High-pressure thermopower technique and its application

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Abstract. In this paper we present details of a technique of measurement of the thermoelectric power (Seebeck effect) at high pressure to 30 GPa. Two examples of its application are displayed as follows: lead (Pb) and bismuth telluride alloys (Bi2Te3 and InxBi2-xTe3). For lead a kink in the pressure dependence of the thermopower near 13 GPa has been established and addressed to the structural fcc \(\rightarrow\) hcp phase transition. The (In,Bi)2Te3 thermoelectrics exhibited a pressure-driven improvement of the thermoelectric parameters, such as thermoelectric power factor (efficiency) and the dimensionless figure of merit. The reasons of this enhancement are discussed.

1. Introduction

Transport properties carry the information about the parameters of charge carriers and electron band structure, and thereby they can clarify pressure-induced changes in conducting materials. Direct in-situ measurements of different transport properties under high pressure still remain challenging. The electrical resistivity is as yet the only distributed and common-use technique in high-pressure experiments. A series of pioneer studies on the electrical resistivity to 10-40 GPa (e.g., [1-3]) established phase transitions in a plenty of semiconductors and metals and so greatly promoted the high-pressure materials science. In this work we present a technique of the thermoelectric power measurements at high pressure up to 30 GPa and display some examples of its application.

2. Experimental details

For measurement of the thermoelectric power under pressure the automated high-pressure setups are utilized, like a one presented at Fig. 1 [4]. Several different anvil-type cells are employed for pressure generation, including those with concave anvils, with flat anvils, and with bevelled anvils. A scheme of a cell with ‘flat’ anvils is presented in Fig. 2. In thermopower measurements an upper anvil is heated (Fig. 2). A temperature difference (\(\Delta T\)) along a sample’s thickness is determined from a temperature difference between fixed points at the upper and the lower anvils (Fig. 2); the latter is directly measured by means of the thermocouples. The validity of this method was proved in calculations of a temperature distribution inside the anvils [5] for various thermal conductivity and thickness of a sample. Normally, the thermopower measurements are performed in three regimes as follows: (i) at fixed pressure under increasing and decreasing of a temperature difference.
Among these three ways, the accuracy of \( \Delta T \) determination is confirmed.

For measurement of a thermoelectric voltage (\( U \)) along a sample only one pair of electrical probes is required. For precise measurements a couple of thin Pt-Ag ribbons of \(~ 5 \mu m\) in thickness is employed as electrical outputs to a sample (Fig. 2). The lithographic stone container is a soft material that preserves the ribbons from a breakup. Well-conducting synthetic diamond anvils also may be used as electrical outputs of a sample; in this case a small parasitic contribution of a cell to a value of the thermopower is beforehand determined by measurements of calibrated materials with close to zero thermopower, e.g. Pb, Au, In, etc. A conventional four-probe resistivity method is also possible in these cells.
Applied force is in-situ measured by a digital dynamometer with resistive-strain sensors [5]. The pressure values in a cell are determined with an uncertainty less than ~ 10% from a calibration “stress-pressure” curve based on the known and well-detectable pressure-driven transitions in Bi, PbS, PbSe, CdSe, ZnS, ZnSe, GaP, etc. [5]. For suppression of the axial components of pressure, a container’s thickness in its central part should be much smaller than a working diameter of the anvils (earlier a threshold ratio of ~ 0.055–0.057 separating (quasi-)hydrostatic and axial contractions has been established [6]). The sharpness of some pressure-driven phase transitions, for instance, those in zinc chalcogenides [7] evidences the absence of significant pressure gradients around a sample.

3. Results and discussion

Below we show two recent examples of the thermopower technique application for lead and bismuth telluride. The former is one of materials that are employed for calibration of thermopower techniques. The latter is a room-temperature thermoelectrics; behaviour of its thermoelectric properties under pressure is of a strong technological interest.

3.1. Lead (Pb). The thermopower of pure poly-crystalline lead (99.9999 %) was measured under pressure up to 19 GPa (Fig. 3). The low-pressure values of the thermopower agreed well with those known from the literature, $S \sim -1.1 \mu V/K$ [8] and $S \sim -1.3 \mu V/K$ [9]. Above ~ 1-1.5 GPa an inversion of the thermopower’s sign was registered. A kink in the dependence near ~ 13 GPa (Fig. 5) may be related to a sluggish fcc $\rightarrow$ hcp phase transition [10,11]. The inset in Fig. 3 presents some of data obtained at fixed pressures of 0 and 19 GPa, while $\Delta T$ is decreasing or decreasing with time. Near ambient pressure the methods gave identical results. At maximal pressure of ~ 19 GPa the thermopower slightly decreased with time, likely owing to a passing of the above-mentioned transition. For this reason a value determined from a slope of a thermoelectric voltage (inset in Fig. 3) is a bit lower than a corresponding value in Fig. 3.

3.2. Bismuth telluride (p-type $In_xBi_{2-x}Te_3$ ($x = 0, 0.04$)) The thermopower of $p$-Bi$_2$Te$_3$ and $p$-$In_{0.04}Bi_{1.96}$Te$_3$ were measured up to respectively ~ 9 and ~ 5.5 GPa (Fig. 4). Near 6-7 GPa a rhombohedral structure (space group $R\bar{3}m$) of Bi$_2$Te$_3$ transforms to another one with a metallic
conductivity (Fig. 4) [12,13]. The pressure dependence of the thermopower showed three maxima, near ~ 1, ~ 2.5 and ~ 4 GPa (Fig. 4). At low temperatures the resembling fluctuations at pressure dependence of the thermopower of Bi$_2$Te$_3$ were registered and addressed to electronic topological transitions [14]. The maxima at the $S(P)$ curves (Fig. 4) might appear owing to a pressure-induced modification of an electron band structure that is characterized by two closely-laying hole bands as well as two electron bands [15]. A structural distortion of the layered rhombohedral lattice [12,16-19] also could be responsible for that. A useful outcome from this finding consists in a possibility of significant enhancement of the thermoelectric performance of Bi$_2$Te$_3$-based elements by compression; likewise, it was found in PbTe [20]. In order to estimate the power factor ($S^2/\rho$) the electrical resistivity was supplementary measured up to the same pressure values (Fig. 4). A falling of the resistivity by approximately one order to 8 GPa agrees with previous reports (e.g. [19,21,22]). By the way the resistivity like the thermopower shows some anomaly near 2-5 GPa too (Fig. 4). The maximal power factor which is achieved in undoped Bi$_2$Te$_3$ near 4 GPa is equal to ~ 6.6 $\times$ 10$^{-3}$ W/(K$^2$×m). This exceeds those in the-state-of-the-art bulk Bi$_2$Te$_3$ thermoelectrics (e.g. [23]). Notice, that other basic thermoelectrics, namely, PbTe exhibited even more significant enhancement of the thermoelectric parameters under pressure [20].

**Figure 4.** The pressure dependencies of the thermoelectric power ($S$) and the electrical resistivity ($\rho$) of p-type single crystals of Bi$_2$Te$_3$ (1) and In$_{0.04}$Bi$_{1.96}$Te$_3$ (2) at 293 K; the electrical resistivity for In$_{0.04}$Bi$_{1.96}$Te$_3$ is omitted. The inset shows a calculated pressure dependencies of the thermoelectric power factor ($S^2/\rho$). It is seen that the power factor drastically grows with pressure and show two or three maxima.

4. **Conclusion**

Two examples of application of our high-pressure thermopower technique evidence its high efficiency for both in-situ measurement of the thermopower values under pressure, and search for pressure-driven phase transitions in conducting materials.

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