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HIGH-PRESSURE INVESTIGATIONS OF MATERIALS SUFFERING ABRUPT JUMPS OF THE SEEBECK EFFECT

Semiconductor compounds based on HgTe, Si, Bi_2Te_3 and PbTe, etc. have been found to suffer abrupt jumps of the Seebeck effect with (or without) the inversion of its sign on exposure to high pressure up to 20 GPa. Possible reasons for the above anomalous behavior of the Seebeck effect have been considered based on the analysis of the electron band structure features, as well as the variation of the defect-impurity system for different kinds of materials.
Key words: Seebeck effect, high pressure, semiconductors

Introduction

High pressure generally produces a strong impact on materials, in particular, it may cause abrupt changes of thermoelectric power (the Seebeck effect, *S*) [1]. These peculiarities are suitable for application in various kinds of electronic devices. The purpose of the present work is searching for materials possessing the above drastic variations of the Seebeck effect, and revealing general reasons for such behavior.

Experimental details

The measurements of the Seebeck effect were carried out in high-pressure chamber of toroidal type with semispherical concave anvils made of tungsten-carbide hard alloy with a diameter of anvil top ~ 1 mm [2, 3]. Typical sample sizes were ~ 200 × 200 × 250 μm^3. The chamber was loaded in an automated high-pressure setup [4]. The pressure values were determined to an accuracy of ~ 10 % from a calibration "stress-pressure" curve based on the known and well-detectable pressure-induced transitions in *Bi*, *PbS*, *PbSe*, *CdSe*, and other compounds [2]. The anvils were characterized by high electrical conductivity, and, therefore, were used as electrical outputs to a sample. In the thermopower measurements an upper anvil was heated [4]. The temperature difference along sample thickness (ΔT) was measured by thermocouples. Possible small contribution to the thermopower values from the anvils themselves was checked by measuring *S* of pure lead having the value of *S* close to zero ($S \approx -1.27$ μV/K) [2-4].

Results and Discussion

The abrupt jumps of *S* under pressure application were first observed in mercury chalcogenides *HgX* (*X*-*Te*, *Se*) in [1] during the pressure-induced phase transition from zinc blende to cinnabar structure near ~ 0.8 – 1.6 GPa corresponding to semimetal – wide-gap semiconductor transformation of electron band structure [5-7]. In the present work, some ternary *HgX*-based compounds as well as

other certain compounds have been examined in search of the above phenomena.

In *HgTe*-based compounds the sign inversion of *S* has been also found both in the initial cubic lattice at low *P* (~ 0.5 GPa for *HgTe*), and in the semiconductor phase near ~ 4 – 6 GPa (Fig. 1) [1]. The inversion of *S* in the semimetal phase of *HgTe* is probably due to electronic transition to gap-less state [8], while the inversion of *S* in semiconductor phase with cinnabar structure corresponds to the variation of the partial contributions of electrons σ_n and holes σ_p into total conductivity $\sigma = \sigma_n + \sigma_p$ from $\sigma_n / \sigma_p > 1$ to $\sigma_n / \sigma_p < 1$. The behavior of $S(P)$ can be described using Eq. 1 [9] for an intrinsic semiconductor:

$$S = -\frac{k}{|e|}\left[\frac{b-1}{b+1}\cdot\frac{E_g}{2kT} + \left(r_n + \frac{5}{2}\right)\frac{b}{b+1} - \left(r_p + \frac{5}{2}\right)\frac{1}{b+1} - \frac{3}{4}\ln\frac{m_p^*}{m_n^*}\right], \qquad (1)$$

where k is the Boltzmann constant, e is the electron charge, $b = \sigma_n / \sigma_p$ is the ratio of partial conductivities of electrons and holes, E_g is energy gap, T is the temperature, r_n (r_p) and m_n^* (m_p^*) are the scattering parameter and density-of-state effective mass of electrons (holes), respectively.

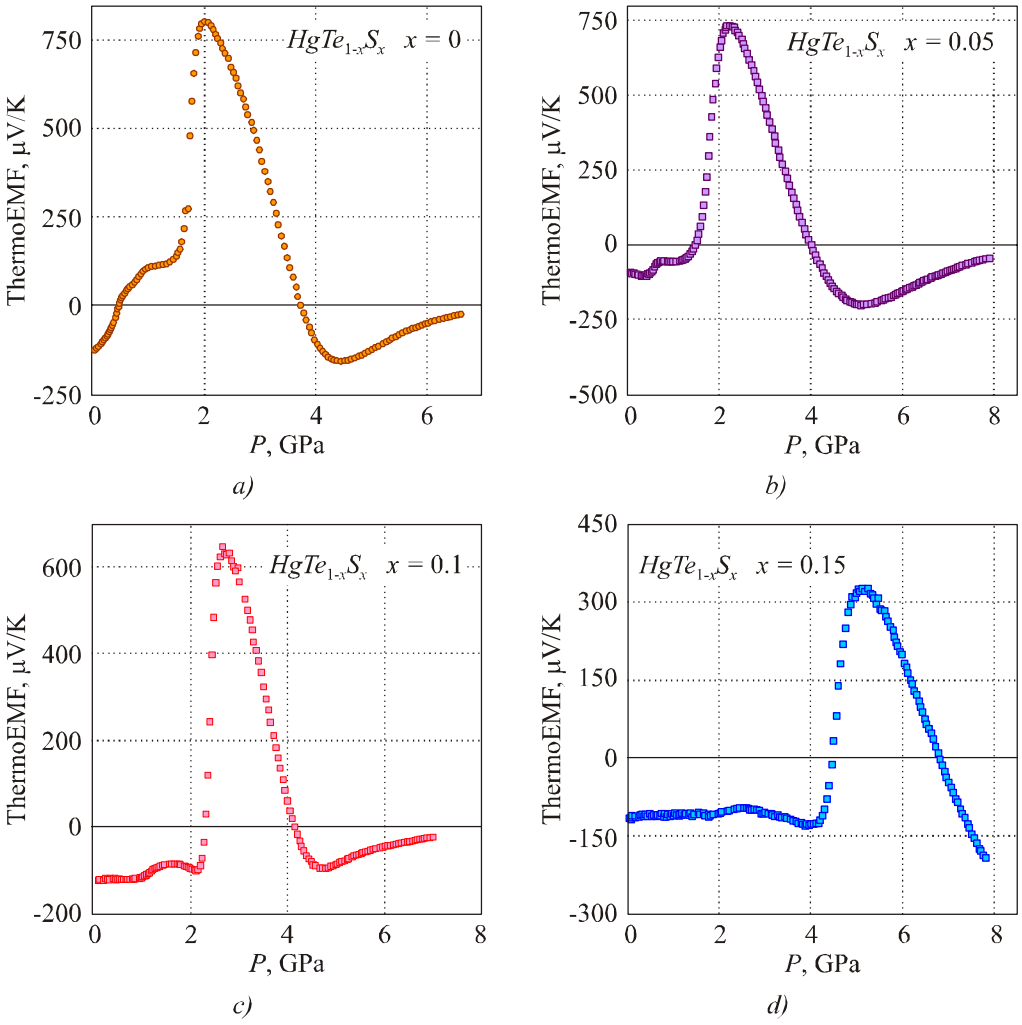

Fig. 1. Pressure dependences of thermoelectric power for $HgTe_{1-x}S_x$ crystals.

The opening of semiconductor gap E_g during semimetal-semiconductor phase transformation tends to an abrupt jump of *S* value, and change in the partial conductivity ratio σ_n / σ_p due to variation of parameters of the electron and hole bands under pressure, namely effective masses and mobilities

of electrons and holes, is the reason for S sign inversion. Both peculiarities are shifted toward higher pressures with increase in sulphur content (x) (Fig. 1). The high-pressure cinnabar phases of *HgTeS* should be good thermoelectrics, similar to *HgTe* [10, 11]. For *HgSe*-based compounds only the first peculiarity of S (abrupt jump) is observed (Fig. 2). Similar behavior of $S(P)$ was also observed in many semiconductors at high pressures up to 30 GPa (*PbX*, *ZnTe*, *GaAs* etc. [10]).

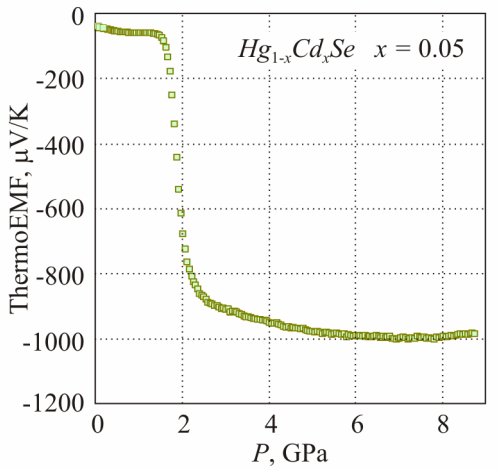

Fig. 2. Pressure dependence of thermoelectric power for $Hg_{1-x}Cd_xSe$.

In $Si_{1-x}Ge_x$ crystals ($x < 0.05$) the abrupt jumps of S with the sign inversion at moderate pressures [12] far from structural phase transitions can be also explained by Eq. 1 assuming the variation of the partial conductivity ratio due to changes in the "impurity-defect" system which tends to effective "doping" of materials. "Thermal donors" in *Si* are related to the interstitial oxygen atoms and structural defects and are known to be pressure dependent [13]. The variation of σ_p and σ_n in this case can be described by Eq. 2 and 3. for a doped semiconductor with two types of charge carriers [14]:

$$n = \frac{n_0}{2} + \left[\left(\frac{n_0}{2} \right)^2 + (4 A_c A_v)^2 \exp\left(-\frac{E_g}{kT} \right) \right]^{1/2}, \tag{2}$$

$$p = -\frac{n_0}{2} + \left[\left(\frac{n_0}{2} \right)^2 + (4 A_c A_v)^2 \exp\left(-\frac{E_g}{kT} \right) \right]^{1/2}. \tag{3}$$

Here, n_0 is the difference between the concentrations of donor and acceptor impurities; k is the Boltzmann constant, E_g is the semiconductor band gap; n and p are the concentrations of electrons and holes; A_c and A_v – are the densities of states in the electron and hole bands. The above change in the "impurity-defect" system leads to the sign inversion of n_0 and thus to the cardinal variation of σ_n / σ_p ratio from $\sigma_n / \sigma_p > 1$ to $\sigma_n / \sigma_p < 1$ (Fig. 3).

For Bi_2Te_3 – based compounds the topology of the Fermi surface occurs under doping because of the complex multi-band electron structure [15]. This topological transition can arise under pressure application [15] tending to the corresponding shift of the electron and hole bands and of the Fermi level position. Doping with In is known to enhance the anomalous behavior of S during the above transformation of electron structure under pressure [15], which becomes apparent in the abrupt jumps of $S(P)$ near ~ 1 GPa (Fig.4) [15].

At pressures $P \sim 3$ GPa another topological transition at Bi_2Te_3 occurs [15], causing the emergence of a peak on $S(P)$ curves for binary [15], as well as at ternary compounds based on Bi_2Te_3 (Fig. 4).

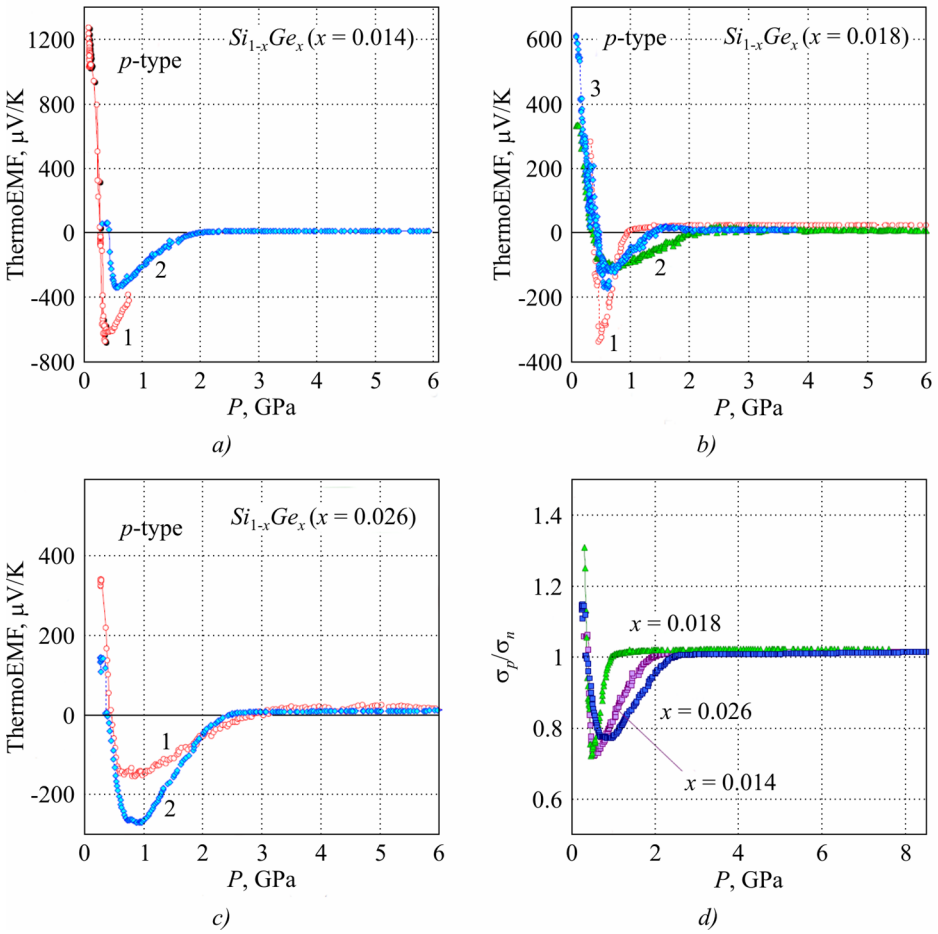

Fig. 3. Pressure dependence of thermoelectric power (a – c) and of hole-electron conductivity ratio (σ_p/σ_n) (d) for $Si_{1-x}Ge_x$ crystals. The figures mark the numbers of microsamples cut from the same $Si_{1-x}Ge_x$ crystal [12].

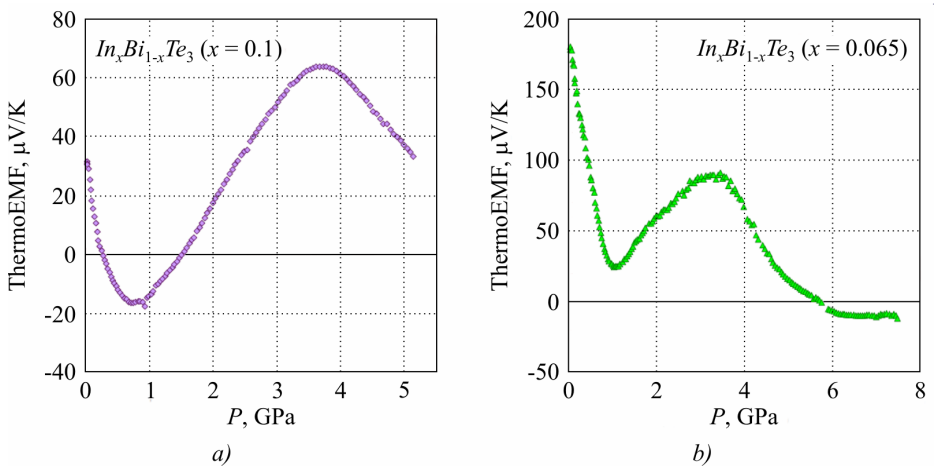

Fig. 4. Pressure dependences of thermoelectric power for $In_xBi_{1-x}Te_3$.

Conclusions

The abrupt jumps and the sign inversions of the Seebeck coefficient have been observed in some compounds under pressure. The main reasons for the above phenomena consist in the opening of semiconductor gap under phase transition and variation of either parameters of electron and hole bands, or the state of "defect-impurity" system under pressure tending to "doping" and compensation of electron (hole) contributions in conductivity. The change in the Fermi surface topology can also

produce the above effects. Certain phases and states arising under high pressure seem to be acceptable for thermoelectric applications [10, 11, 15, 16]. The experimental data of the present paper confirms the realization of the above mechanisms of $S(P)$ variation for different kinds of compounds.

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