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Influence of Vanadium on the Defect Structure and Thermoelectric Properties of GeTe

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The development of new thermoelectric materials based on GeTe is associated with reducing the hole concentration and thermal conductivity. The objects of the present study are GeTe-based solid solutions in the Ge-V-Te ternary system. The goal of the work is to study the character of the change in the structure, mechanical and thermoelectric properties of GeTe under introduction of VTe. The electrical conductivity σ, Seebeck coefficient S, and Hall coefficient R_H were measured in the range of 300 K to 850 K on cast samples and samples prepared by hot pressing; the thermal conductivity λ was measured at room temperature. It was found that the dependences of the unit cell parameters, microhardness, σ, R_H, λ, and S on the VTe content exhibit nonmonotonic behavior. The experimental results were interpreted taking into consideration the complex mechanisms of defect formation in the GeTe crystal lattice under introduction of VTe, the existence of nonstoichiometric vacancies, and percolation effects. It was established that introduction of VTe into GeTe leads to a significant decrease in λ and hole concentration p. The maximum room-temperature values of thermoelectric power factor P and thermoelectric figure of merit Z corresponded to ~2 mol.% VTe. With increasing temperature up to ~550 K, P increases, and the maximum value of P is shifted to ~3 mol.% VTe. The values of P and Z obtained for the cast and pressed samples were practically the same.

Key words: GeTe, solid solutions, VTe, defect formation, thermoelectric properties

INTRODUCTION

The most effective method of controlling the thermoelectric (TE) properties of semiconductor compounds is by introducing new components into a crystal by doping, formation of solid solutions, heterophase structures, etc. All semiconductor compounds in a state of thermodynamic equilibrium under fixed external conditions (temperature, pressure, etc.) have a certain homogeneity region, i.e., can exist in a certain interval of compositions, and are characterized by a certain degree of deviation from stoichiometry. When doping nonstoichiometric phases, it is necessary to take into account the possibility of interactions among intrinsic (native) and impurity defects. An intermediate character of chemical bonds in semiconductors, the appearance of free charge carriers induced by doping, and deviation from stoichiometry determine a great variety of possible mechanisms of such interactions. This is why the development of physicochemical principles of TE materials science must include establishing the role of intrinsic defects in the formation of TE properties of crystals and revealing effects connected with the interaction of intrinsic and impurity defects.

Materials based on the GeTe semiconductor compound are known to be promising for TE applications and have been widely used for the purposes of energy generation.[1–4] GeTe possesses a one-sided, relative to the stoichiometric composition, homogeneity region and is characterized by a high degree of

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