LETTER TO THE EDITOR

Density-of-states effective masses in the system Ge$_{1-x}$Ag$_{x/2}$Bi$_{x/2}$Te (0 ≤ x ≤ 0.333)

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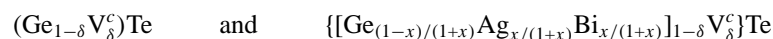Faculty of Physics, University of Sofia, Boulevard James Bourchier 5, BG-1164 Sofia, Republic of Bulgaria

Abstract. The density-of-states effective masses versus composition are calculated. The comparison between density-of-states effective mass and reverse mobility show that the variation of the mobility should be governed by the change in the effective mass.

Among the IV–VI compound family, GeTe is a unique example of a non-stoichiometric, displacive ferroelectric or antiferroelectric narrow-gap semiconductor with three different crystal modifications: the high-temperature phase (β-GeTe) possesses a face-centred-cubic lattice (NaCl-type), but the low-temperature forms are rhombohedral (α-GeTe) at a Te content of less than 50.4% or orthorhombic (γ-GeTe) at a Te content of more than 50.4%. GeTe is always p-type as the homogeneity region is shifted to the Te-rich side of its phase diagram [1]. It is well known that GeTe and solid solutions (SSs) based on it are the most essential p-type thermoelectric materials working at high temperatures (∼700 K) [2–4]. The best thermoelectrics possess a large density-of-states effective mass [4]. The concentration and temperature dependences of the effective mass of the density-of-states (m_d) and conductivity (m_c) of GeTe and some SSs based on it are investigated [5–7]. The concentration dependence of m_d obeys the Kane's model [6], but the concentration dependence of m_c deviates from the theoretical curve calculated using this model [7].

The large difference between the values of m_d and m_c (the ratio m_d/m_c is about 10) is connected with the complicated form of GeTe Fermi surfaces [5, 8].

According to the phase diagram in the system GeTe–AgBiTe$_2$, above 773 K a continuous series of SSs exists. At lower temperatures the solubility is limited by the decomposition of AgBiTe$_2$ and SSs based on it. The solubility is not greater than about 30% AgBiTe$_2$ at 300 K [9]. The GeTe-rich SSs GeTe–AgBiTe$_2$ keep the crystal structure of Ge-rich GeTe, but the phase transition temperature decreases upon increase of the AgBiTe$_2$ content, and from 700 K for Ge-rich GeTe reaches about 300 K for a composition containing ∼23% AgBiTe$_2$ [10]. For the synthesis of the alloys, the stoichiometric GeTe is used (50% Ge and 50% Te). Stoichiometric GeTe contains Ge as a second phase, and the region of homogeneity of this compound is shifted to the Te-rich side of the Ge–Te phase diagram (the region of homogenity of the rhombohedral phase at 573 K is from 50.40% to about 50.44% Te) [1]. The real composition of GeTe-rich and GeTe–AgBiTe$_2$ SSs can be written as

$$(\text{Ge}_{1-\delta}\text{V}_\delta^c)\text{Te} \qquad \text{and} \qquad \{[\text{Ge}_{(1-x)/(1+x)}\text{Ag}_{x/(1+x)}\text{Bi}_{x/(1+x)}]_{1-\delta}\text{V}_\delta^c\}\text{Te}$$

where δ is the number of cation vacancies V_{δ}^{c}. The latter are most probably doubly ionized [1], i.e. are negatively charged. The respective acceptor levels are situated in the valence band. The mechanism of 'self-alloying' ($V_{Ge}^{0} \rightarrow V_{Ge}^{2-} + 2p$) accounts for p-type conductivity of the GeTe and respectively GeTe-rich SSs. The δ-value was estimated by comparison of the densities calculated on the basis of x-ray diffraction results and those measured by picnometry. For GeTe $\delta = 0.029$. At concentrations of AgBiTe$_2$ below that of the vacancy concentration in GeTe, the impurity atoms fill the vacancies and the lattice perfection is improved. At higher AgBiTe$_2$ concentrations the number of vacancies in GeTe-rich SSs increases with x being in the range 0.033–0.042 [11]. As these SSs possess very high values of the Seebeck coefficient (over 200 μV K^{-1} at 500–700 K) [12] it may be expected that they will have good thermoelectric properties. It is therefore interesting to know its density-of-states effective masses, which have not been studied yet.

The aim of the present letter is to find the density-of-states effective mass dependence on alloy composition in the $0 \leqslant x \leqslant 0.333$ range. As the investigated SSs based on GeTe are narrow-gap semiconductors, the band-edge, density-of-states effective masses were calculated from the experimental data of the thermoelectric power S and the carrier concentration p at 300 K using the Kane model for IV–VI compounds [13]

$$p = \frac{(2m_{d}^{*}k_{0}T)^{3/2}}{2\pi^{2}\hbar^{3}} {}^{0}L_{0}^{3/2} \qquad (1)$$

$$S = \frac{k_{0}}{e}\left(\frac{{}^{1}L_{2}^{1}}{{}^{0}L_{2}^{1}} - F^{*}\right) \qquad (2)$$

where ${}^{n}L_{K}^{m}(F^{*}; \beta)$ are the modified two parameter Fermi integrals [14], $F^{*} = F/k_{0}T$ and $\beta = K_{0}T/E_{g}$ are the reduced Fermi energy and non-parabolicity factor, respectively, and E_{g} is the direct energy gap. The Fermi energy is calculated from (2) and the band-edge, density-
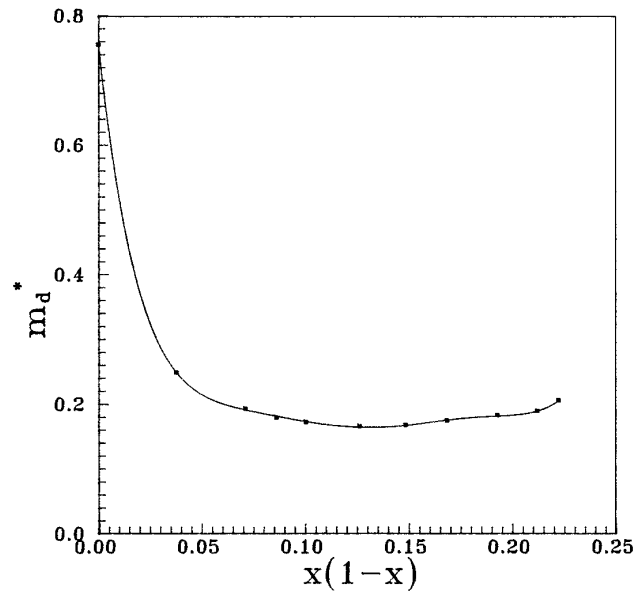

Figure 1. The density-of-states effective masses versus composition in the range $0 \leqslant x(1 - x) \leqslant 0.222$ at 300 K.

of-states effective mass from (1). As only the single valence valley in the α-phase is occupied by carriers, the band-edge density-of-states effective mass refers only to that valley.
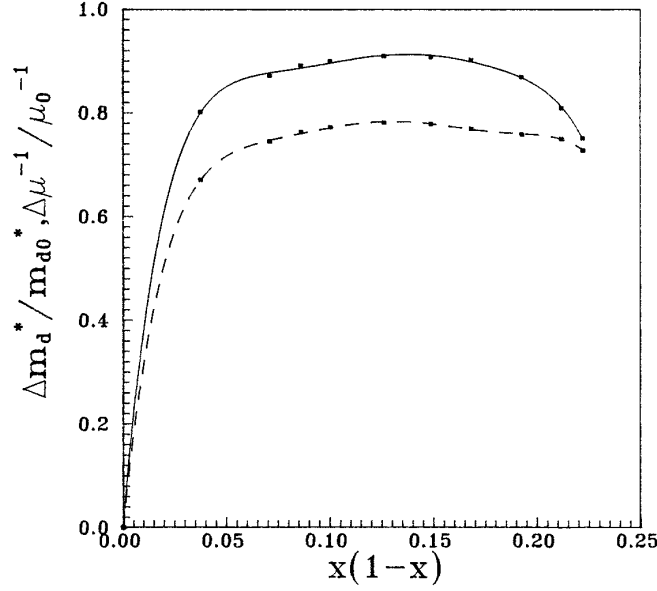

Figure 2. Relative change of the density-of-states effective mass $\Delta m_d^*/m_{d0}^*$ (dashed line) and reverse mobility $\Delta\mu^{-1}/\mu_o^{-1}$ (solid line) versus $x(1-x)$.

The substitution of Ge atoms in cation sublattice by Ag and Bi atoms leads to a rapid decrease in m_d^* at $0 \leqslant x \leqslant 0.076$. At $0.076 \leqslant x \leqslant 0.148$, m_d^* decreases slowly but at $0.148 \leqslant x \leqslant 0.333$ it increases slowly with increasing x (figure 1). This may be connected with the composition changes at the energy gap in rhombohedral SSs at 300 K [12]. According to theory, upon the formation of SSs by substitution a decrease of the effective mass is expected [15]. An estimation of such a decrease can be performed utilizing the formula [16]

$$m_{dx}^* = m_{d0}^* \left(1 - \frac{2x(1-x)\delta^2 m_{d0}^{*2}}{(2\pi N_0)^{4/3}\hbar^4} \right) \qquad (3)$$

where N_0 is the number of atoms per unit volume, δ is the difference between the energy levels which are created from impurity atoms in the end compound and m_{dx}^* and $m_{d0}^*(m_{GeTe}^*)$ are the band-edge, density-of-states effective masses of the SSs and the end compound (GeTe), respectively. Figure 2 represents the plot of the ratio $\Delta m_d^*/m_{d0}^* = (m_{d0}^* - m_{dx}^*)/m_{d0}^*$ versus $x(1-x)$ (dashed curve). From the linear part of the dependence, $0.126 \leqslant x(1-x) \leqslant 0.212$, the value $\delta = 1.2$ eV was estimated. With the assumption that the prevailing scattering mechanisms are acoustic phonon, ion core and lattice potential fluctuations and that the Matthiessen's rule holds, one obtains for the reverse mobility [17]

$$\mu^{-1} = \frac{m_c \rho(E_F)\pi}{eN\hbar} \left(\frac{\Xi^2 k_0 T}{C} + pU_i^2 + \frac{x(1-x)\delta^2}{N_0} \right) |M|^{-2} \qquad (4)$$

where $\rho(E_F)$ is the density of states at the Fermi energy, Ξ the acoustic phonon deformation potential, C a combination of the elastic module, N the number of equivalent extremes, U_i the potential well strength for the cation vacancies in the SSs and p the hole concentration. The estimation of the second and third terms in the brackets of formula (4) has given

$$2 \times 10^{-29} > pU_i^2 > 1.7 \times 10^{-31} \ (eV)^2 \, m^3$$

$$8 \times 10^{-30} < \frac{x(1-x)\delta^2}{N_0} < 8.4 \times 10^{-30} \text{ (eV)}^2 \text{ m}^3$$

as $x(1-x)$ varies from 0.071 to 0.212.

The value of $U_i = 2 \times 10^{-28}$ eV m^3 was taken to be the same as was evaluated for Pb and Sn vacancies in $Pb_{1-x}Sn_xTe$ [17] and $\delta = 1.2$ eV. If the first term does not change drastically with x (all SSs are in the rhombohedral phase), the variation of the mobility should be governed by the change in the effective mass. This can be seen from the plot of $\Delta\mu^{-1}/\mu_0^{-1} = (\mu_0^{-1} - \mu_x^{-1})/\mu_0^{-1}$ versus $x(1-x)$ (the full curve in figure 2), where $\mu_0 = \mu_{GeTe}$. We can see that both curves are on the same scale. The more rapid change of $\Delta\mu^{-1}/\mu_0^{-1}$ at $0 \leqslant x \leqslant 0.076$ compared with $\Delta m_d^*/m_{d0}^*$ can be associated with the more abrupt change of the hole concentration in that region.

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