

Thermoelectric properties of $\text{AgPb}_m\text{SbTe}_{m+2}$ ($12 \leq m \leq 26$) at elevated temperature

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In this study, the thermoelectric properties of $\text{AgPb}_m\text{SbTe}_{m+2}$ (LAST- m , $m=12, 16, 18, 20, 22$, and 26), including the Seebeck coefficient, the electrical resistivity, and the thermal conductivity, were studied in the temperature range from 323 to 773 K. The Seebeck coefficient and the electrical resistivity exhibited the behavior of a degenerate semiconductor. The measured results of the carrier concentration supported the conclusions of the electrical transport properties. The lowest electrical resistivity and the thermal conductivity were observed, which leads to the best thermoelectric performance in LAST-18 and the dimensionless figure of merit ZT value of 0.8 at 773 K. © 2009 American Institute of Physics. [DOI: 10.1063/1.3138803]

I. INTRODUCTION

Thermoelectric devices have attracted more interest in recent years due to their applicability in power generation and electronic refrigeration.^{1,2} The efficiencies of thermoelectric power generation and refrigeration in thermoelectric devices are highly dependent on the dimensionless figure of merit (ZT), which can be expressed as $ZT=S^2T/\rho\kappa$, where S is the Seebeck coefficient (or thermopower), ρ is the electrical resistivity, κ is the thermal conductivity, and T is the absolute temperature.¹ Thus the good thermoelectric performance needs a large value for S and small value for ρ and κ .

Over the past few decades, lead telluride (PbTe) has been presented as a highly attractive thermoelectric material. At the temperature of approximately 700 K, PbTe and its alloys have optimum thermoelectric materials.³ Intensive research has been conducted on improving the thermoelectric performance of PbTe alloys; such research is based on the substitution and addition of other elements for the modification of the thermal conductivity and the carrier concentration of the PbTe alloys. Hsu *et al.*⁴ recently reported that the $\text{AgPb}_m\text{SbTe}_{m+2}$ (LAST- m , $m=10$ and 18) alloys showed n -type properties and the outstanding $ZT=2.2$ at 800 K was higher than that obtained in any other previous PbTe alloys researches. It is known that these enhancements in the ZT value of LAST-10 and LAST-18 alloys were based on the remarkable decrease in the thermal conductivity, which is mainly originated from the Ag–Sb rich nanostructures in the PbTe matrix.^{4,5} Researches by Zhou *et al.*⁶ reported that the off-stoichiometric LAST-18 alloys fabricated by combining mechanical alloying and spark plasma sintering method had $ZT=1.5$ at 700 K and its superior thermoelectric properties were mainly due to the low thermal conductivity originated from nanostructure embedded in the PbTe matrix. However, Kosuga *et al.*⁷ showed that LAST-18 had n -type properties

and the maximum ZT was about 0.015 at 523 K in one study⁸ and 0.08 at 623 K in another. It is believed that these deviations in the thermoelectric properties of the LAST compounds owe to the heterogeneous phase in macroscopic scale, whereas the formation of the heterogeneous phase can be affected by the procedure of the sample preparation.⁹

In this work, a comprehensive investigation of the LAST- m alloys ($m=12, 16, 18, 20, 22$, and 26) on the thermoelectric properties was performed in the temperature range from 323 to 773 K. Most works on the LAST- m compounds have been concentrated on the composition of LAST-18, which was known to have the best thermoelectric performance.^{7,8,10–13} There are a few researches on the effect of the compositional variation, which means the change in the value of m in LAST- m on the thermoelectric properties.^{5,14,15} However, all studies investigated the thermoelectric properties of the LAST- m compounds whose value of m ranges from 0 to 18. Thus the comprehensive investigation of the thermoelectric properties in the LAST- m compounds with varying the values of m is performed in this work. For the LAST- m compounds ($12 \leq m \leq 26$), the thermoelectric properties including the Seebeck coefficient, the electrical resistivity, and the thermal conductivity were investigated at elevated temperatures. Moreover, the carrier concentration was measured to support the conclusions derived from the electrical transport properties.

II. EXPERIMENTAL DETAILS

The samples with the nominal composition of $\text{AgPb}_m\text{SbTe}_{m+2}$ ($m=12, 16, 18, 20, 22$, and 26) were prepared. Each element of Pb, Te, Ag, and Sb granules (5N purity) was cleaned with HNO_3 , HCl, acetone, and ethanol in series for 10 min via ultrasonic cleaning. The weighed elements were loaded into the quartz tubes and evacuated to 10^{-5} Torr. After inserting Ar gas, the tubes were sealed to prevent oxidation during the high temperature melting process. The sealed ampoules were melted in a rocking furnace

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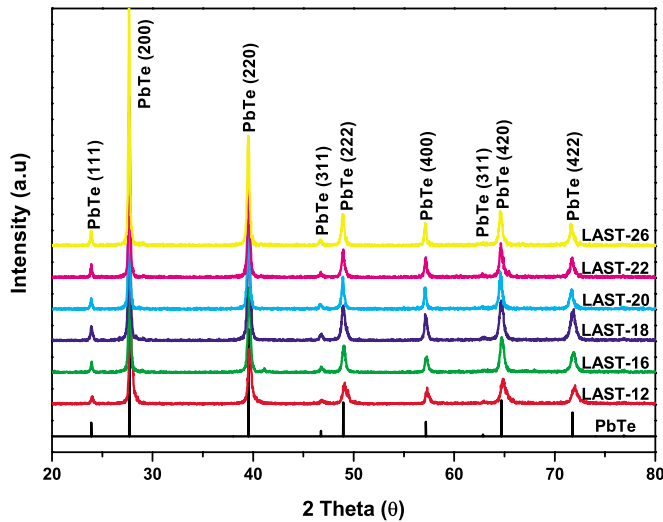


FIG. 1. (Color online) XRD patterns of the LAST- m ($m=12, 14, 16, 18, 20, 22,$ and 26) alloys.

at 1223 K during 10 h. The melted alloys were cooled in the rocking furnace. The obtained alloys were cut into rectangular pieces ($3 \times 3 \times 10 \text{ mm}^3$) for thermoelectric measurement and cylinder pieces (12.7 mm in diameter and 1 mm in thickness) for thermal diffusivity measurement.

The analyses of the phase of the LAST- m alloys were carried out using x-ray diffraction [Rigaku D/max-rc (12 kW)] with Cu $K\alpha$ in the range of 2θ between 20° and 80° . The densities of the melted alloys were measured by the Archimedes method. A differential scanning calorimeter (NETZSCH, DSC 404C) was used for the measurement of the heat capacity of the LAST- m alloys. The thermoelectric properties of the LAST- m alloys were analyzed by ZEM-3 (ULVAC-RIKO, Japan) for the measurements of the Seebeck coefficient and the electrical resistivity. The thermal diffusivity of the LAST- m alloys was measured by the laser flash method (NETZSCH, LFA-457). The thermal conductivity was calculated from the results of the density (d), the heat capacity (C_p), and the thermal diffusivity (α), using the following equation: $\kappa = \alpha C_p d$. The Hall effect measurement was conducted in an electromagnet of 0.55 T for the analysis of the carrier concentration of the LAST- m alloys.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns for the LAST- m alloys. The patterns indicate that all alloys are mostly single phase crystallizing in a NaCl structure. The measured density values of all samples are approximately 8.12 g/cm^3 , which is well above 95% of the theoretical density. We also calculated the unit cell parameters from the patterns. The cell parameters are prone to increase as the value of m in the LAST- m alloys increases. The values of the cell parameters are 0.6443, 0.6437, and 0.6425 nm for the LAST-26, the LAST-22, and the LAST-12 alloys, respectively. The higher value of m in the LAST- m alloys means smaller Ag and Sb concentration in the PbTe matrix. And then the atomic radius of Ag ($\sim 1.60 \text{ \AA}$) and Sb ($\sim 1.45 \text{ \AA}$) is smaller than that of Pb ($\sim 1.80 \text{ \AA}$).¹⁶

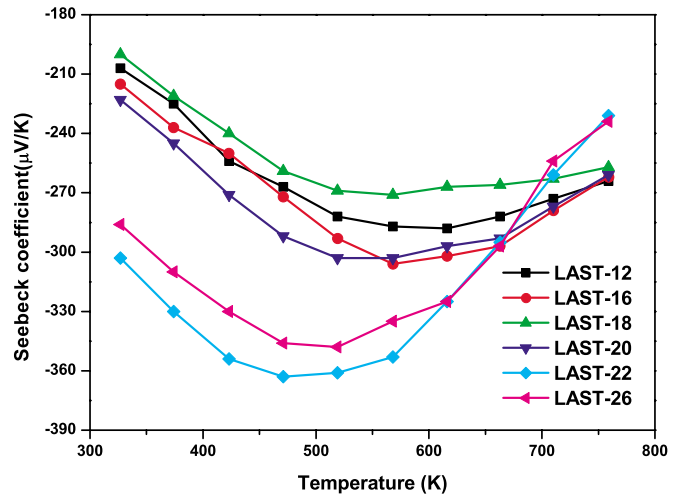


FIG. 2. (Color online) Temperature dependence of the Seebeck coefficient for the LAST- m alloys.

Thus it may be concluded that Ag and Sb are well occupied in the Na site in the NaCl structure the same as Pb.

Figure 2 shows the temperature dependence of the Seebeck coefficient of the LAST- m alloys. The values of the Seebeck coefficient for all alloys are negative, which means that the major carriers are electrons. This behavior is identical with previously reported values for the LAST compounds.⁴ It is noteworthy that the absolute value of the Seebeck coefficient is maximized at the specific temperature, denoted as an on-set temperature hereafter. The absolute values of the Seebeck coefficient are increased in the temperature range from the room temperature to the on-set temperature. And then the values are decreased above the on-set temperature. The former region can be understood as an extrinsic region for the degenerate semiconductor. Assuming single-band conduction in the degenerate semiconductor, the Seebeck coefficients can be expressed by the following:¹⁷

$$S = \frac{\pi^2 k_B}{3 e} \frac{\left(r + \frac{3}{2}\right)}{\eta}, \quad (1)$$

where k_B is Boltzmann's constant, e is the carrier charge, r is the scattering parameter, η is the reduced Fermi energy ($=E_f/k_B T$), and E_f is the Fermi energy. From Eq. (1), it can be deduced that the Seebeck coefficients increase as the temperature increases for the degenerate semiconductor, which is consistent with the experimental results below the on-set temperature. The region above the on-set temperature can be recognized as an intrinsic region. In this region, the electrons are excited across the band gap and the concentrations of the holes are enormously increased as the temperature increases. Thus the contribution of the holes to the total Seebeck coefficient is increased, resulting in the reduction in the absolute value of the Seebeck coefficient. In n -type PbTe, the on-set temperature is apparently observed and dependent on the amounts of the dopant.^{18,19} It is also observed that the on-set temperatures for the LAST- m alloys with larger m values are smaller than that with smaller m values. The on-set temperature is dependent on the position of the Fermi energy in the

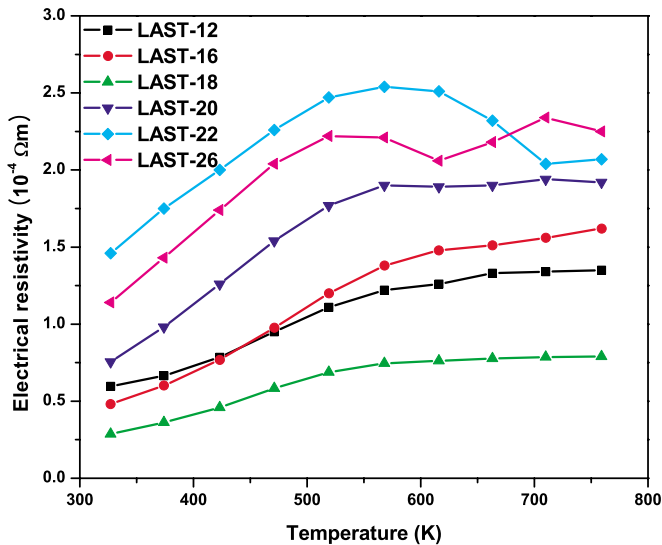


FIG. 3. (Color online) Temperature dependence of the electrical resistivity for the LAST- m alloys.

conduction level for the degenerate semiconductor. If the Fermi energy, which is measured as the energy difference between the Fermi energy and conduction band minimum, is increased, the temperature should be increased for the tail of the Fermi-Dirac distribution to reach on the valence band maximum (VBM). The contribution of holes to the total Seebeck coefficient increases when the tail reaches the VBM. Thus it may conclude that the Fermi energy for the alloys with larger values of m is smaller. This conclusion is also supported by the values of the Seebeck coefficients. The Seebeck coefficient is increased as the carrier concentration is decreased,^{1,20} whereas the carrier concentration is decreased as the Fermi energy is decreased.^{21,22} Therefore, the larger Seebeck coefficient means the smaller Fermi energy. The measured values of Seebeck coefficient are larger in the alloys with larger value of m , which means the smaller Fermi energy as mentioned before.

Figure 3 shows the values of the electrical resistivity for the LAST- m alloys as a function of temperature. The temperature dependence of the electrical resistivity is the typical behavior of the degenerate semiconductor. It is notable that the value of the electrical resistivity of LAST-18 is the lowest among the LAST- m alloys at elevated temperature. Because the electrical resistivity is dependent on the carrier concentration and the mobility, the carrier concentration and the mobility are evaluated from the Hall coefficient measurement.

The measured carrier concentration is shown in Table I. Assuming single-band conduction and a parabolic band model, the carrier concentration at room temperature is calculated from the Hall coefficient using the equation $R_H = 1/ne$, where R_H is the Hall coefficient and n is the carrier concentration. The mobility at room temperature is also calculated from the results of the carrier concentration and the electrical resistivity. The values of the carrier concentration are in the order of 10^{18} cm^{-3} . Moreover the carrier concentration is decreased as the value of m increases, whereas the mobility is increased. Thus the lowest electrical resistivity in

TABLE I. Carrier concentration and mobility of all samples at room temperature.

Samples	Carrier concentration (10^{18} cm^{-3})	Mobility ($\text{cm}^2/\text{V s}$)
LAST-12	6.024	357
LAST-16	4.424	355
LAST-18	3.612	401
LAST-20	2.415	431
LAST-22	1.447	504
LAST-26	1.096	592

LAST-18 at elevated temperature cannot be solely explained in terms of the carrier concentration and the mobility at room temperature. The results of the carrier concentration support what is previously mentioned in the paragraph for the Seebeck coefficient. From the results of the Seebeck coefficient, it can be deduced that the carrier concentration in the LAST alloys is decreased with increasing the value of m , which is in good agreement with the results of the carrier concentration.

The temperature dependence of the power factors for the LAST- m alloys is shown in Fig. 4. The power factor is calculated from the Seebeck coefficient and the electrical resistivity using the following equation: S^2/ρ . The maximum value of the power factor for the LAST- m alloys is achieved in LAST-18. The largest value in LAST-18 is mainly due to the lowest value of the electrical resistivity. In all compounds, the power factor is decreased as the temperature increases.

The temperature dependence of the thermal conductivity for the LAST- m alloys is shown in Fig. 5. The value of the thermal conductivity for the LAST- m alloys except LAST-18 is about 2.0 W/mK at 323 K and decreases at elevated temperature, reaching about 1.4 W/mK at 773 K. The thermal conductivity of LAST-18 is about 1.3 W/mK at 323 K and decreases as the temperature increases, reaching 0.8 W/mK

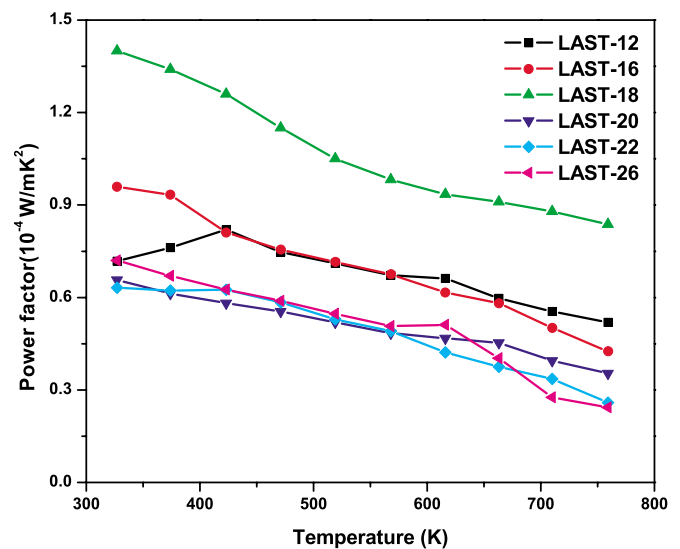


FIG. 4. (Color online) Temperature dependence of the power factor for the LAST- m alloys.

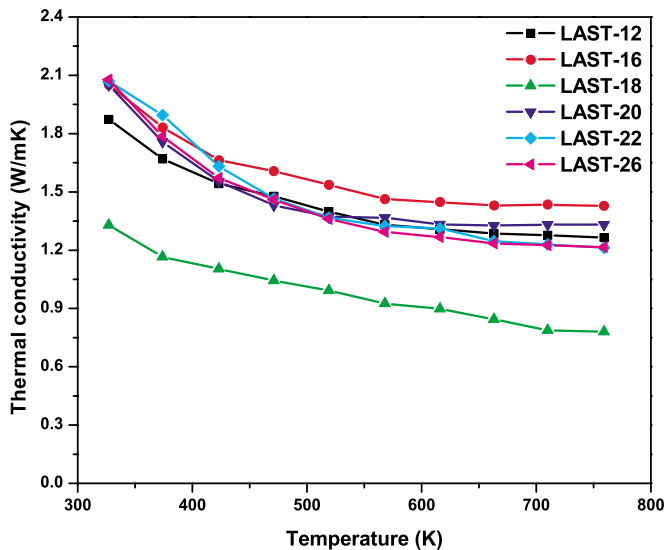


FIG. 5. (Color online) Temperature dependence of the thermal conductivity for the LAST- m alloys.

at 773 K. These values are fairly lower than those reported in Ref. 4 in the whole temperature range, whereas similar with those of LAST-10 in Ref. 4.

The thermoelectric properties of the LAST- m compound are highly dependent on the microstructure at the nanoscopic level. For example, it is thought that the thermal conductivity of LAST-18 is reduced because the nanodots endotaxially embedded in the PbTe matrix efficiently scatter the propagation of phonons, whereas the electrical properties are disturbed little.^{4,6} In addition to the nanodots, the compositional fluctuation in the crystal affects the thermoelectric properties.^{4,6} The compositional fluctuation was observed in LAST-10 in Ref. 4 and in LAST-18 in Ref. 6. It was concluded that the thermal conductivity of the compound was reduced without the significant decrement of the electrical properties, resulted from the presence of the compositional fluctuation.⁶ The reduction in the thermal conductivity in LAST-18 is seemed to be larger in the case of the coherently and endotaxially embedded nanodots in the matrix than the compositional fluctuation features.⁶ But the effect of the nanostructures on the thermoelectric properties is to date not fully understood. It is noteworthy that the existence and the amount of the nanodots and the compositional fluctuation features in the microstructure are dependent on the composition, namely, the value of m in LAST- m , and a fabrication process.^{5,9,23} Thus the lowest thermal conductivity of the present LAST-18 compound can be explained in the same manner. Even though we could not observe the nanodots, the

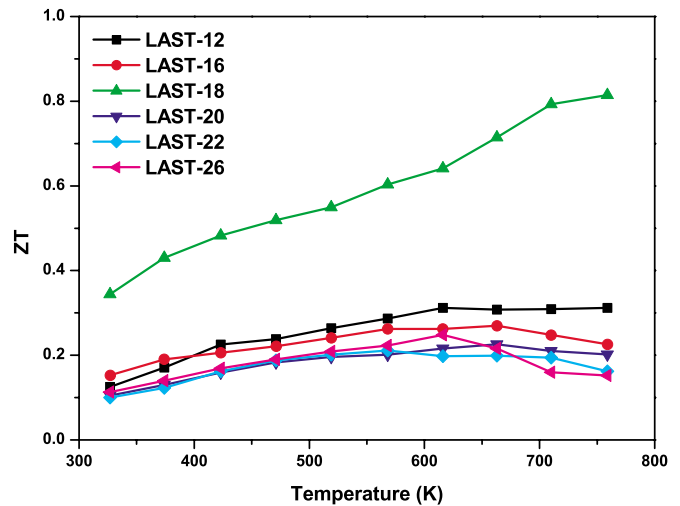


FIG. 6. (Color online) Temperature dependence of the ZT value for the LAST- m alloys.

compositional fluctuation is observed in our preliminary study for the LAST-18 alloy. As a result, the lowest thermal conductivity could be achieved in the LAST-18 alloy, resulting in the highest thermoelectric performance.

Figure 6 shows the temperature dependence of the ZT value for the LAST- m alloys. The maximum ZT value in all samples is 0.8 at 773 K for LAST-18, which is mainly due to the lowest electrical resistivity and the lowest thermal conductivity. It is well known that the superior thermoelectric properties of the LAST compounds are related to the presence of the nanodots.⁴⁻⁶ Moreover, it is reported that the LAST compounds show a compositional inhomogeneity in macroscopic scale and the extent of the inhomogeneity is dependent on a fabrication process such as cooling rates.⁹ Thus the presence of the nanodots in the LAST compounds may be related to the fabrication process, which may support the absence of the nanodots in this research. However, it is noticeable that the best thermoelectric performance among the LAST- m alloys ($12 \leq m \leq 26$) is achieved in LAST-18, consistent with the earlier report in Ref. 4, even though the nanodots are not present in this research and the fabrication processes differ from those in the other.

The ZT value of the present study is quite different from that of Ref. 4. In order to clarify the difference in the thermoelectric properties of the LAST-18 compound, the thermoelectric properties and the electrical transport properties of the LAST-18 compound at room temperature are summarized in Table II. The absolute value of the Seebeck coefficient in the present is larger than that of the previous, while

TABLE II. Seebeck coefficient, electrical resistivity, carrier concentration, carrier mobility, and thermal conductivity of LAST-18 at room temperature.

Sample	Seebeck coefficient ($\mu\text{V}/\text{K}$)	Electrical resistivity ($10^{-3} \Omega \text{ cm}$)	Carrier concentration (10^{19} cm^{-3})	Carrier mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Thermal conductivity (W/mK)
LAST-18	-200	2.87	0.36	401	1.3
LAST-18 ^a	-135	0.54	~ 2.0	~ 800	2.3

^aThe data for LAST-18 were from Ref. 4.

the electrical resistivity of the present is larger by a factor of 5. The large value of the electrical resistivity is mainly due to the smaller carrier concentration in the present than that of the previous. The thermal conductivity of the present is smaller than that of the previous. Consequently, the ZT value of the present is smaller than that of the previous due to the smaller carrier concentration, even though the thermal conductivity is smaller than that of the previous.

IV. CONCLUSIONS

The LAST- m alloys ($12 \leq m \leq 26$) were prepared by using a conventional melting method using a rocking furnace. The investigated LAST- m alloys were polycrystalline with the NaCl-type crystal structure. The transport properties such as the Seebeck coefficient exhibited the behavior of the degenerate semiconductor. The extrinsic and the intrinsic region were well characterized in the result of the Seebeck coefficient. The carrier concentration is increased with decreasing the values of m in LAST- m . The highest ZT value was observed in LAST-18 and reaches 0.8 at 773 K, which is mainly due to the lowest electrical resistivity and the thermal conductivity. Although the thermoelectric performance in the LAST compounds is significantly dependent on the fabrication procedures, LAST-18 is the best alloys among the LAST- m compounds ($12 \leq m \leq 26$), which is consistent with the previous results whose fabrication procedures differ from those of this research.

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- ¹G. J. Snyder and E. S. Toberer, *Nature Mater.* **7**, 105 (2008).
- ²B. C. Sales, *Science* **295**, 1248 (2002).
- ³V. Fano, in *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC, Boca Raton, FL, 1995), p. 257.
- ⁴K. F. Hsu, S. Loo, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis, and M. G. Kanatzidis, *Science* **303**, 818 (2004).
- ⁵E. Quarez, K. F. Hsu, R. Pcionek, N. Frangis, E. K. Polychroniadis, and M. G. Kanatzidis, *J. Am. Chem. Soc.* **127**, 9177 (2005).
- ⁶M. Zhou, J. F. Li, and T. Kita, *J. Am. Chem. Soc.* **130**, 4527 (2008).
- ⁷A. Kosuga, K. Kurosaki, H. Muta, and S. Yamanaka, *Proceedings of the 24th International Conference on Thermoelectrics*, Clemson, SC (IEEE, New York, 2005), p. 45.
- ⁸A. Kosuga, M. Uno, K. Kurosaki, and S. Yamanaka, *J. Alloys Compd.* **387**, 52 (2005).
- ⁹N. Chen, F. Gascoin, G. J. Snyder, E. Muller, G. Karpinski, and C. Stiewe, *Appl. Phys. Lett.* **87**, 171903 (2005).
- ¹⁰A. Kosuga, K. Kurosaki, M. Uno, and S. Yamanaka, *J. Alloys Compd.* **386**, 315 (2005).
- ¹¹A. Kosuga, M. Uno, K. Kurosaki, and S. Yamanaka, *J. Alloys Compd.* **391**, 288 (2005).
- ¹²F. Yan, T. J. Zhu, S. H. Yang, and X. B. Zhao, *Phys. Scr.* **T129**, 116 (2007).
- ¹³T. J. Zhu, F. Yan, S. N. Zhang, and X. B. Zhao, *J. Phys. D* **40**, 3537 (2007).
- ¹⁴J. Sootsman, R. Pcionek, H. Kong, C. Uher, and M. G. Kanatzidis, *Mater. Res. Soc. Symp. Proc.*, Boston, MA (Materials Research Society, Warrendale, PA, 2006), p. 293.
- ¹⁵K. F. Cai, C. Yan, Z. M. He, J. L. Cui, C. Stiewe, E. Müller, and H. Li, *J. Alloys Compd.* **469**, 499 (2009).
- ¹⁶<http://www.webelements.com/>.
- ¹⁷G. S. Nolas, J. Sharp, and H. J. Goldsmid, *Thermoelectrics: Basic Principles and New Materials Developments* (Springer, Berlin, 2001), p. 42.
- ¹⁸Z. H. Dughaish, *Physica B* **322**, 205 (2002).
- ¹⁹D. A. Wright, *Metall. Rev.* **15**, 147 (1970).
- ²⁰M. W. Oh, D. M. Wee, S. D. Park, B. S. Kim, and H. W. Lee, *Phys. Rev. B* **77**, 165119 (2008).
- ²¹B. R. Nag, *Electron Transport in Compound Semiconductors* (Springer, Berlin, 1980), p. 76.
- ²²M. W. Oh, H. Inui, M. C. Kim, M. H. Oh, and D. M. Wee, *J. Kor. Inst. Met. Mater.* **44**, 1 (2006).
- ²³H. Lin, E. S. Božin, S. J. L. Billinge, E. Quarez, and M. G. Kanatzidis, *Phys. Rev. B* **72**, 174113 (2005).