In situ x-ray diffraction, electrical resistivity and thermal measurements using a Paris-Edinburgh cell at HPCAT 16BM-B beamline

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Abstract. We have established a new type of experimental set-up utilizing a Paris-Edinburgh (PE) type large volume press with a dedicated sample cell assembly for simultaneous x-ray diffraction, electrical resistance, and temperature gradient measurements at the High-Pressure Collaborative Access Team (HPCAT) at Advanced Photon Source (APS), Argonne National Laboratory 16BM-B beamline. We demonstrate the feasibility of performing in situ measurements and correlating the measured electrical-thermal-structural properties over a broad range of P-T conditions by observing the well-known solid-solid and solid-melt transitions of bismuth (Bi) up to 5 GPa and 600 °C. The goal of developing this new multi-probe measurement capability is to further improve detection of the onset of solid-solid and solid-melt transitions, relate structural and electrical properties of materials, determine changes in thermal conductivity at high P-T, and ultimately extend the technique for investigating other parameters, such as the Seebeck coefficient of thermoelectric materials.

1. Introduction

The Paris-Edinburgh (PE) type large volume press was developed originally for neutron experiments [1]. The sample assembly design has been modified to be adapted to X-ray experiments for various measurements such as examination of high pressure high temperature (HP-HT) phases of materials, viscosity measurements, HP-HT synthesis of materials, among other techniques [2-5]. For our experiment, a dedicated cell assembly is designed and developed to measure thermal and electrical properties of materials under HP-HT conditions while simultaneously probing the crystal structure of the sample with synchrotron radiation up to 5 GPa and 600 °C. A large variety of materials can be studied using this new technique.

The main goal of this development is to measure the transport and structural properties of thermoelectric materials and their changes with temperature and pressure. The technique will be applicable to mapping the transport properties of metals and alloys at HP-HT conditions. White beam radiography has been utilized to precisely determine the sample dimension in the in situ thermoelectric measurements for studying the high-pressure solid phases [3]. Electrical resistance and heat flow of
solid phases can be simultaneously measured with a four-probe approach using inserted thermocouple wires in the sample cell assembly of the PE cell. Substantial modifications of the existing sample cell assembly components were required in order to add in situ electrodes in and outside of the PE anvils. This new instrumental development opens new opportunities for in situ studies of structure and property correlations, especially the thermoelectric properties, for materials under high P-T conditions.

2. Experimental

A box diagram of the modified cell assembly is shown in figure 1. This diagram is not to scale, but shows the important features of the cell assembly. The sample is sandwiched between two flattened K-type thermocouples, where the alumel and chromel wires were purchased from Omega Engineering, one above the sample and one below the sample (shown in green above and below the sample in figure 1). The thermocouple wires are inserted though the boron-epoxy gasket from the side. Diamond discs are used to aid with heat flow from the graphite heater through the sample and out through the bottom of the cell. Underneath the bottom diamond disc, a metal, made of aluminum or copper, is inserted to ensure the tight contact with Mo foil (shown in purple at both ends of the cell assembly) connected to tungsten carbide anvils above and below the zirconia, ZrO$_2$, caps. The MgO surrounding the sample stack provides thermal insulation and containment for the cell assembly. The MgO disc and mica disc (shown in red) at the top of the cell assembly also provide insulation.

![Figure 1. Box diagram of the sample cell assembly in the PE cell.](image)

The experiments were performed at the beamline 16BM-B of HPCAT at APS, Argonne National Laboratory. The sample shape and the intactness of the inserted wires under pressure were monitored with white-beam radiography images using the beamline’s default white-X-ray camera setup. An example image taken using this camera set-up is shown in figure 2 (left). Having calibrated each pixel to 0.95 µm, the thickness of the sample is determined from the radiography imaging by plotting the brightness of each pixel across the sample [3]. This thickness can be used in future thermal conductivity calculations and is obtainable at any pressure reachable with the apparatus.

To measure electrical resistance of a compressed sample in this cell assembly, a Keithley nanovoltmeter and current source are connected to the thermocouples. The two thermocouple wires inserted at the top and bottom of the sample naturally configures a 4-probe resistance measurement [6]. The voltage was measured across the alumel wires and the current was passed through the chromel wires and into the sample.
Bismuth was chosen as the sample for our initial experiments since a variety of solid-solid phase transitions are accessible in the range of pressure and temperature available to the current PE assembly at HPCAT. The resistance of bismuth is expected to undergo an observable change as the pressure or temperature is increased or decreased through these phase boundaries [7,8]. A phase diagram of bismuth as reported by Chen et al is shown in figure 3 [9]. Varying pressure alone, the solid phases Bi – I, Bi – II, and Bi – III would be achievable. Varying pressure and temperature, the solid-solid phase transition of Bi – I -> Bi – II should be accessible as well. The solid-solid transition from Bi - III -> Bi - IV is also observed within range of the potential pressure and temperature of the apparatus.

Figure 3. Phase diagram of bismuth [9]. The arrows indicate the PT paths taken in these experiments.

3. Results and Discussion
At ambient temperature, the pressure was increased on the Bi sample using a hydraulic oil mechanism. The compression from 1.0 GPa to 4.0 GPa took 16 minutes to complete. While the pressure was increasing, the resistance was determined using the Keithley voltmeter. Figure 4 shows the results of these measurements. The scatter in the resistance represents the error on these measurements for the resistance value. The sudden decrease in resistance between 2.25 GPa and 2.5 GPa corresponds to crossing the Bi - I -> Bi - II phase boundary as seen in the phase diagram in figure 3. The rapid increase in resistance after reaching a minimum around 2.7 GPa corresponds to crossing the Bi - II -> Bi - III phase boundary. This trend seen in the resistance data presented here for Bi agrees well with the previously reported data in the literature [7, 8]. X-ray diffraction (XRD) data has been taken in the
Bi-I region as well as the Bi-III region and example XRD patterns are shown in figure 5. The significant change in the XRD pattern at 2.0 GPa as compared to 3.4 GPa gives further evidence of the phase transformation. The Bi-II region was not measured with x-ray in this experiment, due to the importance of obtaining continuous resistance data throughout the region.

**Figure 4.** Resistance as a function of pressure for bismuth as measured using the modified PE cell assembly set-up. The pressure of the sample was calibrated with the MgO pressure volume data obtained by in situ diffraction.

**Figure 5.** (Left) XRD pattern at 2.0 GPa (Right) XRD pattern at 3.4 GPa

Using a graphite disc as a heater, the temperature of the sample is increased while under compression. This allows access to other parts of the phase diagram. Figure 6 (left) shows a plot of the resistance as a function of temperature at 2.3 GPa. Again, the error on the resistance measurements is the scatter in the data as represented in the graph. The decrease in the resistance value after 120°C corresponds with crossing the Bi-I -> Bi-II phase boundary as seen in the phase diagram in figure 3. Since there is a significant temperature difference across the sample of 30°C, the entire sample would not have changed phase.

Alongside the resistance measurements with temperature, a measurement of the temperature gradient across the sample as a function of heater power was performed. The temperature gradient is determined by the temperature difference between the two thermocouples, one above and one below the sample. The heater power is set as an input to a PID controller and the voltage and current applied to the heater is determined by the PID controller to obtain the set point. The error associated with the temperature measurement is the error typical of K-type thermocouples, which is ± 2.2°C [10]. Due to
the controlled application of voltage and current to the heater, we are confident in the heater power
measurements. However, to determine the heat reaching the sample, extensive modelling is necessary.
A plot of the heater power as a function of this temperature gradient at 2.3 GPa is shown in figure 6
(right). The slope of this plot is related to the thermal conductivity of the sample; however, because an
accurate value for the amount of heat received by the sample is difficult to quantify due to heat loss,
the thermal conductivity was not determined during this set of experiments. Thermal flow modelling is
necessary to achieve this goal.

![Figure 6](image)

Figure 6. (Left) Resistance as a function of temperature at 2.3 GPa for bismuth, (Right) Heater power
as a function of temperature gradient and average temperature of bismuth sample

4. Conclusions
Simultaneous resistance and thermal gradient of bismuth under compression was measured
successfully in a PE cell in addition to in situ x-ray diffraction. The results demonstrate the
modifications to the existing PE cell assembly allow a new type of measurement of thermal and
electrical properties of materials. The resistance measurements provide an excellent determination of
solid-solid phase boundaries as a function of pressure and temperature. Agreement between the known
phase diagram and the results of the resistance measurements provide evidence the modified PE cell
assembly is capable of a variety of useful measurements. The ability to measure the temperature
gradient as a function of heater power allows measurement of the thermal properties of materials.
However, in order to extract the true thermal conductivity of materials, extensive modeling needs to be
conducted to determine heat loss throughout the cell assembly so an accurate value for the heat
entering the sample can be obtained.

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