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Thermal Conductivity in $Bi_{1-x}Sb_x$ Solid Solutions

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$Bi_{1-x}Sb_x$ solid solutions have attracted much attention as promising low-temperature thermoelectric materials. Previously, we observed distinct extrema in the isotherms of the transport and mechanical properties of polycrystalline $Bi_{1-x}Sb_x$ and attributed their presence to the transition from diluted to concentrated solid solutions and to the reconstruction of the energy band structure under increasing Sb concentration. The goal of the present work is a detailed study of the concentration dependences of the thermal conductivity λ for $Bi_{1-x}Sb_x$ polycrystalline solid solutions (x = 0 to 0.09) in the temperature range of 170 K to 300 K. It is established that the $\lambda(x)$ dependences exhibit a nonmonotonic behavior: in certain concentration ranges an anomalous increase in λ with increasing x is observed. It is shown that the concentration dependences of the thermoelectric figure of merit calculated on the basis of the measured λ values are also nonmonotonic. The obtained data represent additional evidence in favor of our assumptions stated earlier about a significant effect of electronic phase transitions observed in $Bi_{1-x}Sb_x$ solid solutions on the concentration dependences of their thermoelectric properties. These results should be taken into account when developing new $Bi_{1-x}Sb_x$-based materials.

Key words: Bi-Sb solid solutions, concentration, thermal conductivity, phase transitions

INTRODUCTION

Solid solutions formed from the semimetals Bi and Sb have attracted much attention from researchers, on the one hand, as promising low-temperature thermoelectric (TE) and magnetoelectric materials for refrigerating devices at temperatures below ~200 K, and, on the other hand, as interesting materials for solid-state physics because of the high sensitivity of their energy band structure to changes in external parameters (composition, temperature, pressure, magnetic field, etc.).[1,2] At present it is known[3–5] that, with increasing Sb concentration, the energy difference between the L_a and L_S bands located at L points of the Brillouin zone decreases, and at a certain critical concentration ($x \approx 0.023$ to 0.04 according to the data of different authors) a gapless state is realized and inversion of bands occurs, and then the energy difference between the L_a and L_S bands increases again. On the other hand, with increasing Sb concentration, the T band corresponding to the top of the valence band sinks in energy, and at $x \approx 0.06$ to 0.07 the L and T bands cross, which results in the transition from a semimetallic to a semiconductor state. It is established that the highest values of the TE figure of merit Z ($Z = S^2 \cdot \sigma/\lambda$, where S is the Seebeck coefficient, σ is the electrical conductivity, and λ is the thermal conductivity) are observed at 80 K to 100 K in the semiconductor region of $Bi_{1-x}Sb_x$ solid solutions ($x \approx 0.07$ to 0.22) for single crystals oriented along the trigonal axis.[1–3] That is why the concentration range corresponding to a semimetallic state (x = 0 to 0.06) has received far less attention and there are practically no detailed studies on the concentration dependences of TE properties in this composition range. However, for manufacturing, for example, thermomagnetic Ettingshausen refrigerators it is desirable to use alloys

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