A Review of thermoelectric properties and study of β-Zn₄Sb₃ structure

Neelam Swarnkar[1]*, Yashwant singh chandel[2]

[1,2]*dept. of Physics, Rajiv Gandhi Prodyogiki Vishwavidhyalaya, Bhopal, M.P., India*

ABSTRACT

Energy plays an important role in our daily life. We use different energy sources for generating electricity. But these energy sources are limited. So we need to discover new sources of energy. Thermoelectric materials are best suited material for doing the desired work. Because thermoelectric material has the ability to convert waste heat into electricity by using the seebeck effect. This waste heat comes from the industry or automobiles. This paper discussed about how to improve the thermoelectric performance like seebeck coefficient, electrical conductivity and figure of merit (ZT). There are so many materials have the quality to convert electricity from heat. We also discussed about the structure of β-Zn4Sb3 thermoelectric material for future requirements and its thermoelectric performance.

KEYWORDS: *Thermoelectric Materials, Zn₄Sb₃, figure of merit (ZT)*

I.   INTRODUCTION

In recent decades, massive attention is given to thermoelectric materials because of their impending and wide utilization in process of refrigeration, power generation and recovery of waste-heat by the means of compact devices without any complex movable parts [1].

Low cost thermoelectric materials (silicides, oxides or skutterudites) and high stability to chemicals (silicides and oxides) provides a trustworthy potential aspect in case of existing commercial applications where vital considerations are low cost and higher durability. On the other hand, advanced nanomaterials for instance nanowires, super lattices or nano composites have raised the opportunity of achieving better performance in optimizing the thermoelectric generators [2].

The efficiency conversion of thermoelectric materials is strongly interlinked with the figure of merit (ZT) the respective material. ZT is demonstrated in Eq. (1) as follows [3].

$$ZT = \frac{S^2 T}{(k_e + k_l)\rho} \tag{1}$$

$$ZT = (S^2 \sigma / K) T$$

Where, S is the Seebeck coefficient, σ is the electrical conductivity, k is thermal conductivity, Ke and Kl electronic and lattice thermal conductivity respectively, T is the absolute temperature, ρ is electrical resistivity. The $S^2\sigma$ (also known as thermo power) is a measuring process which estimates the capacity of thermoelectric material (TE) to produce electricity directly from heat. It is measured in volts per kelvin (V/K) unit. Although in maximum cases microvolts per kelvin (μ V/K) are used. However, seebeck coefficient is dependent on elements, thermodynamic, structural and chemical properties such as structure of molecule, carrier concentration and mass effectiveness [4].

The ideal thermoelectric material should comprise of better electronic properties related to a good single semiconductor crystal but should has thermal properties inter linked with materials which are amorphous in nature such as phonon glass and electron crystal'. β-Zn4Sb3 is a p-type semi-metallic compound which is best suited as a vital material at moderate temperatures, is derived from the three modified versions of Zn₄Sb₃. The Zn₄Sb₃ comprises of three structural phase, known as, α-, β-, and γ-Zn₄Sb₃ in which α- remains stable below 263K, β- remains stable in between 263 K-765K and γ- is stable above 765 K [5]. The highest value of ZT for β- Zn₄Sb₃ is stated as 1.40 at temperature of 675K. In terms of power factor, β- Zn₄Sb₃ is considerably high (∼13Wm−1 K−2 at 675K) whilst it owns an outstanding "phonon-glass" behavior which is descripted by generally lower thermal conductivity of ∼0.9Wm−1K−1 at 300K compared to that of glass [5].

RELATED WORKS

The thermoelectric properties of $(Zn_{1-x}Ag_x)_4Sb_3$ in between 300 – 575 K and its stability at high temperatures which were manufactured by direct plasma sintering method. Doping of Ag at the sites of Zn can enrich the thermoelectric performance comprising the highest value of ZT in case of ~1.2 at 575 K for the $(Zn_{0.9925}Ag_{0.0075})_4Sb_3$ huge sample, and this huge sample attains stability when treated with heat source up to 793 K under conditions of vacuum in addition with it also remains stable when the temperature is increased to 573 K in presence of air (Song et al., 2018). In order to compare the TC lattices in different nanostructures which were simulated using identical parameters by EMD at 300 K, noteworthy overthrow in the nanostructured wires were predicted. The low lattice TC was reported for a particular set of parameters in case of few structures, such as; in case of Si core/Ge shell system the minimum TC of about 2-nm diameter of core was observed to be approx. 7.5W/m-K. Other aspect in terms of consequences of the present work could be based on the robustness of the structure in reference to TC as a result after the fabrication and growth. The distribution of diameter for nanowires is as a result of carrying out bottom-up routes performed for the synthesis of nanowires. Due to the lithography procedure, the Top-down fabrication process exhibits few amount of fabrication tolerance. Hence, the superlattice structures which are depicted are noted to be more robust potentially when it comes to fabrication tolerance while building TE devices [Özden et al., 2016]. [Minnich et al., 2009] explained the accomplishments in the existing time of bulk nanostructured materials. These materials showed on experiments that a higher value of ZT compared to its bulk equivalent counterparts by declining the thermal conductivity to lower levels compared to the estimated values. In terms of practical usability most importantly, the material can be fabricated at lower price, quickly and in such a form which is flexible and compatible with the on-going configurations of thermoelectric devices.

[2] Depicts that thermoelectric materials based on silicon shows substantial space for enhancement and improvement. Attaining the most efficient power generation from heat widely depends on factors such as Seebeck effect, electrical and thermal conductivity. They suggests that these thermoelectric properties can be further optimized in silicide state by means of super saturation through liquid quenching or/in addition with oxides which enables the silicide to reach higher values of excellence from medium to high range of temperatures. [3] Studied the recent progressions and advancements done in β-Zn_4Sb_3 based thermoelectric materials. The band structure engineering (DOS distortion) and Nano structuring (EFE and phonon scattering) are considerably enhanced by the thermoelectric properties. Although, bipolar effect which is not in favor of thermoelectric has obvious rise in the temperature. The bipolar effect is derived from the fact that there are two types of carriers namely electrons and holes. At higher temperatures there is equal number of holes due to the thermal excitations of few electrons from the valence band to the conduction band.

[4]Carried out investigations on thermoelectric properties of Sn-doped PZn,Sb, in order to improve its thermoelectric performance at a better levels. However, in a single phase of PZn,Sb, 3% of Sn was obtained in concentration, there was a negligible change in the lattice constant of Sn-doped samples which indicated that Sn was not the right replacement for Sb. The results from the X-ray diffraction measurement showed that, microcrystals of Sn are distributed among the areas of grain boundaries. This microcrystal of Sn induces the carrier concentration ions and thermal conductivity of Zn_4Sb_3. As a result the value for thermoelectric merit Z barely showed any improvement below -550 K temperature range. Although, improvements were seen above this temperature due to increase in the seeback coefficient of Z. [5] investigated the thermoelectric properties of Nb-doped compounds $(Zn_{1-x}Nb_x)_4Sb_3$ (x = 0, 0.005 and 0.01) within the range of temperature from 300K – 685K. The results showed that there was a significant reduction in the thermal conductivity due to the Nb-doping. On investigation based on temperature it was found that the value of merit ZT in contrast with light doping of compound $(Zn_{0.995}Nb_{0.005})_4Sb_3$ showed improvement, which was two times bigger compared to b-Zn_4Sb_3 at temperature 680 K. [6]investigatedand performed theoretical and experimental based study on the effects of doping of Ag in addition with Cu on the thermoelectric including structural properties of Zn_4Sb_3. The results obtained demonstrated that the resistance and seeback coefficients offered by $(Zn_{1-x}M_x)_4Sb_3$ M =Ag, Cu tends to rise and then decline in reference to the elevating dopant content, which remains stable with the non-repetitive change in behavior of the concentration carriers. [7]Represented thethermoelectric properties of compound $(Zn_{1-x}Ag_x)_4Sb_3$ having Ag doping. The outcomes depicted that lower temperature (T less than 300 K) thermal conductivity λ of light doping of $(Zn_{1-x}Ag_x)_4Sb_3$ (x = 0.0025 and 0.005) declines significantly when compared to case in Zn_4Sb_3

seemingly because of increased impurities dispersion of phonons. The major low temperature thermal conductivity of lattices of $(Zn0.99Ag0.01)_4Sb_3$ in comparison to that of Zn_4Sb_3 might be accredited to the cooperation of impurity phase in ZnSb. The factor of resistance and coefficient of seebeck effect S are observed to be rising and then declining steadily incorporation with increase in the content of Ag which could be accredited to modify the concentration carriers because of the various positions captured by the Ag on elevating the doping content.

Conflicting Thermoelectric Material Properties

The essential aspect of thermoelectric materials is the requirement of optimizing the multiplicity of contradicting properties. In order to obtain maximum value of thermoelectric merit ZT of any material, a huge source of thermo power (utter value of seebeck coefficient), high conduction of electricity, and lower value in terms of thermal conductivity are needed. Since these features of carriers depend on the interconnection of properties of material, a considerable number of quantities are to be optimized in order to get maximum value for ZT.

1.1. Carrier Concentration

It should be made sure that in case of single type carriers, the seebeck coefficient should be in higher amount. Mixed conduction values from *n-type* and *p-type* will result in movement of both charge carriers to the cold region and terminate the seebeck voltages that are induced. Insulators with low concentration of carriers and semiconductors possess bog values for seebeck coefficients.

1.2. Effective Mass

The mass effectiveness of the carrier charge delivers another struggle since high mass effectiveness generates high amount of thermo power value but also lower conduction in electricity.

1.3. Electronic Thermal Conductivity

Surplus material plotting contradicts the base from the requirement of low thermal conductivity. There are two sources of thermal conductivity in case of thermoelectrics: (1) delivery of heat by the electrons and holes, and (2) passing of phonons by the means of lattice. Maximum terminology in terms of electronics is directly connected with electricity conduction by means of Wiedemann–Franz law.

1.4. Lattice Thermal Conductivity

Material glass comprises of the lowest value of lattice in terms of thermal conductivities.

The thermal conductivity in glass is observed as a random scattering of energy by means of a single lattice instead of delivery through phonons in quick transitions, which results in conceptualizing minimum value of thermal conductivity [38]. In fact, although, the glass material creates very low quality thermoelectrics since they do not have the required 'electron-crystal' properties – when compared to the semiconductors which are crystalline in nature which show low flexibility due to the rise in scattering of electrons and decline in mass effectiveness because of wider bands. A good thermoelectric material is thus crystalline in nature which manages to disperse phonons without actively disturbing the conduction through electricity. The flow of heat is accompanied by a phonon spectrum in addition to with huge variation in the wavelengths and mean free paths [39] (less than 1nm and larger than 10 μm), generating the requirement for scattering the phonons at several scale lengths.

Thus thermo electrics need an uncommon material; which is a phonon glass electron crystal [40]. The base prerequisites electron crystal from the fact that semiconductors comprising crystalline nature have proved to be the paramount in meeting the adjustments needed from the side of electronic properties (electricity conduction and seebeck coefficient). The base requirements of phonon glass from the requirement with respect to lower lattice thermal conductivity possible. The traditional thermoelectric materials have utilized insight replacement material (alloys) with elements which are isoelectronic to conserve a structure which is electronically crystalline while generating huge quantity mass to disturb the phonon path. The recent study has been done in the field of thermoelectric shows the successful implementation of these methodologies to attain the phonon glass electron crystal.

II. METHODOLOGY FOR IMPROVING FIGURE OF MERIT (ZT)

Equation 1 shows the material having higher values of ZT which can be attained by calibrating and improving the seebeck coefficient and conduction of electricity, while keeping the thermal conductivity to the minimum value possible. The conduction through electricity σ in reference to thermoelectric material can be written as:

$$\sigma = 1/\rho = ne\mu \text{ ------------------ (2)}$$

Where n is the carrier concentration, e is the charge of unit carrier and μ is the carrier mobility. The enhancement of electrical conductivity can be done by adding chemical

dopants. Doping will, thus decrease the flexibility of charge carriers because of elevated dispersion among carriers and the dopants. Moreover, every single atom of dopant has one higher or lower count in valence electron when compared to the host atoms; hence they raise the density of charge carriers [10]. As per *Powell and Vaqueiro* [11], good thermoelectric material is generally doped strongly and narrow band gap semiconductor in reference with densities of charge carrier within the range of 10^{19} to 10^{21} cm^3 given in the figure 1.
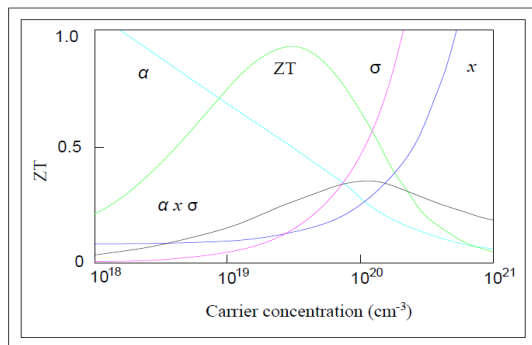

Fig.1 Optimized ZT through carrier concentration tuning. A, maximizing the efficiency (ZT) [8]

A single carrier type among p-type or n-type is retained so as to ensure there is a massive seebeck effect. The combined form of p-type and n-type carriers will move both carriers to reside within the cold area as a result an opposite effect of seebeck effect will be produced which lowers down the thermoelectric power. Huge amount of seebeck effect coefficient might emerge in lower metal concentrations comprising insulators or semiconductors in addition with conduction of electricity as the trade-off. On the other hand high concentrations of carriers in metals have high conduction of electricity but also there is reduction in the seebeck coefficient [10]. The evaluations of thermoelectric properties of insulators, semiconductors, and metals at ambient temperature are depicted in the table below. Although, metals are good conductor of electricity, still have degraded thermoelectric properties due to lower seebeck effect and elevated thermal conductivity. Insulators having maximum width in the bandgaps possess high value of seebeck coefficient but at the same time they have low conduction for electricity which results in lower factor for power and little ZT. Hence the carrier concentrations situated in between semiconductor and metals shows the optimum power factor value.

Table 1: Comparison of thermoelectric properties of metals, semi-metals and non-metals at 300K [41, 42, and 43]

TE property	Metals	Semi-Conductor	Insulator
Seebeck Coefficient	~ 200-300 µV/K [41]	~ 0-3 µV/K [41]	~1000 µV/K [42]
Electrical Conductivity	$>10^5$ (s.m)$^{-1}$ [43]	$10^{-6} < \sigma < 10^5$ (Ω.m)$^{-1}$ [43]	$<10^{-6}$ (Ω.m)$^{-1}$ [43]
Carrier concentration	High	Low	Low

Recent Progress in Environmental Friendly TE Materials

Various noteworthy developments in order to improve the properties of thermoelectrics are displayed. This comprises of chief achievements obtained for ZT around function of year as various decades. It can be seen that advancement in materials of thermoelectrics was prominent in its establishment from 1950s. However, several thermoelectric materials are discovered that attained high value of ZT such as PbTe [20, 21, 22], Bi$_2$Te$_3$and PGEC materials [23], which were the major elements in terms of high performance

although these materials were non-cost effective, toxic, dangerous in use and hazardous to environment.

Accumulate the accomplishment of ZT since many decades from the past as the year function. It was found that there weren't any significant studies done in the field of thermoelectric materials from time period of year 1960s-1990s. The thermoelectric materials reached their defining moment when research from Hicks and Dresselhaus [24] checked for verification in improving the ZT in two dimensional analysis of

Bi_2Te_3 which was possible because of the restricted effects of the quantum. They even proved the decline in thermal conductivity which was the result obtained when a ZT of an anisotropic material in high quantity was raised notably by making layers of super lattices and dispersion of phonons. In the present time, the biggest achievement of ZT (ZT = 3 at 550 K) was obtained by Harman et al.[20] in year 2005, by performing doping on n-type PbSeTe/PbTe quantum dot super lattice (QDSL) which was doped in addition with bismuth.

Silicon-based TE materials

Due to factors like cost effectiveness, availability of the material in high quantity on earth, and non-hazardous to environment; silicon is the most commonly used material as semiconductor in industries around the globe [25, 26]. Although, silicon has high thermal conductivity (kl = 140W/m K) at ambient temperature hence bulk silicon is not suitable thermoelectric material with ZT = 0.01 at 300 K [27]. This shortcoming was resolved by utilizing nanotechnology in order to reduce the size of the grains.

Mg2Si-based TE materials

Mg_2Si is owned by magnesium (IV) family compounds in addition with the process of crystallization in structure of antiflouride comprising Face Centered Cubic positions of Si and tetrahedral sites of Mg. Therefore, Mg_2Si thermoelectric materials were considered as the most potential material in thermoelectrics since 1960s as it can be treated in temperature range between 500 K - 900 K and can attain large values of merit ZT = 1.3[28,29,30].

SiGe-based TE materials

Over past many decades, the material silicon germanium (SiGe) is regarded as the most vital thermoelectric material since it can be used in applications where high temperatures are required.

There, massive research and studies has been done on this material in order to identify its thermoelectric properties and behavior. Properties such as high strength in mechanical, high melting point, low pressure of vapor and good resistance to oxidation caused by atmosphere were found in the alloys of SiGe [31]. Another important benefit of SiGe alloy is that it is friendly to environment and has lower thermal conductivity lattice since germanium particles are added in the matrix structure of silicon. The mixing of Ge particles in Si will result in vast variations in the average free path among its phonons and the electrons; therefore it will substantially decline the thermal conductivity and raise the ZT. SiGe is thus most widely used material as thermoelectrics in generation of power at higher temperatures (~1173 K), hence it has been utilized in space applications during missions as RTG (radioisotope thermoelectric generators) and several other increased temperature applications [32].

High manganese-based TE materials

A thermoelectric material such as HMS (Higher manganese silicide) is regarded as most favorable material since it has two natural elements that are available in plenty amount in earth's crust, they are non toxic in nature and comprises of high value for seebeck coefficient, also has higher resistance for oxidation at high temperatures and bear low resistance [33-35]. Higher manganese silicide resides to a Nowotny chimney ladder (NCL) family which phases with usual geometry structure of $MnnSi_2nm$ and is linked structurally to $TiSi_2$ and $RuGa_2$ [37] The structure is of the $TiSi_2$ type which has two atom substructures, the Mn array being identical to that of the Ti array in $TiSi_2$ and the Si_2 array being identical to that of the Si2 array in TiSi2. Removal of Si leads to a composition MnnSi2nm in which the Mn array is completely unchanged. HMS is the single compound to be known that has Si quantity more than Mn (63-53 at% of Si) [36].

Table 2: Different thermoelectric materials with ZT values [44]

MT	$z \cdot 10^3$	$(T_H)^+$	T_C	zT_H	η (%)
Bi_2Te_3	2.0	450	300	0.9	5.4
$BiSb_4Te_{7.5}$	3.3	450	300	1.5	7.6
Bi_2Te_2Se	2.3	600	300	1.38	11.1
PbTe	1.2	900	300	1.08	12.6
CeS (+Ba)	0.8	1300	300	1.04	14.3

Table 3: Comparison of different thermoelectric materials with ZT values and operating temperature
[45]

Authors	Thermoelectric Material	ZT values	Operating temperature
Harman et al. (2005)	PbSeTe/PbTe	3	550K
Lee, J.-H. and J.C. Grossman (2009)	Si	0.01	300K
Bux, S.K., et al (2011)	Mg2Si	1.3	500-900K
Joshi, G., et al (2008)	SiGe	1-3	~1173K

Structure of β-Zn4Sb3

The structure of β-Zn$_4$Sb$_3$ crystal has been studied and observed by utilizing both the single-crystal and powder X-ray diffraction methods in addition with analysis study over maximum entropy. The structure of β-Zn$_4$Sb$_3$ crystalis hexagon rhombohedral in shape and the constants of the lattices are a = 12.231 ˚A and c =12.428 ˚A with an R-3c comprising group of space [12]. In the current time, there are primarily two separate models and three models which are interstitial that defines the unit cell structure of the β-Zn$_4$Sb$_3$ crystal. In the case of three interstitial models, the density of masses and the composition of the structure of the crystal are noted to be in exact constraints as per the measurements [13, 14]. By the experiments performed it was observed that unit cells of β-Zn$_4$Sb$_3$ contains 30 atoms of Sb, however four of them are in equilibrium positions of Zn in addition with partial functionality: shortage of Zn1 sites with ~90% of occupancy value and the three interstitial model Zn$_2$, Zn$_3$, and Zn$_4$ sites in reference with ~5% of occupancy to adjust the stoichiometric structure, therefore the unit cell contains a total number of 39 Zn atoms [15, 16]. As per the figure 4 shown, the structure of crystal on experimental analysis showed that the stoichiometry of β-Zn$_4$Sb$_3$ is in fact Zn$_{39}$Sb$_{30}$ or Zn$_{13}$Sb$_{10}$ [17, 18]. Since the interstitials of Zn provides massive thermal displacements, the interstitial similar to glass are primarily accounted for the damping of the phonons that degrades the thermal conductivity lattices. Superficially there is disorder Sb in line with the c-axis which can provide thermal conductivity similar to glass. The calculations in the transportation and electronic structure utilizing the structure of crystal found have recognized the compound of the semiconductor as p-type [18], which is as per the outcomes obtained from the experiments in case of doping. It is illustrated that interstitial atoms of Zn performs both as donors of electrons and enhances the thermopower. The thermoelectric properties and calculations for first-principle of structure have also been carried out [19]. The structure of the bands outcomes shows that tendency of electronic covalent of the compound is constant with better measured mobility of the carriers. It was assumed that disorders in Zn structure and the three interstitial occupancies of Zn sites partially provide low thermal conductivity.

However, β-Zn$_4$Sb$_3$ has been recognized as best material of thermoelectric; which demonstrates thermal conductivity like glass; improvements in the performance further are primary concern in its application practically. It is commonly found that factor of power has optimum results compared to concentrations of the carrier. An effective methodology in order to optimize the thermoelectric properties is doping which can be done by balancing the carrier concentrations. In recent times, high factors of power are obtained for β-Zn$_4$Sb$_3$ by optimizing the doping effect.

III. CONCLUSION

Several thermoelectric materials can be used based on the doping element to enhance the ZT values. The present study shows the different materials used by several scholars in order to enhance the ZT merit values of thermoelectric materials. Doping of materials such as BiSb$_4$Te$_{7.5}$, Bi$_2$Te$_2$Se, Mg$_2$Si etc. show good ZT values and show optimum operating temperature. The silicon based materials show lower ZT values hence are not much effective in improving the thermoelectric properties, whereas materials such as PbSeTe/PbTe show higher values of ZT. In order to develop thermoelectric material nanowire, doping of germanium comprising thermoelectric material Zn$_4$Sb$_3$ can be done. This is due to the reason that small size in terms of nanowire will degrade the thermal conductivity of the material, and increase the value for the merit ZT. Also the thermal conductivity is inversely proportional and this results in the enhancement of thermoelectric performance.

REFERENCES

[1]. Song, Lirong, et al. "Enhanced thermoelectric performance and high-temperature thermal stability of p-type Ag-

doped β-Zn 4 Sb 3." Journal of Materials Chemistry A 6.9 (2018): 4079-4087.

[2]. Özden, Ayberk, et al. "Thermal conductivity suppression in nanostructured silicon and germanium nanowires." Journal of Electronic Materials 45.3 (2016): 1594-1600.

[3]. Minnich, AJl, et al. "Bulk nanostructured thermoelectric materials: current research and future prospects." Energy & Environmental Science 2.5 (2009): 466-479.

[4]. Newton, Marcus James, et al. "Meta-study: Analysis of thermoelectric figure of merit parameters for silicides with various doping agents." PAM Review: Energy Science & Technology 3 (2016): 113-125.

[5]. Zou, Tianhua, et al. "Recent developments in β-Zn 4 Sb 3 based thermoelectric compounds." Journal of Nanomaterials 16.1 (2015): 348.

[6]. T. Koyanagi*, K. Hino, Y. Nagamoto, H. Yoshitake and K. Kishimoto "Thermoelectric Properties of f3-Zn4Sb , Doped with Sn", 16th International Conference on Thermoelectrics IEEE 1997.

[7]. Li, D., et al. "Effects of Nb doping on thermoelectric properties of Zn 4 Sb 3 at high temperatures." Journal of Materials Research 24.2 (2009): 430-435.

[8]. Liu, Mian, et al. "Ag and Cu doping and their effects on the thermoelectric properties of β-Zn 4 Sb 3." Physical review B 81.24 (2010): 245215.

[9]. Pan, L., et al. "Effects of Ag doping on thermoelectric properties of Zn4Sb3 at low temperatures." Journal of Alloys and Compounds 489.1 (2010): 228-232.

[10]. Snyder, G. Jeffrey, and Eric S. Toberer. "Complex thermoelectric materials." Materials For Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group. 2011. 101-110.

[11]. Vaqueiro, Paz, and Anthony V. Powell. "Recent developments in nanostructured materials for high-performance thermoelectrics." Journal of Materials Chemistry 20.43 (2010): 9577-9584.

[12]. J. Nyl´en, S. Lidin, M. Andersson et al., "Low-temperature structural transitions in the phonon-glass thermoelectricmaterial β-Zn4Sb3: ordering of Zn interstitials and defects," Chemistry of Materials, vol. 19, no. 4, pp. 834–838, 2007.

[13]. G. B. Bokii and R. F. Klevtsova, "X-ray structure investigation of the β-phase in the zinc—antimony system," Journal of Structural Chemistry, vol. 6, no. 6, pp. 830–834, 1965.

[14]. V. Izard, M. C. Record, J. C. Tedenac, and S. G. Fries, "Discussion on the stability of the antimony-zinc binary phases," Calphad, vol. 25, no. 4, pp. 567–581, 2001.

[15]. G. J. Snyder, M. Christensen, E. Nishibori, T. Caillat, and B. B. Iversen, "Disordered zinc in Zn4Sb3 with phonon-glass and electron-crystal thermoelectric properties," Nature Materials, vol. 3, no. 7, pp. 458–463, 2004.

[16]. H. W. Mayer, I. Mikhail, and K. Schubert, "¨ Uber einige phasen der Mischungen ZnSbN und CdSbN," Journal of The Less-Common Metals, vol. 59, no. 1, pp. 43–52, 1978.

[17]. A. N. Qiu, L. T. Zhang, and J. S. Wu, "Crystal structure, electronic structure, and thermoelectric properties of β-Zn4Sb3 from first principles," Physical Review B, vol. 81, no. 3, Article ID 035203, 2010.

[18]. F. Cargnoni, E.Nishibori, P. Rabiller et al., "Interstitial Zn atoms do the trick in thermoelectric zinc antimonide, Zn4Sb3: a combined maximum entropy method X-ray electron density and Ab initio electronic structure study," Chemistry—A European Journal, vol. 10, no. 16, pp. 3861–3870, 2004.

[19]. S.-G. Kim, I. I.Mazin, and D. J. Singh, "First-principles study of Zn-Sb thermoelectrics," Physical Review B—Condensed Matter and Materials Physics, vol. 57, no. 11, article 6199, 1998.

[20]. Harman, T.C., et al., Nanostructured thermoelectric materials. Journal of Electronic Materials. 34(5): p. L19-L22

[21]. Heremans, J.P., et al., Enhancement of Thermoelectric Efficiency in PbTe by Distortion of the Electronic Density of States. Science, 2008. 321(5888): p. 554-557.

[22]. Biswas, K., et al., High-performance bulk thermoelectrics with all-scale hierarchical architectures. Nature, 2012. 489(7416): p. 414-418.

[23]. Chen, Z.-G., et al., Nanostructured thermoelectric materials: Current research and future challenge. Progress in Natural Science: Materials International, 2012. 22(6): p. 535-549.

[24]. Hicks, L.D. and M.S. Dresselhaus, Effect of quantum-well structures on the thermoelectric figure of merit. Physical Review B, 1993. 47(19): p. 12727-12731.

[25]. Bux, S.K., et al., Mechanochemical synthesis and thermoelectric properties of high quality magnesium silicide. Journal of Materials Chemistry, 2011. 21(33): p. 12259-12266.

[26]. Neophytou, N., Prospects of low-dimensional and nanostructured silicon-based thermoelectric materials: findings from theory and simulation. The European Physical Journal B, 2015. 88(4): p. 1-12.

[27]. Lee, J.-H. and J.C. Grossman, Thermoelectric properties of nanoporous Ge. Applied Physics Letters, 2009. 95(1): p. 013106.

[28]. Bux, S.K., et al., Mechanochemical synthesis and thermoelectric properties of high quality magnesium silicide. Journal of Materials Chemistry, 2011. 21(33): p. 12259-12266.

[29]. Wunderlich, W., et al., Thermoelectric Properties of Mg2Si Produced by New Chemical Route and SPS. Inorganics, 2014. 2(2): p. 351.

[30]. Yang, M., L. Zhang, and Q. Shen, Synthesis and sintering of Mg2Si thermoelectric generator by spark plasma sintering. Journal of Wuhan University of Technology-Mater. Sci. Ed., 2008.23(6): p. 870-873.

[31]. Lee, S.-M., D.G. Cahill, and R. Venkatasubramanian, Thermal conductivity of Si–Ge superlattices. Applied Physics Letters, 1997. 70(22): p. 2957-2959.

[32]. Joshi, G., et al., Enhanced thermoelectric figure-of-merit in nanostructured p-type silicon germanium bulk alloys. Nano Letters, 2008. 8(12): p. 4670-4674.

[33]. Hou, Q.R., et al., Thermoelectric properties of higher manganese silicide films with addition of carbon. physica status solidi (a), 2006. 203(10): p. 2468-2477.

[34]. Kikuchi, Y.M.a.Y., ed. Thermoelectric Nanomaterials. Higher Manganese Silicide, MnSiγ. Vol. 182. 2013, Springer Series: Japan.

[35]. Tae-Ho, A., et al., The Effect of Microstructure on the Thermoelectric Properties of Polycrystalline Higher Manganese Silicides. Japanese Journal of Applied Physics, 2013. 52(10S): p. 10MC11.

[36]. 101. Truong, D.Y.N., Thermoelectric Properties of Higher Manganese Silicides, in Doctor of Philosophy in Chemistry 2015, University of Waterloo: Canada. p. 189.

[37]. Higgins, J.M., et al., Higher Manganese Silicide Nanowires of Nowotny Chimney Ladder Phase. Journal of the American Chemical Society, 2008. 130(47): p. 16086-16094.

[38]. Slack, G. A. (ed.) Solid State Physics (Academic Press, New York, 1979).

[39]. Dames, C. & Chen, G. in &ermoelectrics Handbook Macro to Nano (ed. Rowe, D. M.) Ch. 42 (CRC, Boca Raton, 2006).

[40]. Slack, G. A. in CRC Handbook of &ermoelectrics (ed. Rowe, M.) 407–440 (CRC, Boca Raton, 1995).

[41]. Auparay, N., Room Temperature Seebeck Coefficient Measurement of Metals and Semiconductors. 2013, Oregon State University. p. 23.

[42]. Zheng, J.-c., Recent advances on thermoelectric materials. Frontiers of Physics in China, 2008. 3(3): p. 269-279.

[43]. University of Tennessee, D.o.M.S.a.E., Electrical Properties.

[44]. Alexandre Polozine, Susanna Sirotinskaya, Lírio Schaeffer, "History of Development of Thermoelectric Materials for Electric Power Generation and Criteria of their Quality", Materials Research. 2014; 17(5): 1260-1267

[45]. G. Neeli, D. K. Behara, and M. K. Kumar, "State of the Art Review on Thermoelectric Materials," vol. 5, no. 10, pp. 1833–1844, 201

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