Review Article

Recent Developments in β - Zn_4Sb_3 Based Thermoelectric Compounds

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Received 9 April 2015; Revised 6 August 2015; Accepted 9 August 2015

Academic Editor: Matteo Ferroni

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Thermoelectricity has been recognized as an environmentally friendly energy conversion technology due to its ability to directly achieve conversion between heat and electricity for a long time. β - Zn_4Sb_3 has attracted considerable interest as promising thermoelectric material in the moderate temperature range (500 K–900 K), which is the temperature range of most industrial waste heat sources. In this paper, first we present the structure of β - Zn_4Sb_3 and the traditional doping strategy used to enhance its performance. Next, we review the details of some new methods utilized for improving the thermoelectric properties of β - Zn_4Sb_3 and its thermal stability as well as reliability. Finally, the review finishes with highlighting some promising strategies for future research directions in the material.

1. Introduction

During the last decade, due to their ability to convert heat into electricity directly as well as without moving parts or greenhouse emissions, thermoelectric materials have drawn much attention because of the energy crisis and the environmental concerns of fossil fuel use [1, 2]. When a temperature gradient is applied to a thermoelectric couple consisting of n-type and p-type materials, the charge carriers at the hot side will diffuse to the cold side, producing a thermoelectric voltage. This characteristic is the basis of thermoelectric power generation, known as the Seebeck effect. Conversely, when a voltage is applied to a thermoelectric couple, a temperature difference will be created. This characteristic is the basis of thermoelectric electronic refrigeration, known as the Peltier effect. The conversion efficiency of a thermoelectric material is qualified by the dimensionless figure of merit, ZT , defined as $ZT = (S^2/\rho\kappa)T$, where S , ρ , κ , and T are the Seebeck coefficient, electrical resistivity, thermal conductivity (including the lattice thermal conductivity κ_L , and the carrier thermal conductivity κ_e), and absolute temperature, respectively [3, 4]. A good thermoelectric material should

possess a high power factor $PF (=S^2/\rho)$ and low thermal conductivity. Typically, there are two strategies to improve the ZT of thermoelectric materials: one is to lower the thermal conductivity κ and the other is to boost the PF .

Thermoelectric materials are normally classified into four categories depending on their temperature range of application: (1) cryogenic temperature range: from 4 K to 250 K; (2) near room-temperature range: from 250 K to 500 K; (3) intermediate temperature range: from 500 K to 900 K; and (4) high temperature range: beyond 900 K. As intermediate temperature range is just the temperature range of most industrial waste heat sources, it is very important to research high ZT intermediate thermoelectrics. Among the wide variety of intermediate temperature materials, β - Zn_4Sb_3 compounds with low thermal conductivity and made of relatively cheap and nontoxic elements are pointed out as one kind of most promising thermoelectric materials [5–7].

The ideal thermoelectric material should be a “phonon-glass and electron crystal” material, which possesses electronic properties similar to a good semiconductor single crystal but has thermal properties associated with amorphous materials [8–12]. β - Zn_4Sb_3 , the p-type intermetallic

FIGURE 1: (a) Thermoelectric figure of merit and (b) thermal conductivity of $\beta\text{-Zn}_4\text{Sb}_3$ compared with other materials. Reproduced with permission from [16]. Copyright 2004, Nature Publishing Group.

compound which is most suitable for use as a state-of-the-art material at moderate temperatures, is one of the three modifications of Zn_4Sb_3 . Zn_4Sb_3 is known to have three structural phases, namely, α -, β -, and γ - Zn_4Sb_3 , which are stable below 263 K, between 263 K and 765 K, and above 765 K, respectively [13]. The highest ZT value reported for $\beta\text{-Zn}_4\text{Sb}_3$ is 1.40 at 675 K [13–15]. The power factor in $\beta\text{-Zn}_4\text{Sb}_3$ is reasonably high ($\sim 13 \text{ W m}^{-1} \text{ K}^{-2}$ at 675 K) while it possesses a remarkable “phonon-glass” behavior, characterized by an unusually low thermal conductivity of $\sim 0.9 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K, comparable to that of a glass [13], as shown in Figure 1.

The organization of the review is as follows. First, we would like to provide some important backgrounds by introducing the structure of $\beta\text{-Zn}_4\text{Sb}_3$ and highlight traditional doping method previously used in order to enhance the thermoelectric properties of $\beta\text{-Zn}_4\text{Sb}_3$. We then will review the recent progress in $\beta\text{-Zn}_4\text{Sb}_3$ in details, including the energy filtering effect, distortion of the electronic density of states, *in situ* nanostructures, and its thermal stability. Finally, we identify strategies and research directions which could lead to further research in the material.

2. Structure of $\beta\text{-Zn}_4\text{Sb}_3$ and Traditional Doping Strategy to Enhance ZT for $\beta\text{-Zn}_4\text{Sb}_3$

The detailed crystal structure of $\beta\text{-Zn}_4\text{Sb}_3$ has been determined by using both single-crystal and powder X-ray diffraction methods coupled with maximum entropy analysis [16, 27]. The $\beta\text{-Zn}_4\text{Sb}_3$ has the hexagonal rhombohedral crystal structure and lattice constants are $a = 12.231 \text{ \AA}$ and $c = 12.428 \text{ \AA}$ with a $R\bar{3}c$ space group [28]. To date, there are mainly two different models (*Mayer model* [29] and *three-interstitial model* [16]) to explain the crystal structure of $\beta\text{-Zn}_4\text{Sb}_3$ unit cell. In the three-interstitial model, the mass density and composition of the crystal structure are reported to be in agreement with measurements [30, 31]. In the experimentally determined $\beta\text{-Zn}_4\text{Sb}_3$ unit cell, it contains

30 Sb atoms, but there are four in equilibrium Zn positions with partial occupations: a deficiency of Zn1 site with $\sim 90\%$ occupancy and interstitial Zn2, Zn3, and Zn4 sites with $\sim 5\%$ occupancy to balance the stoichiometry; thus, the number of Zn in the unit cell is 39 [16, 29]. From the experimental crystal structure analysis, the stoichiometry of $\beta\text{-Zn}_4\text{Sb}_3$ is actually $\text{Zn}_{39}\text{Sb}_{30}$ or $\text{Zn}_{13}\text{Sb}_{10}$, as shown in Figure 2 [17, 27]. As the Zn interstitials exhibit large thermal displacements, the glass-like interstitials are mainly responsible for the phonon damping that suppresses the lattice thermal conductivity. There is apparently Sb disorder along the c -axis that can contribute to the glass-like thermal conductivity. Electronic structure and transport calculations using the crystal structure obtained have identified the compound as a p-type semiconductor [27], which is in agreement with experimental findings of the doping trend. It is demonstrated that the Zn interstitial atoms play a dual role as electron donors and thermopower enhancers. First-principles calculations of electronic structure and thermoelectric properties have also been performed [32]. The band structure results reveal the covalent tendency of the compound, consistent with the good carrier mobility measured. It is believed that the Zn disorder in the structure and the three interstitial partially occupied Zn sites attribute to its low thermal conductivity. And the high Seebeck coefficient can be attributed to the strong energy-dependence of the Fermi surface topology near band-filling [32].

Although $\beta\text{-Zn}_4\text{Sb}_3$ has been identified as an excellent thermoelectric material with glass-like thermal conductivity, further improvements of thermoelectric performance are of importance to practical applications. It is well known that the power factor has an optimum versus the carrier concentration. Doping is an effective approach to optimize the thermoelectric properties by adjusting the carrier concentration. In recent years, enhanced power factors through doping optimization are achieved in $\beta\text{-Zn}_4\text{Sb}_3$. Conventional doping such as the substitutions of Pb [33, 34], Bi [35], Nb [36], Mg [37], Cu [38], Cd [39, 40], Sn [33, 41], In [33, 34, 42, 43], Al [42, 44], Ga [42, 44], Ag [38, 45], Hg [46], Fe [47], Te [48],

TABLE 1: List of composition, Seebeck coefficient S , total thermal conductivity κ , and maximum ZT_m obtained from the literatures.

Reference	Composition	S ($\mu\text{V/K}$) ^a (300 K)	κ (W/Km) ^b (300 K)	ZT_m ^c
[34]	$\text{Pb}_{0.02}\text{Zn}_4\text{Sb}_3$	140	0.65	1.12 (605 K)
[36]	$(\text{Zn}_{0.995}\text{Nb}_{0.005})_4\text{Sb}_3$	118	0.71	1.10 (680 K)
[39]	$\text{Zn}_{3.2}\text{Cd}_{0.8}\text{Sb}_3$	—	0.5	1.40 (520 K)
[46]	$\text{Zn}_{3.96}\text{Hg}_{0.04}\text{Sb}_3$	250	1.0	0.30 (300 K)
[47]	$(\text{Zn}_{0.995}\text{Fe}_{0.005})_4\text{Sb}_3$	130	1.0	0.11 (300 K)
[48]	$\text{Zn}_4(\text{Sb}_{0.995}\text{Te}_{0.005})_3$	118	0.76	1.08 (680 K)
[61]	$f(\text{Cu}_3\text{SbSe}_4)/\text{Zn}_4\text{Sb}_3$, $f = 15$	200	1.2	1.23 (648 K)
[21]	$f(\text{Cu}_3\text{SbSe}_4)/\text{Zn}_4\text{Sb}_3$, $f = 3$	120	0.45	1.37 (648 K)
[23]	$(\text{Zn}_{0.998}\text{Sm}_{0.002})_4\text{Sb}_3$	118	0.72	1.10 (615 K)
[78]	$(\text{Zn}_{0.998}\text{Pr}_{0.002})_4\text{Sb}_3$	118	0.83	0.65 (615 K)

^a S is Seebeck coefficient; ^b κ is total thermal conductivity; ^c ZT_m is the maximum ZT value.

FIGURE 2: Crystal structure of (a) $\beta\text{-Zn}_4\text{Sb}_3$ in space group $R\bar{3}c$ with all atoms in full occupancy, the interstitial Zn atoms are presented in smaller spheres, and (b) the $\text{Zn}_{13}\text{Sb}_{10}$ model with occupancy close to the experimental value. Reproduced with permission from [17]. Copyright 2010, American Physical Society.

and Se [49] for $\beta\text{-Zn}_4\text{Sb}_3$ have been investigated. As listed in Table 1, the composition, Seebeck coefficient S , total thermal conductivity κ , and maximum ZT_m reported in some typical literatures are given. The results show that the doping causes a limited improvement of its thermoelectric performance. And it is also found that doping in $\beta\text{-Zn}_4\text{Sb}_3$ is not always beneficial. Liu et al. [34] and Tsutsui et al. [43] investigated the effects of Al, Ga, and In doping on the thermoelectric properties of $\beta\text{-Zn}_4\text{Sb}_3$, respectively. They found that the substitutions increase both the electrical resistivity and the Seebeck coefficient, resulting in a reduction in ZT finally. Pedersen et al. [46] investigated the thermoelectric properties of $\text{Hg}_{0.04}\text{Zn}_{3.96}\text{Sb}_3$, which shows that the Hg doping has a minor influence on the transport properties of $\beta\text{-Zn}_4\text{Sb}_3$ and ZT remains unchanged for both the undoped and the Hg-doped samples.

3. New Strategies to Enhance ZT for $\beta\text{-Zn}_4\text{Sb}_3$

Recently some special physical ideas related to band structure engineering are introduced in thermoelectric research, such

as energy filtering effect (EFE) in PbTe-based nanocomposites embedded with Pb nanoparticles [50, 51], distortion of the electronic density of states (DOS) in Tl doped PbTe [52], and nanostructure approach. In the following we will discuss these new methods in both theory and experiments in the sphere of $\beta\text{-Zn}_4\text{Sb}_3$ based thermoelectric materials.

3.1. Through Energy Filtering to Enhance Thermoelectric Performance in $\beta\text{-Zn}_4\text{Sb}_3$ Based Nanocomposites

3.1.1. Concept and Theory. According to Mott equation, thermopower of a degenerate semiconductor can be expressed as

$$\begin{aligned}
 S &= \frac{\pi^2 k_B^2 T}{3q} \left[\frac{\partial \ln(\sigma(E))}{\partial E} \right]_{E=E_f} \\
 &= \frac{\pi^2 k_B^2 T}{3q} \left[\frac{1}{p} \frac{\partial p(E)}{\partial E} + \frac{1}{\mu} \frac{\partial \mu(E)}{\partial E} \right]_{E=E_f}
 \end{aligned} \tag{1}$$

with carrier mobility $\mu(E) = q\tau/m^*$, where σ is the electrical conductivity, q the carrier charge, E the energy, $p(E)$ and

FIGURE 3: Calculated normalized Seebeck distribution versus energy for heavily doped bulk n-type $\text{Si}_{80}\text{Ge}_{20}$. Reproduced with permission from [18]. Copyright 2009, Royal Society of Chemistry.

$\mu(E)$ energy dependent carrier density and mobility, k_B the Boltzmann constant, m^* the effective mass, and E_f the Fermi energy. Assuming relaxation time τ has power law relation to scattering parameter λ , that is, $\tau = \tau_0 E^{\lambda-1/2}$ (where τ_0 means an energy-independent constant) [53], increasing the scattering time's energy-dependence, $d\tau(E)/dE$, can result in an increase in the energy-dependence of the mobility $d\mu(E)/dE$ through preferentially scattering electrons depending on their energy. In a nanocomposite system, the obvious scattering mechanism to increase the scattering parameter is grain boundary scattering and interface scattering, which can reduce the carrier mobility and preferentially scatters carriers with energies lower than the barrier height [54]. As shown in Figure 3, Minnich et al. calculated the normalized Seebeck distribution versus energy for heavily doped bulk n-type $\text{Si}_{80}\text{Ge}_{20}$ and the results show that low energy electrons will reduce the thermopower because this portion of the Seebeck distribution of low energy electrons is negative [18]. EFE is a good example of how nanostructured materials can be used to improve electrical transport properties by scattering low energy charge carriers while still maintaining low thermal conductivity [55–57].

In metal-based InGaAs/InGaAlAs superlattices, Vashae and Shakouri's work shows that metal-based superlattices with tall barriers can achieve a large ZT (>5) at room temperature through a detailed calculation [58]. Faleev and Léonard used perturbation theory and partial wave method to investigate PbTe based composites dispersed with Pb nanoparticles, and they assume that the electron scattering on spherically symmetrical interface potentials is independent of other scattering mechanisms. The calculated thermopower they got is larger than that of bulk PbTe matrix [59]. Yang and Qin have first proposed a concept of “synergetic scattering” of carriers in a semiconductor matrix dispersed with metallic nanoinclusions [19, 60]. They calculated the scattering parameter and thermopower in both single scattering and

FIGURE 4: (a) Dependences of λ_0 on radius of the metal sphere and the barrier height for synergetic scattering at ionized impurities and the interface potential barriers. (b) Variations in λ_0 with well depth and radius of spherical Pb particles for synergetic scattering at interface potential wells in n-type PbTe/Pb nanocomposites at 300 K. Reproduced with permission from [19]. Copyright 2010, American Institute of Physics.

synergetic scattering of the interface potential barriers and wells formed because of the dispersed nanoinclusions in the matrix. The results indicate that the synergetic scattering of electrons at ionized impurities and the interface potential barriers or wells can produce great scattering parameter and enhanced thermopower. The effects of nanoinclusion radius and energy dispersion relations on the scattering parameter are given in Figure 4.

Theoretically if different types of semiconductors dispersed in a semiconductor matrix to form nanocomposites, two kinds of heterojunctions (nN type and Nn type) will be configured. In principle, the potential energies for carriers in the heterojunctions can be derived by the Thomas-Fermi approximation and depletion layer approximation. The calculation results indicate that scattering parameters depend on temperature T , radii of spheres r , and electron concentrations

FIGURE 5: Calculated Seebeck coefficient as a function of temperature in the case of (a) Nn type and (b) nN type for $n = 0.2 \times 10^{20} \text{ cm}^{-3}$ and $r_0 = 10 \text{ nm}$ (○), 20 nm (△), 30 nm (◇), and 40 nm (☆). The upper curves are for single scattering; the lower curves correspond to synergetic scattering. Reproduced with permission from [20]. Copyright 2013, Elsevier.

n . Seebeck coefficients calculated for synergetic scattering are enhanced compared to those for the single scattering, as shown in Figure 5 [20]. The results demonstrate that heterojunction potentials in semiconductor-based nanocomposites with semiconducting inclusions can give rise to enhanced EFE, which can boost thermopower and thermoelectric performance of the nanocomposite systems.

3.1.2. Experiments Achieved in $\beta\text{-Zn}_4\text{Sb}_3$ Based Nanocompounds. Experimentally, Zou et al. found that EFE can boost the Seebeck coefficient in $f((\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8})/\beta\text{-Zn}_4\text{Sb}_3$ ($f = 0, 0.5, 1$, and $2 \text{ vol.}\%$) nanocompounds and $f(\text{Cu}_3\text{SbSe}_4)/\beta\text{-Zn}_4\text{Sb}_3$ ($f = 0, 1, 3, 5$, and $6 \text{ vol.}\%$) nanocompounds [21, 61], especially in hierarchical nanostructured $\beta\text{-Zn}_4\text{Sb}_3\text{-Cu}_3\text{SbSe}_4$. Through coprecipitation method they got nanoscale inclusions Cu_3SbSe_4 . Cu_3SbSe_4 is another important thermoelectric material with large effective mass and small

band gap in intermediate temperature range [62–67]. Normally if carrier concentration is enhanced, electronic conductivity will be increased and the Seebeck coefficient should be decreased. However, they observed that the thermopower of nanocomposites increases compared with that of the pure $\beta\text{-Zn}_4\text{Sb}_3$, while electronic conductivity increases obviously compared with that of the pure $\beta\text{-Zn}_4\text{Sb}_3$. They calculated λ by using a single parabolic band model, in which effective masses m_d^* and S can be expressed as [13]

$$m_d^* = \frac{h^2}{2k_B T} \left(\frac{p}{4\pi F_{1/2}(\xi_F)} \right)^{2/3}, \quad (2)$$

$$S = \frac{k_B}{e} \left[\frac{[(\lambda + 2) F_{\lambda+1}(\xi_F)]}{[(\lambda + 1) F_{\lambda}(\xi_F)]} - \xi_F \right]$$

with Fermi integral of order i :

$$F_i(\xi_F) = \int_0^\infty \frac{x^i}{1 + e^{(x - \xi_F)}} dx, \quad (3)$$

where h is the Planck constant, ξ_F is the reduced Fermi level $E_f/(k_B T)$, n is the carrier density, e is electron charge, λ is scattering parameters, and k_B is the Boltzmann constant. The calculation results are shown in Figure 6.

In the experiment, increased PF comes from both enhanced Seebeck coefficient because of intensified EFE caused by potential barriers formed at phase boundary between $\beta\text{-Zn}_4\text{Sb}_3$ matrix and nanoscale Cu_3SbSe_4 inclusions and moderate reduction of hall carrier mobility due to hierarchical structures of the nanoscale inclusions, as shown in Figure 7. At room temperature, the band gap E_g of dispersed phase Cu_3SbSe_4 is $0.3\text{--}0.4 \text{ eV}$ [63, 68], which is larger than that (0.26 eV) of matrix $\beta\text{-Zn}_4\text{Sb}_3$ [17]. When they contact each other, due to band bending (the schematic at the bottom in Figure 7(b)) caused by the transfer of holes from dispersed phase Cu_3SbSe_4 to the matrix $\beta\text{-Zn}_4\text{Sb}_3$ to guarantee the equal chemical potentials on both sides, valence band offset appears at heterojunction interfaces (Figure 7(a)) and p-p type heterojunction barriers form at the interface in the nanocomposites. Due to significant increase in PF and drastic reduction in thermal conductivity, ZT reaches 1.37 at 648 K in the composite system with $5 \text{ vol.}\%$ of nanophase Cu_3SbSe_4 . Present results demonstrate that simultaneous enhancement of power factor and phonon blocking can be achieved via proper design of a material system and its microstructures, resulting in large increase in ZT of a material system.

3.2. Through Resonant Levels to Enhance the Density of Electrical States

3.2.1. Concept and Theory. From (1), the second approach to enhance the Seebeck coefficient is the introduction of resonant distortion of electrical density of states near the Fermi level (E_f) reflected by increased effective mass m^* . The use of impurity band energy levels to increase the thermopower has resulted in an obvious increase in ZT value [52, 69]. Previously resonant impurity is a concept introduced in solid state physics for metals [70–72]. Theoretically Hicks

FIGURE 6: (a) Variation of scattering parameter λ with Cu_3SbSe_4 content at 300 K. (b) Variation of Seebeck coefficient with carrier concentration for $f(\text{Cu}_3\text{SbSe}_4)/\beta\text{-Zn}_4\text{Sb}_3$ ($f = 0, 1, 3, 5$, and 6 vol.%) at 300 K. The solid line is Pisarenko relation for $\beta\text{-Zn}_4\text{Sb}_3$. Reproduced with permission from [21]. Copyright 2014, American Institute of Physics.

FIGURE 7: Cross sectional schematics of (a) the energy bands for Cu_3SbSe_4 (band gap E_{g1}) and $\beta\text{-Zn}_4\text{Sb}_3$ matrix (band gap E_{g2}) before contact (where E_{c1} and E_{c2} are the conduction band bottoms and E_{v1} and E_{v2} are the valence band tops), and (b) p-p type interface potential barriers (lower schematic) with an effective barrier height V_{eff} formed from band bending, where the upper schematic shows the corresponding Cu_3SbSe_4 particle with hierarchical nanostructures embedded in $\beta\text{-Zn}_4\text{Sb}_3$ matrix, where dP is the particle size of Cu_3SbSe_4 , and μ_1 , μ_2 , and μ are the chemical potentials for the inclusions, matrix, and the composite system, respectively. Reproduced with permission from [21]. Copyright 2014, American Institute of Physics.

and Dresselhaus [73] and Mahan and Sofo [74] predict an enhancement in thermoelectric properties due to an increase in the electronic density of states first. The resonant level can be regarded as a bound level with an energy that falls above the conduction band edge or below the valence band edge [22], creating a local maximum in the density of states, as shown in Figure 8. The figure represents schematically the case for In:PbTe , where the resonant states are in the conduction band. Band structure calculations show that not only impurities create sharp DOS peaks close to the Fermi

level, but also those peaks should be of the similar character as the host band structure. Results show that d- or even f-state impurities are useful to improve the thermopower of metals, but s- or p-state resonance levels are more suited to improve thermoelectric properties of semiconductors [75–77].

3.2.2. Experiments Achieved in $\beta\text{-Zn}_4\text{Sb}_3$ Based Compounds. Wang et al. investigated thermoelectric properties of Sm-doped compounds $\beta\text{-(Zn}_{1-x}\text{Sm}_x)_4\text{Sb}_3$ ($x = 0, 0.001, 0.002$, and 0.003) and Pr-doped compounds $\beta\text{-(Zn}_{1-x}\text{Sm}_x)_4\text{Sb}_3$

FIGURE 8: Schematic energy versus distance diagram where the spheres on the bottom represent atoms. The periodic potential of the host atoms of the solid is experienced by conduction electrons and results in the formation of conduction and valence bands, extended states available to the nearly-free electrons. Reproduced by permission from [22]. Copyright 2012, Royal Society of Chemistry.

($x = 0, 0.001, 0.002$, and 0.003) at the temperatures from 300 K to 615 K [23, 78]. The results indicate that Sm doping and Pr doping can cause the resonant distortion of density of states of β - Zn_4Sb_3 and result in about a 2-fold increase in effective mass m_d^* of β - Zn_4Sb_3 in these two compounds. Sm doping and Pr doping result in $\sim 50\%$ and $\sim 65\%$ increases of the Seebeck coefficient for the doped samples, compared with that ($\sim 75 \mu\text{V/K}$) of the undoped sample. Furthermore, thermal conductivity decreases substantially by Sm doping and Pr doping.

They observed an interesting phenomenon that the thermopower of nanocomposites increases minorly compared with that of the pure β - Zn_4Sb_3 , as shown in Figure 9. The obtained effective mass m_d^*/m_e (where m_e is the free electron mass) as functions of temperature in the temperature range of 300 K to 615 K is shown in Figure 10(a). The solid line in Figure 10(b) is carrier concentration dependence of thermopower for the undoped β - Zn_4Sb_3 , which is calculated by using formulae (2) for $m_d^* = 1.47 m_e$. And this resonant distortion of DOS results in obvious increase in thermopower for the doped compounds at room temperature, as shown in Figure 10(b). The larger effective masses indicate that there is strong resonant distortion of DOS around the Fermi level. These data are above the black line, including the experimentally measured Seebeck coefficient of the Sm doped at room temperature in Figure 10(b), indicating strong DOS resonant distortion effect achieved. Finally, ZT value of β -($\text{Zn}_{1-x}\text{Sm}_x$) $_4\text{Sb}_3$ ($x = 0.002$) is about 53% larger than that of the undoped sample and reaches 1.10 at 615 K in the study.

3.3. Through Melt Spinning-Spark Plasma Sintering (MS-SPS) to Get In Situ Nanostructures. Over the past decade, one successful strategy that has been used to boost the performance

is nanostructure in several thermoelectric materials, and the nanostructure approach significantly enhances the ZT values by drastically reducing the lattice thermal conductivity [73–84]. Recently, it is reported that, in addition to the reduction of the lattice thermal conductivity, nanostructure can also increase the power factor in some nanocomposites [85–87]. In other words, it is possible that in some material systems the three interrelated thermoelectric properties can be uncoupled by introducing nanostructures. High-energy ball milling [88] and melt spinning (MS) [80, 81, 89–94] techniques have been utilized to produce nanostructured bulk materials (nanosize powders or precursors containing nanoinclusions) for commercial applications, and the corresponding bulk compacted materials with nanoinclusions show notably improved ZT values.

Wang et al. used MS-SPS (melt spinning-spark plasma sintering) technique to prepare nanostructured β - Zn_4Sb_3 compounds with minute Cd-doping [24]. As shown in Figure 11(a), each ribbon is composed of two different surfaces: one is contact surface which directly contacts the copper roller and the other is the free surface. Figure 11(c) displays the morphology of the free surface and Figure 11(d) displays the corresponding high-resolution picture for MS ribbon. Many flower-like clusters of nanosheets or nanoneedles are distributed on the free surface, and these ~ 10 nm nanosheets or nanoneedles grow perpendicular to the surface. These $\sim 1 \mu\text{m}$ flower-like clusters are adhered to the surface of ribbon.

The MS-SPS technique generates multiscale nanostructures in the ribbon-shape samples and the compacted bulk materials. Figure 12 shows the microstructures of the undoped MS-SPS bulk sample. These unique multiple nanostructures result in reductions in lattice thermal conductivities, particularly for samples with some ZnSb nanodots with sizes of 10–30 nm, as displayed in Figure 12(a). These nanostructures originate from the multiscale nanostructures in melt spinning ribbons, as well as the subsequent chemical reactions during the following spark plasma sintering process [28]. High-resolution transmission electron microscopy observations were used on the undoped MS-SPS bulk sample and are presented in Figures 12(b)–12(d).

In the MS-SPS experiments, Cd-doping affects the electrical properties by minorly reducing the electrical conductivity and distinctly increasing the thermopower. As a result, the nonstructural strategy combined with the Cd-doping remarkably improves the final figure of merit. A peak ZT value of 1.30 is achieved for ($\text{Zn}_{0.99}\text{Cd}_{0.01}$) $_4\text{Sb}_3$ sample at 700 K, which is $\sim 13\%$ and $\sim 23\%$ larger than the undoped MS-SPS sample and the 1% Cd-doped melt ingot at the same temperature.

4. Recent Research about Stability and Reliability of β - Zn_4Sb_3 for Commercialization

Stability and reliability are very important requirements for a candidate thermoelectric material to practical application. Several studies have focused on the thermal stability and

FIGURE 9: Temperature dependence of (a) electrical resistivity and (b) thermopower. Reproduced with permission from [23]. Copyright 2013, American Institute of Physics.

FIGURE 10: (a) Temperature dependence of the ratio of density of states effective mass m_d^* to that of the free electron. (b) Variation of thermopower with carrier concentration for β -($\text{Zn}_{1-x}\text{Sm}_x$) $_4\text{Sb}_3$ ($x = 0, 0.001, 0.002$, and 0.003). Reproduced with permission from [23]. Copyright 2013, American Institute of Physics.

decomposition process of β - Zn_4Sb_3 [95–98]. *Ab initio* calculations [99, 100] and multitemperature synchrotron powder X-ray diffraction measurements [101] suggest a decomposition process: $\text{Zn}_4\text{Sb}_3 \rightarrow 3\text{ZnSb} + \text{Zn}$. Some studies have proposed a starting temperature of 500 K for decomposition of β - Zn_4Sb_3 into ZnSb and Zn [102–104] while some research reported instabilities of β - Zn_4Sb_3 that have also happened below 500 K [105, 106]. On the other hand, there are experimental reports of an outstanding ZT of about 1.30 at around

670 K for pure β - Zn_4Sb_3 [107, 108]. In the following we will show two typical studies about stability and reliability of β - Zn_4Sb_3 .

4.1. Highly Enhanced Thermal Stability Achieved in β - Zn_4Sb_3 - TiO_2 Nanocomposites. Yin et al. investigated impact of nano-sized TiO_2 and ZnO ceramic inclusions on the high temperature stability of β - Zn_4Sb_3 by using multitemperature synchrotron powder X-ray diffraction [25]. The test temperature

FIGURE 11: (a) Sketch of the MS process; (b) photograph of the MS ribbons; (c)–(f) FESEM images and the corresponding high-resolution images for MS ribbon; (c, d) showing the free surface and (e, f) the contact surface. Reproduced with permission from [24]. Copyright 2011, Elsevier Ltd.

of the experiment is up to 625 K. In their study, it is observed that 9 nm TiO_2 nanoparticles dispersed in $\beta\text{-Zn}_4\text{Sb}_3$ powder can effectively block the mobile Zn atoms to improve the stabilization of the samples. The stabilization effect of 80 nm ZnO nanoparticles is much worse than that of 9 nm TiO_2 , indicating that the stability of the nanocomposites depends on the size of the nano-inclusions as well, as illustrated in Figure 13(a). From Figure 13(b) we can see that, after three heating cycles, samples with 9 nm TiO_2 nano-inclusions still keep remarkable stability. The experiments show us that Zn atoms diffusion is the main factor responsible for the decomposition of $\beta\text{-Zn}_4\text{Sb}_3$ synthesized by quenching [101]. Because TiO_2 is a kind of cheap and available nanoparticles, it seems to be a promising method for the thermal stability of $\beta\text{-Zn}_4\text{Sb}_3$. Although the nanocomposites exhibit an obvious improvement in thermal stability, they show a significant degradation of the thermoelectric properties at

the same time. Increased resistivity and thermal conductivity and reduced thermopower resulted in ZT value decreasing from 0.7 for pure $\beta\text{-Zn}_4\text{Sb}_3$ to 0.3 for the $\beta\text{-Zn}_4\text{Sb}_3\text{-TiO}_2$ nanocomposites at 575 K. So, in order to take advantage of the thermal stabilization, another method useful for the thermoelectric properties for the nanocomposite is needed to introduce into the material system.

4.2. Unexpected High-Temperature Stability of $\beta\text{-Zn}_4\text{Sb}_3$.

Recently, Lin et al. investigated the fabrication of single-phase $\beta\text{-Zn}_4\text{Sb}_3$ and its thermoelectric transport across a wide temperature range [26]. The time-temperature-transformation curve of $\beta\text{-Zn}_4\text{Sb}_3$ can be described in Figure 14(a). If $\beta\text{-Zn}_4\text{Sb}_3$ is heated along the red curve to 425 K, there is the first transition around 425 K. After 425 K, the Zn–Sb bonds of $\beta\text{-Zn}_4\text{Sb}_3$ will break, allowing significant diffusion of Zn atoms. In the process, Zn atoms can depart from crystalline sites

FIGURE 12: (a) Field emission scanning electron microscopy image of the fracture surface of the MS-SPS neat bulk sample; ((b)–(d)) high-resolution transmission electron microscopy images for the neat bulk sample. Reproduced with permission from [24]. Copyright 2011, Elsevier Ltd.

FIGURE 13: (a) Refined weight fractions of β - Zn_4Sb_3 phase as a function of temperature during the first heating cycle. Data for a pure sample are shown for comparison. (b) Refined weight fraction of β - Zn_4Sb_3 phase for all nanocomposites during thermal cycles. Data for a pure sample are shown for comparison. Reproduced by permission from [25]. Copyright 2013, Royal Society of Chemistry.

FIGURE 14: (a) Schematic of the time-temperature-transformation curve for β - Zn_4Sb_3 and (b) microstructure of after different heat treatments following rapid cooling. Reproduced with permission from [26]. Copyright 2013, American Chemistry Society.

to interstitial positions. Then β - Zn_4Sb_3 becomes metastable and gradually decomposes into Zn and ZnSb phase, respectively. Microstructure of β - Zn_4Sb_3 following different heat treatments after rapid cooling is shown in Figure 14(b). At room temperature grain boundaries and inner grains are both obvious. After a 523 K heat treatment, nanostructures with sizes around 30 nm are found in the inner grain which are derived from the decomposition of β - Zn_4Sb_3 [109]. In the experiments, additional phonon scattering results in a significant decline of thermal conductivity above 425 K. When the temperature reaches 565 K, Zn begins to react with ZnSb above the second transition temperature again. β - Zn_4Sb_3 becomes thermodynamically stable and the damage caused by decomposition can be recovered as well. This is the reason for its state-of-the-art thermoelectric performance at high temperature: the maximum ZT value reaches 1.40 at 748 K. Since the thermal stability is a prerequisite for thermoelectric application, the study provides insight into the search of new high-temperature thermoelectric materials.

5. Conclusion and Outlook

In this paper, we have briefly reviewed the recent progress and advances in β - Zn_4Sb_3 based thermoelectric materials. The thermoelectric properties are enhanced significantly by band structure engineering (DOS distortion) and nanostructuring (EFE and phonon scattering). However, bipolar effect, which is not thermoelectric favorable, will be very obvious at high temperature [61, 110, 111]. The bipolar effect derives from the truth that there are two types of carriers, electrons and holes. At high temperature some electrons are thermally excited from the valence band to the conduction band, resulting in an equal number of holes. As holes and electrons have opposite charges, the thermopower will be suppressed if electrons

and holes are both present. Thus, reducing the bipolar effect can improve the figure of merit of β - Zn_4Sb_3 by creating a nanostructure which scatters minority carriers preferentially [18]. Even though both the resonant distortion of density of states of electron and the energy filtering effect can enhance the Seebeck coefficient or ZT , successful joining of the two approaches to improve the thermoelectric performance is still elusive. If we can join the two effects in one system to enhance its thermopower and thermoelectric properties, then we may provide a new mechanism to prepare high performance thermoelectric materials.

Conflict of Interests

The authors declare that they have no conflict of interests.

Acknowledgments

Tianhua Zou, Wenjie Xie, Jian Feng, and Anke Weidenkaff gratefully acknowledge the Deutsche Forschungsgesellschaft within the DFG Priority Program SPP 1386 for financial support. Xiaoying Qin acknowledges financial support from National Natural Science Foundation of China (nos. 11174292, 11374306, and 51101150) gratefully.

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