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Carrier distribution in multi-band materials and its effect on thermoelectric properties

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Abstract

Band convergence is one of the most interesting topics in recent studies of thermoelectrics. However, its effect on thermoelectric properties is only simply stated as improving band degeneracy. In this paper, the enhanced thermoelectric performance due to band convergence is clarified from the viewpoint of distribution of carriers in the electronic bands. The n-type $Mg_2Sn_{0.75}Ge_{0.25}$ is used as a case study, and the effect of band offset E on its thermoelectric properties is investigated based on the three-band model, *i.e.*, one light conduction band, one heavy conduction band, and one valence band. The results show that E has a decisive effect on controlling the distribution of carriers in the two conduction bands, thus affecting the thermoelectric properties. Since the optimal carrier concentration n_{opt} is related to the density of state effective mass m^* at a given temperature, an appropriate distribution of carriers should be a higher carrier concentration in the heavy band (with larger m^*) and a lower carrier concentration in the light band (with smaller m^*). In order to achieve a proper distribution of carriers, E should be as small as possible at any temperature, which explains the reason why band convergence could lead to the enhanced thermoelectric performance.

Keywords: Thermoelectric; Band convergence; Three-band model; Distribution of carriers; Optimal carrier concentration

1. Introduction

By utilizing the Seebeck effect and its inverse phenomena, *i.e.*, the Peltier effect, thermoelectric materials are capable of converting thermal energy into electricity and vice versa [1–6]. Therefore, it can be used to recover the waste heat as well as cooling the electronics. The performance of thermoelectric materials is governed by materials' dimensionless figure of merit (ZT) that is defined as $ZT = S^2\rho^{-1}\kappa^{-1}T$, where S, ρ, κ, and T are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively. For the thermal conductivity, it contains three components, *i.e.*, lattice thermal conductivity, electronic thermal conductivity, and bipolar thermal conductivity.

For materials with multiple electronic bands, the band offset E (*i.e.*, the energy difference between the bands) between the top of valence bands (p-type semiconductors) or the bottom of conduction bands (n-type semiconductors) can be affected by temperature, pressure, and composition. Therefore, E could be within few $\pm k_BT$ (k_B is the Boltzmann constant) under certain conditions, which means the electronic bands are effectively converged, so-called band convergence. Recently, band convergence becomes a highly interesting topic in the research of thermoelectrics. It has already been demonstrated to be an effective route to improve the power factor PF ($S^2\rho^{-1}$) and hence the ZT in several material systems, *e.g.*, $Mg_2Sn_{1-x}Si_x$ [7,8], $Mg_2Sn_{1-x}Ge_x$ [9,10], $PbTe_{1-x}Se_x$ [11], $Pb_{1-x}Sr_xSe$ [12], $Pb_{1-x}Mg_xTe$ [13], $Sn_{1-x}Mn_xTe$ [14–17], and skutterudite [18].

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However, in most cases, the beneficial contribution of band convergence is only simply ascribed to the improved band degeneracy [11]. For band convergence, the band offset E is a critical parameter. Nonetheless, its effect on thermoelectric properties is seldom investigated in detail. Moreover, several important questions are rarely discussed for multi-band thermoelectric materials, *i.e.*, how are the carriers distributed in each of electronic bands, and how will this distribution affect the thermoelectric properties? Solving these questions can provide us with a better understanding on band convergence, and may enable us to achieve an even better thermoelectric performance by proper band engineering.

Band model is an effective tool to understand the thermoelectric properties of materials. The multi-band model for describing the thermoelectric properties of materials was firstly reported by Simon [19,20]. In his papers, he mainly focused on utilizing the two-band model, *i.e.*, one conduction band and one valence band, to understand the effect of material parameter β, band gap E_g, and scattering parameter r on the figure of merit ZT. Slack et al. [21] predicted the maximum possible energy conversion efficiency of n-type SiGe by utilizing three-band model, *i.e.*, one light conduction band, one heavy conduction band, and one valence band. Liu et al. [22] investigated the effect of additional conduction band on thermoelectric properties of skutterudite by three-band model. Pei et al. [11] demonstrated the effect of band convergence on thermoelectric properties of p-type $PbTe_{1-x}Se_x$ by three-band model.

To the best of our knowledge, the effect of E on thermoelectric properties has never been investigated by band model. Therefore, this work is trying to achieve a better understanding of band convergence *via* investigating the effect of E on thermoelectric properties in the framework of three-band model. Since $Mg_2Sn_{0.75}Ge_{0.25}$ is an n-type material, which demonstrates a good thermoelectric performance due to the convergence of two conduction bands, therefore it is chosen as the platform for this study. Moreover, the three-band model is chosen because it gives a reasonable description of the thermoelectric properties of $Mg_2Sn_{0.75}Ge_{0.25}$. The calculations shed new light on the influence of band convergence on thermoelectric properties, which demonstrates that the distribution of carriers in the electronic bands can be effectively controlled by tuning E. An appropriate distribution of carriers can be achieved when E approaches zero, which explains the reason why band convergence can lead to enhanced thermoelectric properties.

2. Results and discussion

2.1. Three-band model

Fig. 1 shows the schematic view of three-band model for $Mg_2Sn_{0.75}Ge_{0.25}$. The C_L, C_H, and V are the light conduction band, heavy conduction band, and valence band, respectively. The details of three-band model are presented in the supporting information. The thermoelectric properties of $Mg_2Sn_{0.75}Ge_{0.25}$ are taken from a previously published paper [9]. The materials' parameter for three-band calculation is shown in Table S1 (supporting information).

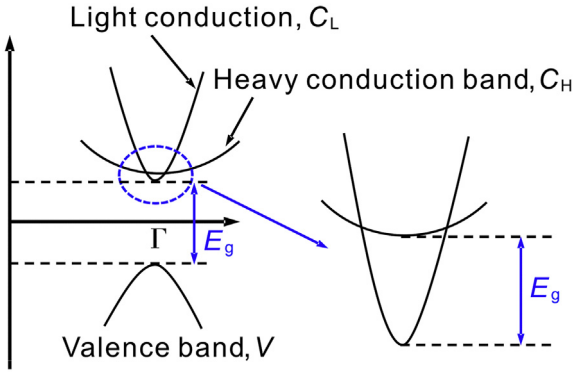

Fig. 1. Schematic view of three-band model for $Mg_2Sn_{0.75}Ge_{0.25}$.

2.2. Calculated thermoelectric properties of $Mg_2Sn_{0.75}Ge_{0.25}$

Fig. 2 shows the thermoelectric properties of $Mg_2Sn_{0.75}Ge_{0.25}$ calculated by using the three-band model. The calculated results by considering three bands show a reasonable agreement with the experimental data, indicating that three-band model can indeed provide a reasonable description of the thermoelectric properties of $Mg_2Sn_{0.75}Ge_{0.25}$. Also, the relative contribution of each band to the total thermoelectric properties can be clearly revealed by utilizing the three-band model. Thus, it enables the following discussion of the effect of distribution of carriers in electronic bands on the thermoelectric properties. Based on the calculated thermoelectric properties of $Mg_2Sn_{0.75}Ge_{0.25}$, the band offset E is perturbed and its effect on thermoelectric properties is further investigated based on the model.

2.3. Effect of E on thermoelectric properties of $Mg_2Sn_{0.75}Ge_{0.25}$

The band offset E of conduction bands can be expressed as

$$E = E_0 - T\frac{dE}{dT} \quad (1)$$

where E_0 is the band offset of conduction bands at 0 K, and dE/dT is the dependence of E on temperature. It is evident that due to the existence of dE/dT, band convergence is definitely a temperature-dependent phenomenon. For the following calculations, E_0 is perturbed in order to change E, which is mainly due to the fact that E_0 can be practically controlled by tuning the composition of $Mg_2Sn_{1-x}Ge_x$ [23]. In the following discussion, the δE_0 stands for the variation of E_0, *i.e.*, when δE_0 is -95% the E_0 of $Mg_2Sn_{0.75}Ge_{0.25}$ is reduced by 95%, while when δE_0 is $+50\%$ the E_0 of $Mg_2Sn_{0.75}Ge_{0.25}$ is increased by 50%.

In Fig. 3(a) and (b), the electrical resistivity and the Seebeck coefficient decrease gradually with δE_0. Fig. 3(c) shows