Journal of Alloys and Compounds 691 (2017) 151–158

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Theoretical study of thermoelectric properties of p-type $Mg_2 Si_{1-x} Sn_x$ solid solutions doped with Ga

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ARTICLE INFO

Article history:
Received 2 May 2016
Received in revised form
15 August 2016
Accepted 27 August 2016
Available online 28 August 2016

Keywords:
Thermoelectric materials
Thermoelectric figure of merit
Electrical transport properties
Thermal transport properties
Mg_2SiSn systems

ABSTRACT

Mg_2 Si-Mg_2 Sn solid solutions are a promising class of thermoelectric materials. The thermoelectric properties of p-type $Mg_2(Si_{0.3}\ Sn_{0.7})_{1-y}\ Ga_y$ solid solutions with the doping levels as $y = 0.05$ and $y = 0.07$ are investigated in the temperature range of 300 K–800 K. By using the nearly-free hole approximation and the Fermi-Dirac statistics, the temperature dependences of Fermi level (E_f), Seebeck coefficient (S), and electrical conductivity (σ) are calculated theoretically and compared with related experimental measurements. The thermal conductivity contributions from carriers (namely acceptor holes in this present work, κ_c), electron-hole pairs (κ_{bp}), and phonons (κ_{ph}) are included by employing Wiedemann-Franz law, Price's theory, and Srivastava's scheme, respectively. A maximum thermoelectric figure of merit (ZT) of 0.355 is theoretically achieved for the $Mg_2(Si_{0.3}\ Sn_{0.7})_{0.95}\ Ga_{0.05}$ sample arising from a high Seebeck coefficient of 175.71 μV/K and low total thermal conductivity of 1.82 W m^{-1} K^{-1} at 650 K where its experimental ZT value was reported as 0.356 at 620 K.

1. Introduction

As the global demand for energy increases, the demand for alternative energy source has become completely a major social issue. More than 60% of the energy released is lost as waste heat and in spite of low efficiency, thermoelectric materials can convert waste heat into useful electrical energy and thus they will play an important role as a source of alternative energy in future energy utilizations and managements [1,2]. Compared to a mechanical refrigeration device or power generation device, a thermoelectric device is of no noise, no pollution, long life, and free maintenance. Thermoelectric conversion efficiency is directly proportional to materials dimensionless thermoelectric figure of merit (ZT) which is determined by,

$$ZT = \frac{\sigma S^2}{\kappa_{total}} T, \quad (1)$$

where T is the absolute temperature, S is the Seebeck coefficient, σ is the electrical conductivity and κ_{total} is the total thermal conductivity which has three different contributions; κ_c is the carrier thermal conductivity (i.e., from electrons for n-type materials and from holes for p-type materials), κ_{bp} is the bipolar thermal conductivity (i.e., from electron-hole pairs) and κ_{ph} is the lattice thermal conductivity (i.e., from phonons). Good thermoelectric materials (i.e., namely for $ZT \geq 1$) should have a high power factor ($PF = S^2\sigma$) and a low total thermal conductivity ($\kappa_{total} = \kappa_c + \kappa_{bp} + \kappa_{ph}$). Due to the interdependence of the three thermoelectric material parameters (S, σ, and κ_{total}) maximizing the thermoelectric efficiency is quite challenging task and the major research in the field of thermoelectrics has been focused on this issue. There are several ways to enhance the power factor such as carrier energy filtering [3,4], convergence of electronic band valleys [5–8] and generating resonant levels in electronic bands at near to the Fermi level [9,10]. Additionally, to decrease the κ_{total} there are various routes to follow; scattering of heat carrying phonons with introducing point defects by making alloys, embedding nano-inclusions, and second phase precipitates into the matrix [11–13], nano/mesoscale grain boundaries [11–14], and intrinsic bond anharmonicity [15–18].

Owing to the rich reserves of raw materials, along with their environmentally friendly, non-toxic, and lightweight nature Magnesium based thermoelectric materials, known as ecofriendly thermoelectric semiconductors, are promising candidates to be applied at middle temperature range between 400 K and 800 K. Mg_2 X semiconductors crystallize in the cubic anti-fluorite structure whose number of states in the Brillouin zones with space

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http://dx.doi.org/10.1016/j.jallcom.2016.08.278
0925-8388/

group Fm3m. These semiconductors have indirect band gaps as $E_g(Mg_2Si) = 0.78$ eV and $E_g(Mg_2Sn) = 0.36$ eV [19] and also their electronic properties can be controlled by appropriate doping. Among Mg_2Si-Mg_2Sn, Mg_2Si-Mg_2Ge, and Mg_2Sn-Mg_2Ge solid solutions in the Mg_2X systems, especially the $Mg_2Si_{1-x}Sn_x$ solid solution is expected to have much higher thermoelectric efficiency due to its reduced phonon thermal conductivity sourced from the greater difference in atomic mass between Si and Sn [20], enhanced short wave-length phonon scattering by the introduction of point defects and optimized band structure such as band inversion and splitting [21]. In general, $Mg_2Si_{1-x}Sn_x$ solid solution is applied to utilize waste heat from industrial plants and exhaust gas of cars [22]. To produce the thermoelectric generator from $Mg_2Si_{1-x}Sn_x$ solid solution, the thermoelectric performances of both p- and n-type materials must be balanced. It is thus very important to investigate the thermoelectric properties of both types thermoelectric materials. In line with this, the low ZT of p-type doped $Mg_2Si_{1-x}Sn_x$ solid solution is the biggest problem that needs to be overcome first. Although a reasonable amount of information about thermoelectric properties of n-type doped Mg_2Si based solid solutions does exist, there is a dearth of information about its p-type doped solid solutions. Effectively high thermoelectric figure of merit values were gained for n-type doped $Mg_2(Si,Sn)$ ternary series, such as for Sb doped $Mg_2Si_{0.6}Sn_{0.4}$ solid solution $ZT = 1.1$ nearly at 800 K [23], for Sb doped $Mg_2Si_{0.3}Sn_{0.7}$ solid solution $ZT = 1.3$ near 700 K [24], and Bi doped $Mg_2Si_{0.4}Sn_{0.6}$ solid solution $ZT = 1.4$ at $T = 800$ K [25]. In $Mg_2(Si,Sn)$ series, the Sn-rich side exhibits higher ZT values but Si-rich side seems to be more appropriate for applications owing to the lower density, rather higher melting points and higher strength. Additionally, very recently, a very high figure of merit $ZT = 1.4$ was reported for Bi-doped Si-rich $Mg_2Si_{1-x-y}Sn_xGe_y$ ($x = 0.4$, $y = 0.05$) solid solution at 800 K [26]. The selection of compositions and doping elements plays an important role on the hole concentration and electronic transport properties thus the thermoelectric efficiency of p-type doped Mg_2Si based semiconductor compounds. The thermoelectric properties of p-type materials were investigated for $Mg_2Si_{0.25}Sn_{0.75}$ double doping with Ag and Li and ZT was found to be nearly 0.32 at 610 K [27] and for $Mg_{2.1}Si_{0.3}Sn_{0.7}$ doped with Ga ZT was gained as 0.35 at 650 K [28]. Despite these lower ZT values, Noda et al. [29] studied on Ag doped $Mg_2Si_{0.6}Ge_{0.4}$ solid solutions and reported the ZT value as high as 1.68 at 629 K. Conversely, latter studies achieved rather much smaller ZT value as 0.26 nearly at 850 K [30].

In this present study, the temperature dependence of thermoelectric properties of p-type $Mg_2(Si_{0.3}Sn_{0.7})_{1-y}Ga_y$ solid solutions with the doping levels as $y = 0.05$ and $y = 0.07$ is investigated theoretically and compared with available experimental measurements in the temperature range between 300 K and 800 K. For the theory of electronic transport properties (S, σ, κ_c) the temperature dependent Fermi level covering the extrinsic and intrinsic conditions [31] is taken into account and the calculations are identified by using Hicks-Dresselhaus' procedure [32]. The temperature variations of κ_{bp} and κ_{ph} are worked out by employing Price's theory [33] and Srivastava's scheme [34], respectively. For both solid solutions (doping levels as $y = 0.05$ and $y = 0.07$), the frequency as well as percentage contributions from different polarisations (transverse and longitudinal) towards the phonon thermal conductivity are studied in detail. Moreover, our calculated results for the thermoelectric transport coefficients are compared with the experimental values obtained by Liu et al. [35] and a detailed discussion is provided to explain the experimental measurements. We hope that this present theoretical explanation will allow us to give an insight into thermoelectric properties of p-type doped Mg_2Si based semiconductor compounds and the reason for their low thermoelectric efficiency values compared to their n-type doped solid solutions.

2. Theory

The methods for calculating Seebeck coefficient (S), electrical conductivity (σ), total thermal conductivity κ_{total} (including carrier thermal conductivity, κ_c, bipolar thermal conductivity, κ_{bp}, and lattice thermal conductivity, κ_{ph}) and hence ZT for p-type doped semiconductors have already been described in our previous study [36]. For the calculation of ZT in (3D) bulk materials temperature dependence of Fermi level (E_f) is strongly required for the electronic transport properties which is given in the extrinsic regime as [37]

$$E_f^{ext} = \frac{1}{2}(E_a + E_v) + \frac{k_B T}{2}\ln\frac{N_a}{2U_v} - k_B T \sinh^{-1}\left[\sqrt{\frac{U_v}{8N_a}}\exp\left(\frac{-\Delta E_i}{2k_B T}\right)\right], \tag{2}$$

where E_v is the valence band edge, E_a is the acceptor energy level, N_a is the concentration of acceptor impurity atoms, $\Delta E_i = E_a - E_v$ is the acceptor ionisation energy, and $U_v = 2((m_p^* k_B T)/(2\pi\hbar^2))^{3/2}$ with m_p^* as the hole effective mass, k_B is the Boltzmann constant, and $\hbar$ is the reduced Planck's constant. The Fermi level at zero temperature, $E_f = (E_v + E_a)/2$, lies exactly midway between the acceptor level and the valence band. As the temperature increases, the Fermi level first decreases slowly and then increases up until it reaches the value where the acceptor level becomes fully ionized [37]. Thus, from this point the material behaves like an intrinsic semiconductor and the temperature dependence of E_f is expressed as [37]

$$E_f^{int} = \frac{E_v + E_c}{2} + \frac{3}{4}k_B T \ln\left(\frac{m_p^*}{m_n^*}\right), \tag{3}$$

where E_c is the conduction band edge and m_n^* is the electron effective mass. In narrow band gap semiconductors, band gap variation with temperature plays a major role especially in the intrinsic regime. Thus, by setting the valence band edge as zero ($E_v = 0$) Fermi level in the intrinsic regime can be re-written in terms of the energy band gap as

$$E_f^{int} = E_c - \frac{E_g(T)}{2} + \frac{3}{4}k_B T \ln\left(\frac{m_p^*}{m_n^*}\right), \tag{4}$$

where the temperature dependence of energy band gap is expressed by following Yelgel's formula as [36]

$$E_g(T) = \left[E_g(0) - \frac{\alpha T^2}{\beta + T}\right] + \frac{\eta T}{\beta + T}, \tag{5}$$

with $E_g(0)$ is the value of E_g at 0 K, and α, β and η are treated as adjustable parameters.

The electronic transport properties are described by assuming a single-band nearly free-hole model and can be summarized in the following forms. For p-type semiconductors the Seebeck coefficient is given as

$$S = \frac{k_B}{e}(\delta - \zeta^*), \tag{6}$$

where e is the hole charge, $\zeta^* = E_f/k_B T$ is the reduced chemical