials available today for devices have the ZT value of about 1. It is believed that the ZT value of 3 or 4 is necessary for practical thermoelectric generators.[1] Thus, the current research on thermoelectric materials is focused on finding thermoelectric materials with larger possible value of ZT.[2]

Several approaches have been adopted to improve thermoelectric properties of materials, such as the synthesis of new bulk materials[3] and quantum-well[4] structures. Besides the ambient pressure synthesis methods, pressure tuning is another efficient way.[5] Pressure tuning may offer new means to rapidly explore the phase space composed of the interaction parameters (e.g. orbital overlap, orbital energy, and magnetic coupling, etc) that determine the material properties, potentially increasing the rate of discovery of improved materials.[6−8] Badding *et al.* found that the ZT values of some materials including heavily doped semiconductors and rare earth intermetallic compounds were considerably improved at high pressure and room temperature.[9,10] Observation of improved properties under pressure provides targets for synthesis by other approaches, although the higher ZT value induced by pressure can not be retained at ambient pressure. It is well known that the high-pressure and high-temperature (HPHT) synthesis is the most direct method to obtain the high pressure phase materials, such as the diamond and hBN. In our previous work, we synthesized some thermoelectric materials under HPHT, and we found that the ZT values of PbTe synthesized under HPHT were considerably higher than those of ones synthesized at ambient pressure.[11,12] In order to obtain a better understanding of the roles that temperature and pressure play in the course of synthesis, in situ measurements of thermopower and resistance under HPHT were conducted in this work.

Although some in situ thermopower measurement techniques have been used in anvil cells and self-clamped cells, there has been no report so far about such kind of measurements being conducted on cubic anvil high-pressure apparatus.[13−15] Because the cubic anvil is the synthesis apparatus, in which it is easy to control the temperature, we can obtain the thermopower and resistance functions of temperature at different pressures.

In this work, in situ measurements of thermopower and resistance of PbTe under HPHT are conducted on cubic anvil high pressure apparatus with the pressures ranging from 1.8 to 5 GPa and the temperatures ranging from 300 to 800 K. It is found that the thermoelectric property of PbTe increases with pressure.

Sample synthesis and in situ measurements at HPHT are carried out in the cubic anvil apparatus. The sketch of the assembly is shown in Fig. 1. A graphite tube was introduced as heater. Due to the heating fashion and the geometry of the chamber, there exists an axial temperature gradient that can

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be used to perform the thermopower measurements without any supplementary heater. One end of the sample was placed at the centre of the chamber where the temperature was the highest. The K-type thermocouples were used to measure the thermopower of the sample and the temperature of the chamber.

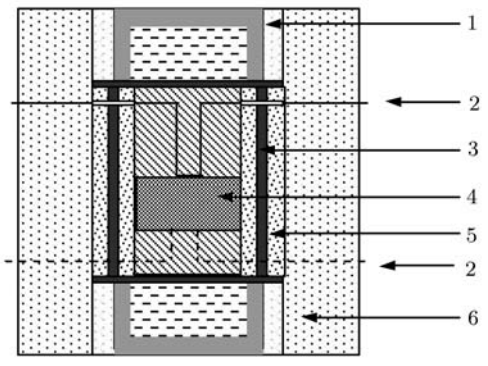


Fig. 1. Schematic diagram of the experimental setup for the sample synthesis and in situ measurements: (1) ring, (2) K-type thermocouple (the perpendicular ones are shown by dashed lines), (3) graphite heater, (4) sample, (5) insulation tube (NaCl + 20 wt.% ZrO_2), (6) pyrophyllite.

High pure (99.999%) lead and tellurium powder were mixed with 1:1 (at.%) ratio in an agate mortar under argon atmosphere. Then the mixture was pressed into pellets of 6 mm in diameter and 6 mm in length. The samples were heated for 30 min under the condition of 1300 K and 1.8 GPa, then quenched to room temperature. The pressure was estimated by the oil press load, which was calibrated by the pressure-induced phase transitions of bismuth, thallium and barium metals under high pressure. The temperature was measured by K-type thermocouples.

Two pairs of K-type thermocouples which connected the anvils and sample were used to measure thermopower and resistance. They were insulated from graphite heater by ceramic pipe. The thermocouples were connected with anvils as shown in Fig. 1. The details of the technique (e.g. experimental configuration and the principle of measurement thermopower, etc) have been described elsewhere. Conventional four-probe dc resistance measurements were performed on a sample loaded in the same way as those loaded for thermopower measurements. Voltages were measured by an HP 3458A multimeter.

Figure 2 shows the temperature dependence of the thermopower, $S(T)$, under different pressures for the PbTe sample synthesized under HPHT. All the $S(T)$ values are negative, which means that the PbTe are an n-type semiconductor due to the excess of lead. At different pressures, $S(T)$ values have the same variation tendency in which $S(T)$ increases with increasing temperature and then slightly decreases. At 1.8 GPa, for example, the thermopower increases from 51 μV/K at 330 K to 197 μV/K at 600 K and decreases to 165 μV/K at 780 K. As a transport coefficient, thermopower depends on the energy band structure of a material. The PbTe is one of the few materials where the temperature coefficient ($\partial E_{\rm gap}/\partial T \approx 4.7 \times 10^{-4}$ eV/K) is positive, which means that the semiconducting gap increases with temperature.[16] Moreover, the thermopower is inversely proportional to the carrier density that decreases as $E_{\rm gap}$ becomes broader. However, when the temperature goes over a value, the carrier density increases slightly because the contribution of thermal excitation is dominant at high temperature. Therefore, the thermopower of PbTe increases to a maximum value at one temperature and then slightly decreases. The thermopower also depends on the pressure. Figure 2 shows that $S(T)$ is smaller at higher pressure, which is marked at high temperature. The pressure coefficient is negative for PbTe.[15] Thus, $E_{\rm gap}$ becomes narrower as pressure increases, which means that the carrier density increases. Thus the thermopower decreases with pressure.

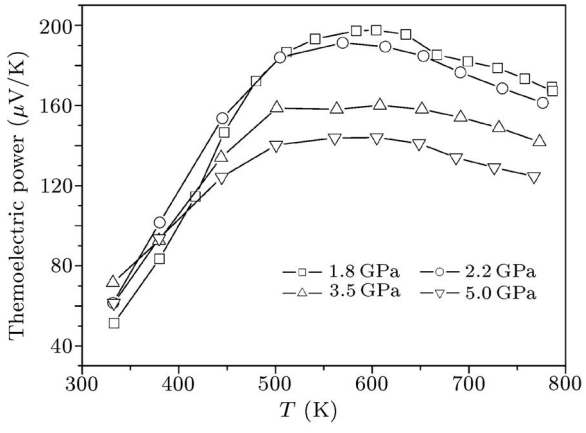


Fig. 2. Temperature dependence of thermopower $S(T)$ of PbTe under different pressures.

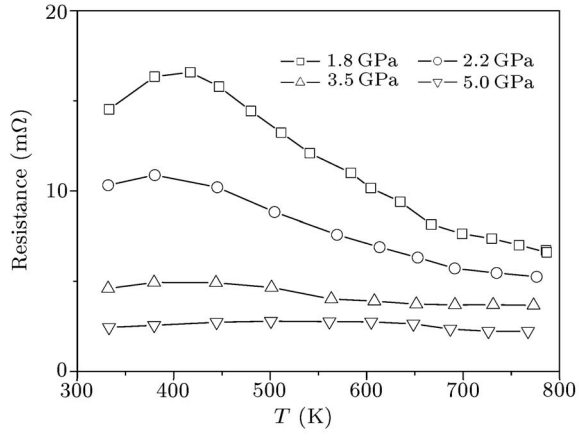


Fig. 3. Temperature dependence of resistance $R(T)$ of PbTe under different pressures.

The measurements of resistances were conducted simultaneously as the measurements of thermopower. Because of the temperature gradient, the sample voltage has the temperature component V_T, i.e. $V = IR + V_T$. Therefore, the resistances can be calculated by the linear fit of the voltage. Figure 3 shows that the temperature dependence of resistances of PbTe at different pressures. The changing tendencies of resistances with temperature and pressure are the same as that of thermopower. Similarly, the resistance is inversely proportional to the carrier density. Moreover, compared with thermopower, the resistance is more sensitive to pressure. Table 1 exhibits that the effect of pressure on resistance is larger than that on thermopower at 600 K.

Table 1. The effects of pressure on thermopower and resistance at 600 K.

Pressure (GPa)	1.8	2.2	3.5	5.0
S (P)/S (1.8 GPa)	1.00	0.97	0.81	0.73
R (P)/R (1.8 GPa)	1.00	0.66	0.36	0.25

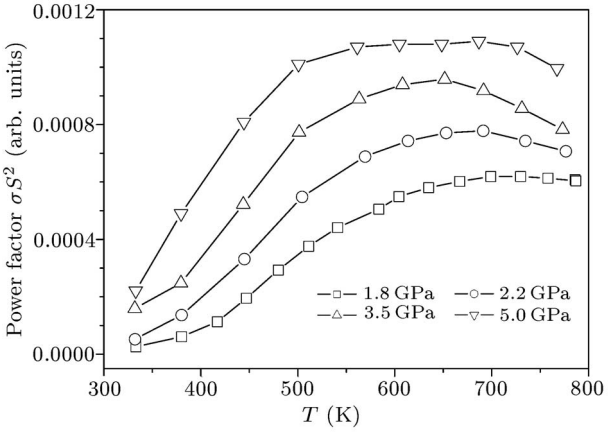


Fig. 4. Temperature dependence of power factor σS^2 of PbTe under different pressures.

The power factor, $S^2\sigma$, is determined by thermopower and the electrical conductivity that can be calculated by the resistance and the geometric factor. In HPHT experiments, the geometric factor will have a small change that is not able to be in situ measured at cubic anvil. Thus, the relative conductivity is calculated by the same geometric factor. Figure 4 shows the temperature dependence of the power factor under different pressures for PbTe. At high pressures, the maximum values appear in the range 600–700 K, which is in good agreement with the results at the ambient pressure. At a certain temperature, the values of the power factor increase as the pressure increasing. This indicates that the increasing effect of pressure on electrical resistivity is so large that it can compensate for the loss of thermopower. To determine ZT at high pressure, it is also necessary to have the thermal conductivity which consists of two contributions, one from the electrical carriers κ_e, and the other from the thermal lattice vibrations (phonon) κ_{ph} that is the main portion for PbTe. Comparing with S and R, we found that κ_{ph} has a smaller decrease with pressure.[12] Thus the ZT value should increase with the increasing pressure.

In summary, in situ measurement of the electrical property of PbTe has been conducted at high pressure. The thermopower and resistance of PbTe decrease with increasing pressure, however the decreasing rate of resistance is higher than that of thermopower. Therefore the power factor of PbTe increases with pressure. This indicates that this method is an efficient tool for synthesizing good thermoelectric materials at HPHT.

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