A review of CoSb₃-based skutterudite thermoelectric materials

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Abstract: The binary skutterudite CoSb₃ is a narrow bandgap semiconductor thermoelectric (TE) material with a relatively flat band structure and excellent electrical performance. However, thermal conductivity is very high because of the covalent bond between Co and Sb, resulting in a very low ZT value. Therefore, researchers have been trying to reduce its thermal conductivity by the different optimization methods. In addition, the synergistic optimization of the electrical and thermal transport parameters is also a key to improve the ZT value of CoSb₃ material because the electrical and thermal transport parameters of TE materials are closely related to each other by the band structure and scattering mechanism. This review summarizes the main research progress in recent years to reduce the thermal conductivity of CoSb₃-based materials at atomic-molecular scale and nano-mesoscopic scale. We also provide a simple summary of achievements made in recent studies on the non-equilibrium preparation technologies of CoSb₃-based materials and synergistic optimization of the electrical and thermal transport parameters. In addition, the research progress of CoSb₃-based TE devices in recent years is also briefly discussed.

Keywords: skutterudite; CoSb₃-based materials; lattice thermal conductivity; synergistic optimization; thermoelectric properties; thermoelectric devices

1 Introduction

Thermoelectric (TE) materials can directly convert thermal energy to electrical energy, which have attracted wide attention due to their fascinating applications in power generation and refrigeration [1–4]. The performance of TE materials is characterized by the dimensionless figure of merit ZT ($ZT = \sigma\alpha^2T/\kappa$), which

is mainly determined by the Seebeck coefficient (α), electrical conductivity (σ), and thermal conductivity (κ), where T is the absolute temperature, and $\sigma\alpha^2$ is the power factor. α and σ are decided by the electronic structure and carrier transport properties (Hall coefficient R_H , carrier concentration n , carrier mobility μ_H), which are used to characterize the electrical transport properties of the material. κ is the thermal conductivity written as the sum of electronic (κ_E) and lattice (κ_L) components, which is used to characterize the thermal transport properties of the material. High $\sigma\alpha^2$ and low κ are required to obtain high ZT . However, these parameters

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are closely related to each other and mutually constrained by the band structure and the scattering mechanism. Therefore, it is very difficult to decouple the electrical and thermal performance parameters. The κ_E is closely related to the σ according to the Wiedemann–Franz law $\kappa_E = L\sigma T$, while the κ_L is less related to the electrical transport properties. Therefore, researchers initially used various optimization methods to reduce the κ_L of materials, which is a very effective way to improve the ZT values. The κ_L of TE materials has been significantly reduced by alloying, element filling, the introduction of nanoscale second-phase, nano-interface or nanopore, copper ion-like behavior, and anharmonic phonon coupling [5–12]. It can even be reduced to near the theoretical minimum [7]. The electrical transport properties of TE materials can be also effectively increased by energy band engineering, such as high energy valley degeneracy or energy band convergence, resonance energy level, Peierls distortion, electron orbit hybridization, energy filtering, multi-band optimization, and optimized bandwidth [13–20]. In recent years, the key to further improve the ZT value is to decouple the interrelated electrical and thermal transport parameters by the magnetic nanocomposite [21,22], all-scale hierarchical structuring, endotaxial nanostructuring and valence-band offset engineering, and hierarchical compositionally alloyed nanostructures [23–27]. According to the applicable temperature of TE materials, it can be divided into low-, medium-, and high-temperature TE materials. Skutterudite is recognized as the most promising TE material in the mid-temperature range due to its excellent electrical transport properties. Some research progresses [4,28–30] about skutterudite materials have been systematically reviewed in recent years. However, research progresses on how to reduce the thermal conductivity of CoSb₃-based TE materials at atomic-molecular scale and nano-mesoscopic scale, and how to optimize synergistically the electrical and thermal transport properties, are rarely reported.

Figure 1(a) shows the energy band structure of binary CoSb₃ TE material [31–34]. It can be seen that it is a narrow bandgap semiconductor material with a band gap of about 0.22 eV. Therefore, it has a large carrier concentration and electrical conductivity. In addition, CoSb₃ has a large carrier effective mass and Seebeck coefficient because of its flat energy band. However, the thermal conductivity of CoSb₃ is very high due to the covalent bond between Co and Sb (see Fig. 1(b)), resulting in a very low ZT value. Therefore,

Fig. 1 (a) Band structure (reproduced with permission from Ref. [31], © American Physical Society 2008) and (b–d) crystal structure of CoSb₃.

it has become the focus by reducing the thermal conductivity without deteriorating the electrical properties of the CoSb₃ material. As we mentioned above, the lattice component in thermal conductivity is independent of the electrical transport performance. Therefore, reducing lattice thermal conductivity by enhancing phonon scattering without causing significant changes in σ and α becomes a very effective way to increase the ZT value of CoSb₃ TE materials. In addition, some advanced preparation processes can also achieve the purposes of reducing the κ_L and increasing ZT value.

In this review, the main research progresses on how to reduce the thermal conductivity of CoSb₃-based materials at atomic-molecular and nano-mesoscopic scale in recent years were summarized. A simple summary of achievements made in recent studies on the non-equilibrium preparation technologies of CoSb₃-based materials and synergistic optimization of the electrical and thermal transport parameters was also provided. In addition, the investigations related to fabricating CoSb₃-based TE device have garnered a lot of attention in recent years. Therefore, we also briefly summarize the research progresses of CoSb₃-based TE devices in recent years.

2 Optimization of the thermal performance

CoSb₃ material has better electrical transport properties based on its band structure. However, thermal conductivity of CoSb₃ is very high due to the covalent bond between

Co and Sb (see Fig. 1(b)), resulting in a very low ZT value (only about 0.1). The κ_L of the single crystal CoSb_3 material at room temperature prepared by the Bridgman method is up to $10 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ [35]. Therefore, how to reduce the κ_L of CoSb_3 material is the key to improve the TE performance. The decrease of κ_L is mainly achieved at the atomic-molecular scale and the nano-mesoscopic scale.

2.1 Optimization at atomic-molecular scale

There are two main ways to reduce the κ_L of CoSb_3 -based materials at the atomic-molecular scale: (i) forming solid solution alloy by doping; (ii) introducing other atoms into the Sb_{12} icosahedral void of CoSb_3 to form the filled skutterudites.

Forming solid solution alloy by doping. As early as the 1950s, Ioffe and Ioffe [36] proposed that the formation of solid solution alloys by doping can effectively reduce the κ_L of materials. The cations (or anions) in the crystal structure of CoSb_3 can be partially replaced by similar atoms at Co or Sb site to form ternary or multicomponent solid solutions. The κ_L of solid solution formed by partial substitution is significantly decreased. This is mainly due to the existence of high concentration point defects in solid solution. A large number of point defects can significantly scatter phonons, thereby reducing the lattice thermal conductivity. These point defects mainly come from the fluctuations of mass and strain fields because of the difference of the mass and radius between the foreign atom and the guest atom. In the solid solution, the point defects caused by doping will lead to lattice distortion and strong phonon–phonon, free electron–phonon coupling based on the polaron theory [37–40]. Therefore, it is possible that the polaron theory can also effectively explain the decrease of κ_L caused by point defects.

In addition, Callaway [41] proposed a phenomenological model for the calculation of κ_L . A simplified version of Callaway model is given in Eq. (1):

$$\kappa_L = \frac{4\pi k_B}{v} \left(\frac{k_B T}{h} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\tau^{-1}(e^x - 1)} dx \quad (1)$$

where $x = h\omega/4\pi k_B T$ (ω is the phonon frequency, k_B is the Boltzmann constant), v is the phonon velocity, and θ_D is the Debye temperature, h is the Planck constant, τ is the effective relaxation time, and τ can be expressed by the following Eqs. (2)–(7) [41–47]:

$$\tau^{-1} = \frac{V}{4\pi v^3} (\Gamma_B + \Gamma_S) \bar{\omega}^4 + \frac{\gamma^2 h}{2\pi M v^2 \theta_D} \bar{\omega}^2 T \exp(-\theta_D/3T) + C\bar{\omega} + v/d \quad (2)$$

$$\tau^{-1} = \tau_{PD}^{-1} + \tau_U^{-1} + \tau_{PE}^{-1} + \tau_B^{-1} \quad (3)$$

$$\tau_{PD}^{-1} = \frac{V}{4\pi v^3} (\Gamma_B + \Gamma_S) \bar{\omega}^4 \quad (4)$$

$$\tau_U^{-1} = \frac{\gamma^2 h}{2\pi M v^2 \theta_D} \bar{\omega}^2 T \exp(-\theta_D/3T) \quad (5)$$

$$\tau_{PE}^{-1} = \frac{E_{\text{def}}^2 m^{*2}}{4\pi^2 h^3 \rho v_l} \bar{\omega} \quad (6)$$

$$\tau_B^{-1} = v/d \quad (7)$$

where τ_{PD} is the effective relaxation time caused by scattering of point defects, τ_U is the effective relaxation time caused by phonon–phonon U-scattering, τ_{PE} is the effective relaxation time caused by free electron–phonon scattering, τ_B is the effective relaxation time caused by grain boundary scattering, d is the average grain size, Γ_B and Γ_S are the disorder scattering parameters due to mass and strain field fluctuations, respectively. γ is the Grueneisen parameter, which strongly depends on the anharmonicity of the bonding, and is given as $\gamma = (3\beta B_m V_m)/C_v$, where β , V_m , B_m , C_v are the linear thermal expansion coefficient, molar volume, isothermal bulk modulus, and heat capacity, respectively. E_{def} is the deformed potential of conduction band, which is related to the strength of electron lattice interaction, m^* is the carrier effective mass, ρ is the density, and v_l is the phonon longitudinal velocity.

Based on the Callaway model and the effective relaxation time caused by different types of scattering, the κ_L of materials is closely related to point defect scattering, phonon–phonon, free electron–phonon, and boundary scattering, which all significantly affect the κ_L of materials. Similarly, in solid solution materials, the scattering of point defects, phonon–phonon scattering, and free electron–phonon scattering caused by mass and strain field fluctuations can significantly reduce the κ_L , which is consistent with the results of polaron theory.

Figure 2 shows the timeline of room-temperature κ_T and κ_L for several typical CoSb_3 -based solid solution alloy materials. It can be seen that the room-temperature κ_T and κ_L of the CoSb_3 -based solid solution alloy formed by doping are greatly reduced compared to that of the

Fig. 2 Timeline of room-temperature thermal conductivity (κ_T) and lattice thermal conductivity (κ_L) for several typical CoSb_3 -based solid solution alloy materials.

binary CoSb_3 material. The solid solution of CoSb_3 is mainly obtained by substitution of atoms of the same and different families in periodic table of elements [5,48–65]. The κ_L of the formed solid solution by the partial substitution with the isoelectronic atoms has an obvious decrease because of the increase in point defects induced by the big difference between atomic radius and mass between guest atoms and host atoms. Zhou *et al.* [49] reported that a large number of point defects in the ternary CoSb_3 -based solid solution formed by substituting Sb with As could strongly scatter the phonons, which effectively reduced the κ_L . In addition to increasing point defects to reduce the κ_L , the solid solution formed by partial substitution with non-isoelectronic heteroatom can also be used as donor doping to regulate the carrier concentration. In the Te-doped CoSb_3 -based ternary solid solution alloy, Te provides a large amount of electrons as a donor when Te replaces Sb, causing the Fermi level of the CoSb_3 to rise, which significantly improves the electrical conductivity. At the same time, the point defects in the solid solution enhance the phonon scattering when Sb is partially substituted with Te, resulting in the remarkable decrease of the κ_L . Te-doped ternary alloy $\text{CoSb}_{3-x}\text{Te}_x$ prepared by Liu *et al.* [5] has a high ZT value of 0.93 at 800 K. In addition, the single doped atoms have the problem of solid solubility limit because of the existence of the size and charge difference between atoms. In particular, some atoms have a lower solid solution quantity in CoSb_3 . Therefore, researchers try to form multi-component solid solution by multi-element doping to further improve the solid solution limit and reduce the κ_L [58]. Su *et al.* [59,60] reported that Te doping limit was significantly

increased for the quaternary compound $\text{CoSb}_{3-x-y}\text{Ge}_y\text{Te}_x$ formed by Ge-doped $\text{CoSb}_{3-x}\text{Te}_x$ with the charge compensation of Ge. The presence of the group IV Ge compensates for the charge of the group VI Te, in turn, increases the solubility (doping limit) of Te. For Ge and Te co-doped skutterudite $\text{CoSb}_{3-x-y}\text{Ge}_y\text{Te}_x$, the solid solubility of Te on the Sb site is higher than that of single-doped Te due to partial charge compensation by Ge. The valence electron numbers of Ge, Sb, and Te are 4, 5, and 6, respectively. A Ge atom substituting for Sb on the $[\text{Sb}_4]^{4-}$ rings compensates for the charge of Te substituted for Sb on the same $[\text{Sb}_4]^{4-}$ rings and effectively increases the solubility of Te in CoSb_3 [60]. In addition to the phonon point-defect scattering induced by the co-doping of Ge and Te, the nanostructures formed in situ may also contribute to the decrease of lattice thermal conductivity. As a result, maximum ZT value of the quaternary compound $\text{CoSb}_{3-x-y}\text{Ge}_y\text{Te}_x$ reached 1.1 at 800 K. In recent years, nanostructured CoSb_3 -based solid solution alloys have also been formed by some synthetic methods (such as high temperature and high pressure synthesis [66–70], plasma pulse sintering [71], magnesium reduction method [72], and microwave synthesis [73]). The κ_L of the CoSb_3 -based solid solution alloys prepared by these synthetic methods is significantly reduced, resulting in great increase of the ZT value.

Introducing the filling atom. The most interesting feature of the crystal structure for CoSb_3 material is that there are two intrinsic voids (Sb_{12} icosahedron composed of twelve Sb atoms) occupying 2a position in the crystal lattice, as shown in Fig. 1(d). In the past 20 years, electropositive elements (such as alkali metals, alkaline earth metals, and rare earth metals) [34,74–107] or electronegativity elements (such as S, Se, Br, and Cl) [108–111] have been filled into the larger Sb_{12} icosahedral void to form filled skutterudite $\text{R}_x\text{Co}_4\text{Sb}_{12}$ (R for filled atom). A large number of studies found that the filling degree and filling amount of different kinds of filling atoms are different, and there is a problem of the upper limit of the filling amount. Shi *et al.* [112] predicted theoretically the upper limit of the filling amount of a series of filled atoms for filled skutterudites and proposed a simple electronegativity selection rule for the stability of CoSb_3 , that is $x_{\text{Sb}} - x_{\text{R}} > 0.80$. In other words, the electronegativity difference between Sb atom and filled atom R must be greater than 0.80 to form a stable filled skutterudite compound. Filled atoms that satisfy the principle of electronegativity

proposed by Shi *et al.* is generally electropositive element, such as alkaline earth metals, alkali metals, and rare earth elements. The filled atoms act as a rattling center in the skutterudite void [113] and can strongly scatter the lattice phonons, causing a significant decrease in the κ_L . In addition, the filled atoms can also serve as the donor atom to effectively adjust the carrier concentration because the donor atom has different electronegativity from the framework atom Sb, which is more electronegative than the donor atom. Therefore, the introduction of filled atoms can improve significantly the TE transport properties of CoSb₃ material.

The earliest research on filled skutterudites can be traced back to 1977. Jeitschko and Braun [114] first filled the lanthanide metal atoms (also called rare earth metal atoms) into the icosahedral voids of skutterudite, and prepared a series of filled skutterudite TE materials. Then in 1995, Slack [115] proposed a concept of “phonon-glass electron-crystal” (PGEC), that is, a good TE material should have the same excellent electrical properties as a crystalline material and a low thermal conductivity like a glass material. It is also proposed that the filled skutterudite meets the characteristics of PGEC. Sales *et al.* [6] first reported the MFe_{4-x}Co_xSb₁₂ (M = La, Ce) filled skutterudite materials and studied the electrical and thermal transport properties in 1996. It was experimentally confirmed that the filled skutterudite materials have the transport properties of PGEC. Since then, the study of filled skutterudite materials has entered a research climax.

Although the TE performance of CoSb₃ has been greatly improved by the single atom filling [34,74,75, 82,84,86,88,90–103], the TE properties of single-filled CoSb₃ skutterudites can be further improved by doping other elements at Co or Sb sites [111,116,117]. Recently, Trivedi *et al.* [117] found that the *ZT* value of single element Dy-filled CoSb₃ skutterudites can be significantly enhanced by the microstructure and doping effect of Ni. The Dy_{0.4}Co_{3.2}Ni_{0.8}Sb₁₂ material has a high *ZT* value of up to 1.4 at 773 K. To further reduce the κ_L , the research on the filled skutterudite TE material system has gradually developed from single- to multiple-filled [118]. Theoretical and experimental results showed that multiple atomic filling can reduce the κ_L more effectively than single atom filling. The *ZT* value of the filled CoSb₃-based material was increased from about 1.0 for single filling [74] to about 2.0 for the multiple filling [7,87]. The *ZT* values of these n-type filled CoSb₃-based materials are obviously better than that of

p-type Fe₄Sb₁₂-based skutterudite materials [119–121]. Zhao *et al.* [77] found that there was a 5p orbital coupling between the filled atom In and Sb in the n-type multiple-filled CoSb₃ TE materials. The symmetry of Sb₄ ring (Fig. 1(c)) in the CoSb₃ structure was significantly improved, resulting in the remarkable enhancement in TE transport properties for the filled CoSb₃ materials, as shown in Figs. 3(a) and 3(b). The multiple-filled skutterudite TE material Ba_uLa_vYb_wCo₄Sb₁₂ prepared by Shi *et al.* [7] has a high *ZT* value of 1.7 at 850 K (Fig. 3(e)). The high *ZT* value benefits from the following two aspects: (i) controlling the filling fraction of multiple filled atoms to optimize the carrier concentration, leading to a higher power factor, as shown in Fig. 3(d); (ii) strong scattering of wide-band phonons can be achieved by different rattling frequencies of the multiple atomic filling in the icosahedral voids of CoSb₃ TE material, making the κ_L close to the theoretical minimum (Fig. 3(d)). Filling atoms that satisfy the principle of electronegativity selection proposed by Shi *et al.* [112] are generally electropositive element. It has rarely been reported that the stable filled skutterudite compounds can be formed by using electronegative elements (such as S, Se, Br, Cl, etc.) as filler. Duan *et al.* [108] reported that elements with negative charge can be filled into the icosahedral voids of CoSb₃ by certain charge compensation, forming the stable filled skutterudite compounds (Fig. 4). The filling of negatively charged elements can cause strong covalent interactions between guest and host atoms, and significantly lower κ_L by a unique “cluster vibration” characteristic as shown in Figs. 4(a)–4(c). The n-type S_{0.26}Co₄Sb_{11.11}Te_{0.73} filled skutterudite material has a high *ZT* value of up to 1.5 at 850 K. Figure 5 shows the timeline of *ZT* for several typical CoSb₃-based filled skutterudite TE materials in recent 20 years. It can be seen that the *ZT*_{max} value of the CoSb₃-based TE materials is between 1.0 and 2.0, which is significantly improved compared with that of the binary CoSb₃. Therefore, introducing foreign atoms into the intrinsic icosahedral void is a very effective way to improve significantly the TE properties of the CoSb₃ TE materials.

2.2 Optimization at nano-mesoscopic scale

Low dimensional CoSb₃-based materials. The low-dimensionalization of the material structure can cause significant changes in the electrical and thermal transport properties of the material. The changes of electrical transport properties are reflected mainly in the increase

Fig. 3 (a) Improvement of symmetry of the rectangular Sb_4 ring for n-type $\text{Ba}_7\text{In}_3\text{Co}_4\text{Sb}_{12}$ materials induced by the 5p orbital hybridization between the filler In and Sb; (b) temperature dependence of ZT values for $\text{Ba}_7\text{In}_3\text{Co}_4\text{Sb}_{12}$ materials. Reproduced with permission from Ref. [77], © American Chemical Society 2009. (c) Power factors at 850 K as a function of room-temperature carrier density for single-, double-, and multiple-filled skutterudites, and the solid line shows a trend for both the calculated and measured data; (d) high-temperature (850 K) lattice thermal conductivity as a function of total filling fraction; (e) temperature dependence of ZT for $\text{Ba}_x\text{La}_y\text{Yb}_w\text{Co}_4\text{Sb}_{12}$ multiple-filled skutterudites. Reproduced with permission from Ref. [7], © American Chemical Society 2011.

Fig. 4 CoSb_3 skutterudite TE materials with the electronegative guests. Calculated charge density difference at Sb four-ring plane in (a) $\text{Br}_{0.063}\text{Co}_4\text{Sb}_{12}$ and (b) $\text{S}_{0.063}\text{Co}_4\text{Sb}_{11.5}\text{Te}_{0.5}$; (c) phonon spectra in filled skutterudites with electronegative guests. Temperature dependence of (d) electrical conductivity, (e) lattice thermal conductivity κ_L , and (f) dimensionless figure of merit ZT for the electronegative guest filled CoSb_3 skutterudite materials. Reproduced with permission from Ref. [108], © The Royal Society of Chemistry 2016.

Fig. 5 Timeline of ZT for several typical CoSb₃-based filled skutterudites TE materials.

of the α . The increase in α is mainly attributed to the increase in the density of electronic states near Fermi energy [122] induced by the quantum confinement effect after the low-dimensionalization [123], as shown in Fig. 6. The changes of thermal transport properties after the low-dimensionalization are reflected in the decrease in the κ . The decrease in κ is mainly due to the fact that the high-density nano-interfaces in the low

Fig. 6 Electronic density of states of different dimensions. Reproduced with permission from Ref. [122], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2007.

dimensional materials enhance significantly the scattering of electrons and phonons. In the past ten years, TE properties of CoSb₃ materials have been improved significantly by the nanocrystallization of CoSb₃-based materials [124–140] or the preparation of thin film materials [141–147]. Toprak *et al.* [125] reported a novel chemical alloying method to prepare CoSb₃ materials with different nanoparticle sizes. This novel chemical alloying method (or solution chemistry route) from a thermodynamic modelling [148–150] of the equilibria

Table 1 Room-temperature thermal conductivity (κ_T) and lattice thermal conductivity (κ_L) of several typical CoSb₃-based solid solution alloy materials, and ZT values of several typical CoSb₃-based filled skutterudites TE materials

CoSb ₃ -based TE materials	κ_T (W/(m·K))	κ_L (W/(m·K))	CoSb ₃ -based TE materials	κ_T (W/(m·K))	κ_L (W/(m·K))	ZT	CoSb ₃ -based TE materials	ZT
CoSb ₃ [35]	10	—	CoSb _{2.75} Te _{0.20} Sn _{0.05} [62]	2.3	0.7	—	(R,Ba,Yb) ₃ Co ₄ Sb ₁₂ (R = Sr, La, 2.0 Mm, DD, SrMm, SrDD) [87]	—
Co _{1-x} Fe _x Sb ₃ [54]	3.5	—	CoSb _{2.85} Te _{0.15} [61]	2	—	—	In _{0.27} Co ₄ Sb _{11.9} [88]	1.2
Co(Sb _{1-x} As _x) ₃ [49]	4.4	—	Ni _{0.06} Co _{0.94} Sb ₃ [72]	5.1	—	—	(Sr,Ba,Yb,In) ₃ Co ₄ Sb ₁₂ +9.1wt% [89]	1.8
Co ₄ Sb _{12-x} Te _x [56]	4	3.4	CoSb _{3-x} Te _x [73]	3.3	3	—	In _{0.4} Co ₄ Sb ₁₂ [89]	—
Co _{1-x} Ir _x Sb ₃ [48]	4.8	—	Co ₄ Sb _{12-x} Te _x [67]	4.4	3.4	—	Yb ₃ Co ₄ Sb ₁₂ [34]	1.2
Co _{1-x} Ni _x Sb ₃ [53]	5.2	4.4	Yb _x Co ₄ Sb ₁₂ [74]	—	—	1.0	Sm ₃ Co ₄ Sb ₁₂ [90]	1.3
Co _{1-x} Fe _x Sb ₃ [55]	2.9	2.4	Ba _x Co ₄ Sb ₁₂ [75]	—	—	1.1	Yb _{0.3} Co ₄ Sb ₁₂ [91]	1.5
Co ₄ Sb _{12-x} Te _x [5]	2.6	—	Ba _x Yb _x Co ₄ Sb ₁₂ [76]	—	—	1.36	In _x Co ₄ Sb ₁₂ [92]	1.5
Co ₄ Sb _{12-x} Te _x [57]	4.5	3.6	Ba _x In _x Co ₄ Sb ₁₂ [77]	—	—	1.34	In _{0.15} Ba _{0.35} Co ₄ Sb ₁₂ [93]	1.18
CoSb _{2.75} Ge _{0.25-x} Te _x [60]	4.2	3.2	In _x Ce _x Co ₄ Sb ₁₂ [78]	—	—	1.43	In _{0.12} Yb _{0.20} Co _{4.00} Sb _{11.84} [94]	1.48
CoSb _{2.75} Ge _{0.25-x} Te _x [59]	2.4	1.9	Sr _x M _y Co ₄ Sb ₁₂ (M = Yb, Ba) [79]	—	—	1.32	Yb _x Co _{4-3x} Fe _{3x} Sb ₁₂ [95]	1.34
Co _{4-x} Ni _x Sb _{11.6} Te _{0.2} Se _{0.2} [50]	3.6	3.3	Yb _x Ca _y Co ₄ Sb ₁₂ [80]	—	—	1.03	S _{0.26} Co ₄ Sb _{11.11} Te _{0.73} [108]	1.5
CoSb _{2.8} Sn _x Te _{0.2-x} [63]	2.6	1.7	Ba _{0.3} In _{0.2} Co _{3.95} Ni _{0.05} Sb ₁₂ [81]	—	—	1.2	S _{0.25} Co _{3.4} Ni _{0.6} Sb ₁₂ [110]	0.8
Co ₄ Sb _{11.5-x} Te _{0.5} Sn _x [68]	2.3	—	Ba _{0.30} Ga _x Co ₄ Sb _{12+x} [83]	—	—	1.35	Yb _x Co ₄ Sb ₁₂ [96]	1.0
Co _{3.5} Sb _{11.8} Pd _{0.5} Se _{0.2} [67]	4.8	2.6	Li _x Co ₄ Sb ₁₂ [84]	—	—	1.3	A _{0.4} (Ga _{0.15} In _{0.15})Co ₄ Sb ₁₂ [104]	1.4
CoSb _{3-x} Se _x [66]	2	1.4	In _x M _{0.2} Co ₄ Sb ₁₂ (M = Ba and Pb) [85]	—	—	0.8	Multiple-filled X-CoSb ₃ skutterudites (X = Yb, Ca, Ba, Al, Ga, In, La, Eu) [107]	1.22
Co ₄ Sb _{11.7-x} Te _x Sn _{0.3} [69]	2.4	2.3	Ce ₃ Co ₄ Sb ₁₂ [86]	—	—	1.3	Al _x La _{0.5} Co ₄ Sb ₁₂ (0 < x < 0.5) [106]	1.36

of chemical reactions involved has been developed by Toprak *et al.* [151] and Wang *et al.* [152]. High-density grain boundaries produced by nanocrystallization can strongly scatter electrons and phonons, leading to the decrease in the κ of CoSb₃ material. Compared to single crystal and annealed polycrystalline CoSb₃ materials, the room-temperature κ is significantly reduced by nearly one order of magnitude, reaches 1.5–2.2 W/(m·K). Yu *et al.* [126] used MA-SPS technology to prepare CoSb₃ bulk TE materials with a minimum average particle size of 150 nm. There is a little effect on κ_E , whereas the κ_L is remarkable reduced when the grain size of the material is reduced from micrometer scale to nanometer scale. CoSb₃ bulk materials with an average grain size of 150 nm were prepared by solvothermal method combined with SPS technique. The ZT value of this CoSb₃ nanocrystalline material reached 0.61 at 725 K because of the remarkable decrease in κ and the increase in the α [133].

Rogl *et al.* [138] prepared a series of nanostructured (Mm,Sm)₃Co₄Sb₁₂ materials by a technology that consists of rapid reaction melting, high energy ball milling, and hot pressing. A lower κ was obtained because of a large number of nanostructures in the material (Figs. 7(a) and 7(c)). The maximum ZT value reached 1.6 at 825 K under certain ball milling and hot pressing conditions

as shown in Fig. 7(d). Yb-filled CoSb₃ skutterudite films were prepared by DC-reactive magnetron sputtering [142]. Higher electrical and thermal transport properties were presented after the heat treatment at 1020 K as shown in Figs. 7(e)–7(g). The ZT value reached 0.48 at 700 K for the film with a thickness of 130 nm (Fig. 7(h)). This ZT value of the film is only between half and one third of the bulk materials because of the lower mobility. Recently, Ag-doped CoSb₃ thin films were prepared by inter-layer diffusion method [145]. This film has a higher power factor value of 0.11 mW·m⁻¹·K⁻² at 573 K, which is 5 times that of undoped CoSb₃ samples. In summary, the low-dimensionalization of the material structure is also an effective way to improve the TE transport properties of the CoSb₃-based materials.

Introducing special structure. The results of theoretical and experimental studies showed that the phonon thermal conductivity can be significantly reduced without the deterioration of electrical transport properties by the introduction of special structures (such as micro-nanopores, nano-core shell structures, etc.) in bulk materials [10,153,154]. Therefore, these special structures may be introduced into the TE material to decrease significantly the κ_L and further improve its TE properties by enhancing the multi-scale phonons scattering. Porous (Ba,In) double-filled skutterudite materials with pore

Fig. 7 CoSb₃-based TE materials with low dimensional nanostructure. (a) SEM image of the broken surface of (Mm,Sm)₃Co₄Sb₁₂ (S50HBBHP sample); temperature dependence of (b) Seebeck coefficient, (c) thermal conductivity λ and lattice thermal conductivity λ_{ph} , and (d) ZT values of n-type (Mm,Sm)₃Co₄Sb₁₂; the inset in (b) shows the temperature dependence of power factor. Reproduced with permission from Ref. [138], © Acta Materialia Inc. 2014. (e) SEM surface image of Yb_xCo₄Sb₁₂ thin film (1020 K heat treatment Y4 sample); (f) Seebeck of 1020 K heat treated Yb_xCo₄Sb₁₂ thin films with different thicknesses; (g) thermal conductivity of Yb_xCo₄Sb₁₂ film at different thicknesses with temperature dependent; (h) figure of merit, ZT values of Yb_xCo₄Sb₁₂ films with different thicknesses. Reproduced with permission from Ref. [142], © AIP Publishing LLC. 2015.

diameter about 1–4 μm containing a disordered arrangement of microporous structures have been prepared by the decomposition of metastable ZnSb inclusions induced by the Zn sublimation [155], as shown in Fig. 8. The electron filtering effect caused by the nanostructures on the surface of the pore structure increased the α . The percolation effect of conducted network composed of filled skutterudites did not change the electrical conductivity. The κ_L was dramatically decreased because of the enhanced pore-edge boundary scattering of long-wavelength phonons. As a result, a maximum ZT of 1.36 was obtained at 800 K, increased by 22.5% as compared to that of the bulk material with the same chemical composition. Recently, Ni-induced nuclear-shell structures [156] and micro-nanoporous structures [157] were also introduced in CoSb_3 -based materials, as shown in Fig. 9. By using the strong scattering of these special structures on phonons, the κ_L of CoSb_3 -based materials was significantly reduced and the ZT value was also remarkably improved. Therefore, the introduction of the special structure is also considered to be an effective method for improving the TE properties

of CoSb_3 -based materials.

In addition, some special structures (such as in situ nanostructures [158], dislocation arrays [159,160], nanocrystalline polymer, and lattice distortion [161]) can also be introduced into the CoSb_3 -based materials by the microstructure and composition engineering [158,162], dislocation engineering [159] or grain boundary engineering [160], pressure regulation [161], and novel preparation methods [163–165]. The introduction of these special structures can also significantly improve the TE properties of CoSb_3 -based materials.

Nanocomposite. The introduction of the nanoscale second-phase is also an effective way to significantly improve TE properties of CoSb_3 -based materials at the nanometer- and mesoscopic-scale in addition to the low dimensionality and the introduction of special structure discussed above. The study found that the TE properties of the matrix material can also be significantly improved by introducing the nanoscale second-phase into the matrix to form nanocomposite TE materials [166]. Intragranular and grain boundary dispersion are generally the dispersion state of the nanoscale second-phase in the matrix material.

Fig. 8 Microstructure and thermoelectric properties of the dense (DM) and microporous $x\text{Zn}/\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$ materials (PM), Zn particles were added in the as-prepared $\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$ powders before SPS sintering according to molar ratio of $\text{Zn}:\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12} = x:1$ ($x = 0, 0.3, 0.5$). The dense materials were named as DM00, DM03, and DM05, respectively. All the dense materials were annealed at 753 K for 72 h to obtain $\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$ porous materials (PM). The resulting porous materials were termed as PM00, PM03, and PM05, respectively. (a) SEI photographs of PM03; (b, c) FEFSEM photographs of the porous structures of PM03. Temperature dependence of (d) power factor, (e) lattice thermal conductivity, and (f) ZT values for the DM and PM materials. Reproduced with permission from Ref. [155], © AIP Publishing LLC. 2014.

Fig. 9 CoSb₃-based materials with special structure. (a) A sketch map for the whole forming process of the “core–shell” structure in Yb_{0.2}Co₄Sb₁₂+xwt%Ni samples. The large blue polygons represent the normal Yb_{0.2}Co₄Sb₁₂ grains in the sintered bulk materials. (b) SEM fractograph of the Yb_{0.2}Co₄Sb₁₂+0.2wt%Ni samples. Reproduced with permission from Ref. [156], © The Royal Society of Chemistry 2015. (c) Schematic illustration and SEM fractographs of CoSb_{2.75}Si_{0.075}Te_{0.175} material with pristine and porous; (d) temperature dependence of ZT values for CoSb_{2.75}Si_{0.075}Te_{0.175} material with pristine and porous. Reproduced with permission from Ref. [157], © The Author(s) 2016.

The nanoscale second-phase dispersed in the intragranular and grain boundaries of the matrix material is smaller than the mean free path of the phonon, which can effectively scatter phonons to reduce the κ_L . The electron is not easy to be scattered because of the size of the nanoscale second-phase is much larger than the mean free path of the electron, which has little effect on the electrical properties. The preparation of CoSb₃-based nanocomposites by in-situ generation [78,167–177] or mechanical addition of nanoinclusions [178–193] is a common method to introduce the second phase. In_xCe_yCo₄Sb₁₂ nanocomposites containing in-situ formed InSb nanophases (10–80 nm) were prepared by melt quenching, annealing, and spark plasma sintering [78], as shown in Figs. 10(a) and 10(b). The strong scattering of phonons by InSb nano phase resulted in the significant decrease in the κ_L . Combined with the filling effect of the In and Ce atoms, the ZT value of In_{0.2}Ce_{0.15}Co₄Sb₁₂ nanocomposite reached 1.43 at 800 K. Xiong *et al.* [169] prepared a Yb_{0.26}Co₄Sb₁₂/0.2GaSb nanocomposite containing GaSb nanoinclusions (5–20 nm) by in-situ method (Fig. 10(c)). The metastable filling atom Ga reacts with an excess of Sb to form GaSb nanoinclusion during the sample cooling process. Nanoscale GaSb

can not only significantly enhance the power factor by the energy filtering effect generated by the interface potential between the nanoscale GaSb and Yb_{0.26}Co₄Sb₁₂ matrix, but also significantly reduce the thermal conductivity. The Yb_{0.26}Co₄Sb₁₂/0.2GaSb nanocomposite sample had a highest ZT value of 1.45 at 850 K. CoSb₃-based nanocomposites were also prepared by mechanically adding nanoinclusions (Ag [179], AgSbTe₂ [183], Bi₂Te₃ [189], MoS₂ [190], etc.) in the CoSb₃-based material, as shown in Figs. 10(e)–10(h). The κ_L can be reduced significantly through the strong scattering of phonons by nano inclusions, even like metal Ag nanoinclusions [179], the electrical transport properties can be significantly improved, and thus the TE properties of CoSb₃ materials can also be significantly improved.

Recently, we prepared a series of magnetic nanocomposites BaFe₁₂O₁₉/Ba_{0.3}In_{0.3}Co₄Sb₁₂ by introducing BaFe₁₂O₁₉ magnetic nanoparticles into the (Ba,In) double-filled CoSb₃ matrix material [21]. BaFe₁₂O₁₉ magnetic nanoparticles (~20–150 nm) are uniformly dispersed on the grain boundary and interface of Ba_{0.3}In_{0.3}Co₄Sb₁₂ matrix (Fig. 11(a)). Some BaFe₁₂O₁₉ magnetic nanoparticles with less than 10 nm in diameter were embedded into the matrix grains (Fig. 11(b)). The

Fig. 10 Microstructure of CoSb₃-based nanocomposite TE materials. (a, b) FESEM photographs of In_xCyCo₄Sb₁₂ nanocomposite materials with in situ forming nanostructured InSb phase. Reproduced with permission from Ref. [78], © American Institute of Physics 2009. (c) FESEM photograph of Yb_{0.26}Co₄Sb₁₂/0.2GaSb nanocomposite material. Reproduced with permission from Ref. [169], © Acta Materialia Inc. 2010. (d) HETEM photograph of YbCo₄Sb₁₂/rGO nanocomposite material. Reproduced with permission from Ref. [170], © The Royal Society of Chemistry 2015. (e) TEM photograph of Ag/Ba_{0.3}Co₄Sb₁₂ nanocomposite material. Reproduced with permission from Ref. [179], © The Royal Society of Chemistry 2012. (f) FESEM and TEM photographs of AgSbTe₂/Yb_{0.2}Co₄Sb₁₂ nanocomposite material. Reproduced with permission from Ref. [183], © The Royal Society of Chemistry 2015. (g) TEM photograph of Bi₂Te₃/CoSb₃ nanocomposite material. Reproduced with permission from Ref. [189], © IOP Publishing Ltd. 2018. (h) TEM photograph of MoS₂/CoSb₃ nanocomposite material. Reproduced with permission from Ref. [190], © Elsevier B.V. 2017.

Fig. 11 Performance deterioration of Ba_{0.3}In_{0.3}Co₄Sb₁₂ matrix in the intrinsic excitation region can be suppressed through the magnetic transition of permanent magnet nanoparticles. (a) FESEM image of the 0.45%BaFe₁₂O₁₉/Ba_{0.3}In_{0.3}Co₄Sb₁₂ (MNC45) magnetic nanocomposite TE material; (b) HRTEM MNC45 sample; (c) Curie temperature of BaFe₁₂O₁₉ nanoparticles; temperature dependences of (d) carrier concentration n , (e) Seebeck coefficient, (f) electronic thermal conductivity κ_e , (g) lattice thermal conductivity κ_L , and (h) ZT figure of merit of x BaFe₁₂O₁₉/Ba_{0.3}In_{0.3}Co₄Sb₁₂. The inset in (e) shows the temperature dependences of power factor ($\alpha^2\sigma$) for x BaFe₁₂O₁₉/Ba_{0.3}In_{0.3}Co₄Sb₁₂. Reproduced with permission from Ref. [21], © Macmillan Publishers Limited, part of Springer Nature 2016.

magnetic phase transition temperatures of these BaFe₁₂O₁₉ magnetic nanoparticles from ferromagnetic to

paramagnetic are about 669–673 K (Fig. 11(c)), which is very close to the intrinsic excitation temperature

(675 K) of the matrix. $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles with ferromagnetic state below 675 K can capture electrons by the spherical micromagnetic field induced by the electron spin of Fe^{3+} [194]. $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles with paramagnetic state above 675 K released the captured electrons because of disappearance of the micromagnetic field, leading to a significant increase in electron concentration (Fig. 11(d)). $\text{BaFe}_{12}\text{O}_{19}$ magnetic nanoparticles played an “electronic repository” role. Insulating $\text{BaFe}_{12}\text{O}_{19}$ magnetic nanoparticles caused the decrease in the σ and the increase in the α of the composites. The α of the composites significantly improved (Fig. 11(e)) combined with the magnon-drag effect caused by $\text{BaFe}_{12}\text{O}_{19}$ magnetic nanoparticles. The magnetic phase transition produced by $\text{BaFe}_{12}\text{O}_{19}$ magnetic nanoparticles from ferromagnetic to paramagnetic significantly affected the TE transport properties of the matrix, especially the high-temperature electron thermal conductivity, as shown in Fig. 11(f). The high-temperature ZT value of the composites is greatly improved because of the significant decrease of high-temperature thermal conductivity. The maximum ZT value reached 1.6 at

850 K, increased by 22% compared with that of the matrix (Fig. 11(h)). Very recently, we also prepared a series of magnetic nanocomposites $\text{BaFe}_{12}\text{O}_{19}/\text{In}_{0.25}\text{Co}_4\text{Sb}_{12}$ by introducing $\text{BaFe}_{12}\text{O}_{19}$ nanometer suspension into the In-filled CoSb_3 matrix material [195]. $\text{BaFe}_{12}\text{O}_{19}$ nanometer suspension can not only solve the agglomeration phenomenon of nanoparticles in nanocomposites (Figs. 12(a) and 12(b)), but also suppress the deterioration of high-temperature thermoelectric properties of In-filled skutterudite by suppressing the decrease of high-temperature Seebeck coefficient (Figs. 12(c) and 12(d)). The decrease of high-temperature Seebeck coefficient was significantly suppressed by the magnetic phase transition of $\text{BaFe}_{12}\text{O}_{19}$ magnetic nanoparticles from ferromagnetism to paramagnetism. These results further confirmed that the magnetic phase transition of $\text{BaFe}_{12}\text{O}_{19}$ magnetic nanoparticles can significantly suppress the deterioration of high-temperature thermoelectric properties of filled skutterudite materials.

In addition, we also prepared $\text{Co}/\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$ magnetic nanocomposites by introducing the soft magnetic Co nanoparticles (or Fe, Ni nanoparticles) in (Ba,In)

Fig. 12 (a) FESEM image of 0.45% $\text{BaFe}_{12}\text{O}_{19}/\text{In}_{0.25}\text{Co}_4\text{Sb}_{12}$ (BaM45) bulk material produced by an ultrasonic mixing of $\text{BaFe}_{12}\text{O}_{19}$ nanometer suspension and $\text{In}_{0.25}\text{Co}_4\text{Sb}_{12}$ matrix material combined with spark plasma sintering; (b) HRTEM image of BaM45 bulk material; temperature dependences of (c) Seebeck coefficient and (d) ZT values of $\text{In}_{0.25}\text{Co}_4\text{Sb}_{12}$ matrix and $\text{BaFe}_{12}\text{O}_{19}/\text{In}_{0.25}\text{Co}_4\text{Sb}_{12}$ nanocomposites; T_W is the work temperature, T_C is the Curie temperature. Reproduced with permission from Ref. [195], © American Chemical Society 2019.

double-filled CoSb₃ materials [22]. Co nanoparticles were uniformly dispersed on the grain boundaries and interfaces of the Ba_{0.3}In_{0.3}Co₄Sb₁₂ matrix, as shown in Figs. 13(a) and 13(b). Even some Co nanoparticles with 5–10 nm in diameter were embedded into the grains of the matrix (Fig. 13(c)). These uniformly dispersed nanoparticles on the grain boundaries and surface of the matrix significantly enhanced phonon scattering and caused the significant decrease in the κ_L of the composite material, which leads to a significant decrease in the total thermal conductivity, as shown in Fig. 13(d). The superparamagnetic transition temperature of Co nanoparticles with 5–10 nm in diameter (Fig. 13(e)) was approximately 442 K (Fig. 13(f)), which was basically consistent with the M – H experimental test result of 450 K (Fig. 13(g)). The random turning of magnetic

domains in Co nanoparticles with superparamagnetic state can cause multiple scattering of electrons (Fig. 13(h)), which enhanced the scattering factor r of the composites, resulting in the increase of the α , as shown in Fig. 13(k). In addition, based on the metal and semiconductor contact theory [196], the difference of work function between the Co nanoparticles and the matrix caused a charge transfer (Fig. 13(i)). The charge transfer of the 4s electrons from the Co nanoparticles to the matrix caused the increase in the σ of the composites (Fig. 13(j)). Charge transfers of superparamagnetic Co nanoparticles can remarkably improve the electrical transport properties of composites. At the same time, the multiple scattering of electrons caused by random turning of magnetic domains can significantly increase the α and enhance phonon scattering. The ZT value of

Fig. 13 Superparamagnetic enhancement of TE performance in $x\text{Co}/\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$ magnetic nanocomposite TE materials. (a–c) Microstructures of the as-prepared powders and bulk materials of $x\text{Co}/\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$ with $x = 0.2\%$ (MNC02R); (d) temperature dependences of thermal conductivity κ for $x\text{Co}/\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$; the inset in (d) shows the temperature dependence of lattice thermal conductivity κ_L ; (e) TEM image of the Co nanoparticles (diameters of 5–10 nm); (f) ZFC and FC M – T curves of Co nanoparticles; (g) M – H curves at 300 and 450 K of Co nanoparticles; (h) multiple scattering of electrons (indicated by the small red dashed arrows) as a result of the random turning of magnetic domains (indicated by the small purple dashed arrows) within the superparamagnetic Co nanoparticles; (i) schematic of the charge transfer of 4s electrons from the Co nanoparticles to the matrix; E_{vac} is the vacuum energy, $E_{\text{F,m}}$ and $E_{\text{F,s}}$ are the Fermi levels of the Co nanoparticles and the matrix, respectively, E_{C} is the energy of the conduction band minimum, E_{V} is the energy of the valence band maximum, and E_{g} is the bandgap; ϕ_{m} and ϕ_{s} are the work functions of the Co nanoparticles and the matrix, respectively; temperature dependences of (j) electric conductivity σ , (k) Seebeck coefficient α , and (l) figure of merit ZT for $x\text{Co}/\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$; the inset in (k) highlights the abnormal temperature dependence of the Seebeck coefficient for MNC01R (blue). Reproduced with permission from Ref. [22], © Macmillan Publishers Limited, part of Springer Nature 2017.

the composites was significantly improved combining with the strong scattering of phonons by Co nanoparticles at the grain boundaries and surface of the matrix. The maximum ZT value reached 1.8 at 850 K, increased by 32% compared with that of the matrix. The magnetic composites composed of Fe or Ni nanoparticles and $\text{Ba}_{0.3}\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$ matrix were also studied. It was found that the TE properties of the composites can be also significantly improved by the superparamagnetic Fe or Ni nanoparticles.

In addition, introducing nanoscale second-phase into CoSb_3 -based materials to form nanocomposites can not only significantly reduce the thermal conductivity, but also may significantly affect the mechanical properties [158,177,197–201] of CoSb_3 -based materials. Rogl and Rogl [199] reviewed systematically that nanoparticles can obviously change the mechanical properties of skutterudite TE materials. They claimed that as long as the nanoscale second-phases do not increase the porosity of the samples, the smaller and more nanoscale second-phases can significantly enhance the mechanical properties of the nanocomposites. This is mainly due to the establishment of a resistance against crack growth, a pinning effect in the embedded skutterudite matrix and a stronger interface between skutterudite matrix and nanoscale second-phases. The mechanical properties of different kinds of CoSb_3 -based nanocomposites were obviously changed by introducing some nanoparticles like Yb_2O_3 [158], TiN [181,200], CoAl [197], CoSi [179], and SiC [198]. Qin *et al.* [177] prepared $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}$ with in situ formed CoSi nanoprecipitates by adding the extra Co and Si. Microstructure with multiscale CoSi nanoparticles shows that mechanical properties (hardness and indentation fracture toughness) were significantly improved owing to particle hardening, making it more competitive for practical applications.

3 Non-equilibrium preparation

Preparation of CoSb_3 -based TE materials by conventional melt, anneal, SPS process needs a long period (about 10 days). It is not conducive to large-scale production and impedes the final commercial use of CoSb_3 -based TE materials for power generation. Therefore, some non-equilibrium preparation methods, such as melt spinning combined with spark plasma sintering (MS-SPS) [202–204], self-propagating high-temperature synthesis (SHS) method [205–209], and high pressure synthesis

[66–70,210,211], have been adopted in recent years. Using these non-equilibrium preparation methods, the preparation period of the material was greatly shortened. Materials prepared by non-equilibrium have the following advantages: (i) higher density; (ii) refined grain (nanostructure) and uniform element distribution; (iii) competitive transport properties compared with the materials prepared by traditional methods, and even higher than their properties.

3.1 MS-SPS

An improved MS-SPS preparation method based on the traditional preparation method has emerged in order to prepare CoSb_3 -based TE materials more quickly and cheaply. This method directly melts and spins the original raw materials. The entire process time was highly shortened from about 8 days for conventional method to less than about 40 h. The microstructure and low-temperature TE transport properties of the materials prepared by MS-SPS method were systematically studied. The results showed the grain of the sample was arranged more closely. No obvious pores were observed between the large grains with smooth surface and the flocculent small grainy areas. Compared with the samples prepared by traditional methods, the grain of the MS-SPS sample was significantly refined, and the element distribution was also more homogeneous. Li *et al.* [202,203] prepared nanostructured $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$ and $\text{In}_x\text{Ce}_y\text{Co}_4\text{Sb}_{12+z}$ skutterudite TE materials by MS-SPS method, as shown in Fig. 14. The preparation cycle was significantly reduced from about 10 days of the traditional method to less than about 40 h. Under this rapid preparation process, the grains of the bulk material after sintering were greatly refined, and a large number of nanoparticles (Yb_2O_3 and InSb) were also found on the matrix grains. A wide range of phonon was strongly scattered by these multi-scale grains. The κ_L was remarkably decreased and ZT value was significantly enhanced compared with that of the materials prepared by traditional methods. ZT value of the $\text{In}_{0.2}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ sample reached about 1.5 at 850 K.

3.2 SHS

Self-propagating high-temperature synthesis (SHS) rapid preparation technology has been proposed by the Soviet Union for more than 50 years since the 1960s. It has been developed in the 1970s–1990s and widely used in the preparation of high temperature refractories [205],

Fig. 14 Nanostructured $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$ and $\text{In}_x\text{Ce}_y\text{Co}_4\text{Sb}_{12+z}$ skutterudite TE materials prepared by the MS-SPS. FESEM photographs of bulk nanostructured $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$ after SPS: (a) $y = 0.3$, (b) $y = 0.6$. Temperature dependences of (c) power factor, (d) thermal conductivity, and (e) ZT values for $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$ materials. Reproduced with permission from Ref. [202], © American Institute of Physics 2008. (f, g) FESEM and (h) HRTEM photographs of $\text{In}_{0.15}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ sample prepared by MS-SPS; temperature dependences of (i) lattice thermal conductivity and (j) ZT values for $\text{In}_x\text{Ce}_y\text{Co}_4\text{Sb}_{12+z}$ skutterudite TE materials. Reproduced with permission from Ref. [203], © The Chinese Ceramic Society 2017.

high purity ceramic materials [206], and intermetallic compounds [207]. Spontaneous combustion wave is the basic feature of the reaction, which depends on exothermic reaction. The combustion synthesis reaction is very fast, usually in the time range of seconds. The synthesis is initiated by heating part of the sample locally, and once the heating ignition starts, the combustion wave will quickly pass through the remaining sample because the melting heat released in one zone is enough to maintain the reaction in the adjacent zone. The propagation of the combustion wave is fast, usually in a matter of seconds, and the final product usually has a higher purity. In other words, the heat released during SHS not only maintains the reaction but propagates it through the whole sample. For more than 40 years, SHS technology has not been used for synthesis of TE materials. Su *et al.* [208] applied SHS technology for the first time to rapidly prepare high-performance TE materials, which breaks the view that TE material cannot be synthesized by SHS based on traditional thermodynamic criteria. They also proposed a new criterion of thermodynamic universality for SHS reaction. Te-doped CoSb_3 materials were first synthesized by SHS-PAS (plasma activated sintering) technology [209] as shown in Fig. 15. Te-doped CoSb_3 -based TE material prepared by this method has the following advantages: (i) the preparation time is greatly shortened from a few days of the conventional process to less than 20 min (Fig. 15(a)); (ii) this rapid preparation method allows a large amount of nanostructures to be retained in the material (Figs. 15(b)–15(d)), which is

helpful to improve the thermal transport performance (Fig. 15(g)); (iii) compared with samples prepared by traditional processes, the samples prepared by SHS-PAS technology have good density and good electrical properties (Figs. 15(e)–15(f)). Therefore, the TE performance can also be significantly improved. The ZT value of $\text{CoSb}_{2.85}\text{Te}_{0.15}$ sample prepared by SHS-PAS technology reached 0.98 at 820 K (Fig. 15(h)).

4 Synergistic optimization

To obtain high ZT value, the TE material is required to have a high Seebeck coefficient and electrical conductivity, while having a low thermal conductivity. However these parameters are strongly interdependent and maximizing one transport parameter inevitably leads to diminishing the others. Therefore, it is very difficult to realize the decoupling of electrical performance and thermal conductivity. In recent years, some important progresses [212–215] have been made in the research of synergistic optimization of electrical and thermal transport properties for TE materials. These methods of synergistic optimization include structural phase transition [216], disordered structure [11,217], all-scale hierarchical architectures [26], band convergence [14], and so on. For CoSb_3 -based TE materials, there are many ways to achieve the synergistic optimization of their electrical and thermal transport properties, such as doping to form solid solution alloy [36,61,218], introducing filler atoms

Fig. 15 Te-doped CoSb_3 materials prepared by the SHS-PAS technique. (a) Different stages of the SHS process; (b, c) FESEM images of bulk $\text{CoSb}_{3-x}\text{Te}_x$ compounds after the SHS process; (d) FESEM image of the bulk $\text{CoSb}_{3-x}\text{Te}_x$ compound after SHS-PAS processing; temperature dependence of (e) electrical conductivity, (f) Seebeck coefficient, (g) thermal conductivity, and (h) the dimensionless figure of merit ZT of $\text{CoSb}_{3-x}\text{Te}_x$ compounds prepared by the SHS-PAS technique. Insets in (e), (f), and (g) show TE properties of pure CoSb_3 skutterudite. Reproduced with permission from Ref. [209], © The Royal Society of Chemistry 2014.

[7,108,219], nanocomposites [21,22,172], and other means mentioned in the previous section.

The solid solution alloy formed by doping is realized by atom substitution at Co or Sb sites. Atomic substitution can not only reduce the phonons thermal conductivity by point defects induced by the fluctuations of mass and strain fields because of the difference of the mass and radius between the foreign atom and the guest atom, but also improve the electrical transport performance by the adjustment of the carrier concentration, so as to realize the synergistic optimization of electrical and thermal transport properties. The filled CoSb_3 materials are formed by introducing the other atoms into the Sb_{12} icosahedral void of CoSb_3 . The introduction of foreign atoms can not only reduce the lattice thermal conductivity by the rattling of filled atoms in the CoSb_3 void, but also improve the electrical transport performance by the adjustment of the carrier concentration. This is because the filled atoms can serve as the donor atom. Filled atom has different electronegativity from the framework atom Sb, which is more electronegative than the donor atom. Therefore, the synergistic optimization of electrical and thermal transport properties can also be achieved by introducing the filled atoms. Zhao *et al.* [219] found that the electrical and thermal transport properties of n-type In-filled skutterudite TE materials $\text{In}_y\text{Co}_4\text{Sb}_{12}$ can be optimized synergistically by three types of coexisting multi-localization transport behaviours in an

independent way due to the introduction of foreign In atom, as shown in Figs. 16(d)–16(f). These are heat-carrying phonon-localized resonant scattering (Fig. 16(a)), accelerated electron movement (Fig. 16(b)) and increased density of states near the Fermi level (Fig. 16(c)).

In addition, introducing magnetic nanoscale second-phase into CoSb_3 -based materials to form magnetic nanocomposites can also achieve the synergistic optimization of electrical and thermal transport properties. As we mentioned in the previous discussion, magnetic nanocomposites were prepared by introducing hard magnetic nanoparticles ($\text{BaFe}_{12}\text{O}_{19}$ nanoparticles) and soft magnetic nanoparticles (Co, Fe, or Ni nanoparticles) into the filled CoSb_3 material [21,22]. The electrical and thermal transport properties of the composite materials were simultaneously improved by the magnetic phase transition of these introduced magnetic nanoparticles, strong phonons scattering by nanoparticles, and charge transfer between magnetic metal nanoparticles and CoSb_3 -based materials matrix. The decoupling of electrical properties and thermal conductivity was achieved, and the ZT value of the composite materials was greatly enhanced.

5 CoSb_3 -based TE devices

TE energy conversion devices have attracted wide

Fig. 16 Synergistic regulation of electrical and thermal transport properties in $\text{In}_y\text{Co}_4\text{Sb}_{12}$ TE materials. (a) Temperature dependences of lattice thermal conductivity for CoSb_3 and filled CoSb_3 in the range of 300–800 K; (b) temperature dependences of Hall mobility for filled CoSb_3 in the range of 10–300 K; the inset shows the temperature dependences of Hall mobility for filled CoSb_3 in the range of 100–300 K; (c) carrier concentration dependences of the Seebeck coefficient of n-type filled CoSb_3 at room temperature; (d) filling Sb_{12} icosahedron voids at the 2a sites; (e) differential charge density of $\text{In}_{0.125}\text{Co}_4\text{Sb}_{12}$ projected on the (111) plane; (f) total DOS and partial DOS near VBM and CBM of CoSb_3 and $\text{In}_{0.125}\text{Co}_4\text{Sb}_{12}$. Reproduced with permission from Ref. [219], © Macmillan Publishers Limited 2015.

attention because they have no moving parts and are capable of high power densities, scalable in size, and potentially highly reliable [220]. In order to obtain high conversion efficiency of TE devices, the key factor is that the TE material has high ZT value. The ideal efficiency of thermal to electrical energy conversion for a TE material is expressed as [221]:

$$\eta = \left(\frac{T_H - T_C}{T_H} \right) \cdot \frac{\sqrt{1 + ZT_{\text{avg}}} - 1}{\sqrt{1 + ZT_{\text{avg}}} + (T_C / T_H)} \quad (8)$$

where T_H is the hot-side temperature, T_C is the cold-side temperature, $T_{\text{avg}} = (T_H + T_C)/2$ is the arithmetic average of the T_H and T_C , and $\Delta T = (T_H - T_C)$ is the temperature difference. The conversion efficiency is also obtained with Eq. (9) [222]:

$$\eta = \frac{P}{P + Q_c} = \frac{IV}{IV + Q_c} \times 100\% \quad (9)$$

where P is the output power for a given load resistance. The electrical current (I) and the released heat (Q_c) can be calculated by area integration of the current density or the heat flux over a selected cross section. The terminal voltage (V) can be probed on the cold-side

electrode. The maximum output power (P_{max}) and the maximum conversion efficiency (η_{max}) can be determined by applying a parameterized load resistance.

Skutterudite-based TE materials are recognized as the most promising TE materials in the mid-temperature range because they have adequate TE performance and are mechanically robust. Especially, n-type CoSb_3 -based materials have high ZT values ($ZT_{\text{max}} \approx 2.0$ [7,22,87]). They are usually used as an ideal n-leg of skutterudite-based TE devices. The structure of a conventional module of TE device follows the Π -shaped configuration as shown in Fig. 17(a). In addition, there are the tube-shape module (Fig. 17(b)) and Y-shaped configuration (Fig. 17(c)). The schematic diagram of a typical Π -shaped skutterudite-based TE uni-couple is shown in Fig. 17(d). Skutterudite-based TE uni-couple is composed of one n-type skutterudite material, one p-type skutterudite material, intermediate layers, and electrodes. N-type leg or p-type leg has electrodes at both the hot side and the cold side. In order to prevent the diffusion between the skutterudite TE material and the electrode and to release the stress at the joint, an intermediate layer or a barrier layer is usually employed between them. Some attempts

Fig. 17 Schematic diagrams of (a) Π -shaped, (b) tube-shaped, and (c) Y-shaped TE module. (d) Schematic diagram of a typical Π -shaped skutterudite-based TE uni-couple. Reproduced with permission from Ref. [223], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2015.

[224–236] have been made to join TE materials onto different electrodes (such as Mo–Cu alloys [225,229,236], Ag–Cu [233], Cu [235]) with different barrier layers or intermediate layer (such as Cr–Si alloys [225], Ti–Al alloys [227], Ni [228], Ti [229,230], TiCoSb [231], ZrO_2/Ti [232], Co [233], Al–Ni [234], Fe–Ni [237]) in recent years. The lower contact resistance, stable interface, and high mechanical properties of the device can be obtained by selecting the appropriate electrode and barrier layers to connect with the CoSb_3 -based material. In this way, the TE devices can obtain higher output performance and conversion efficiency.

In recent years, some CoSb_3 -based TE modules (uni-couple [238–241] and multipair [236,237,242–250])

have been widely studied. The output performance and service behavior of CoSb_3 -based TE devices were greatly improved by the design and optimization of electrode, interface and barrier layer, and the protection coating [225,232,234,251,252] for preventing Sb sublimation and oxidation. Table 2 summarizes some available CoSb_3 -based TE devices reported in recent years. Although some progresses have been made in CoSb_3 -based TE devices, there are still many challenges and technical problems to be solved for further large-scale application.

6 Conclusions and outlook

We have reviewed the research progress of CoSb_3 -based TE materials in recent years. The commonly adopted strategies to reduce the thermal conductivity of CoSb_3 -based materials and optimize their TE properties at the atomic-molecular scale and nano-mesoscopic scale were mainly reviewed. Furthermore, the research works of some advanced preparation technologies and synergistic optimization of electrical and thermal transport parameters for CoSb_3 -based materials were also summarized and analyzed. The research progresses of CoSb_3 -based TE devices were also briefly summarized in recent years. Although the ZT value of CoSb_3 -based TE materials has made some progress, however, the conversion efficiency of the TE device corresponding to the ZT value of the material is still low. Therefore, the ZT value of CoSb_3 -based TE materials still needs to be further improved. At present, some problems in the

Table 2 A summary of the reported CoSb_3 -based TE devices in recent years

Materials of p-legs	Materials of n-legs	Type	Electrode of hot side	Electrode of cold side	Barrier layer	Open-circuit voltage (mV)	$P_{\max}$ (W)	$\eta_{\max}$ (%)	ΔT (°C)	Ref.
$\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$	CoSb_3	Uni-couple	Metallic	Metallic	None	204.2	0.67	10.7	27–700	[238]
$\text{In}_{0.25}\text{Co}_3\text{FeSb}_{12}$	$\text{In}_{0.25}\text{Co}_{3.95}\text{Ni}_{0.05}\text{Sb}_{12}$	Uni-couple	Mo–Cu	Cu	Ti	143	0.796	—	55–598	[239]
$\text{NdFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$	$\text{Yb}_{0.35}\text{Co}_4\text{Sb}_{12}$	Uni-couple	Co–Si	—	—	—	—	9.1	70–550	[240]
$\text{Yb}_{0.25}\text{Fe}_{0.25}\text{Co}_{3.75}\text{Sb}_{12}$	$\text{La}_{0.7}\text{Ti}_{0.1}\text{Ga}_{0.1}\text{Fe}_{2.7}\text{Co}_{1.3}\text{Sb}_{12}$	Uni-couple	Mo	Cu	Ga–Sn	80	0.337	7.2	40–406	[241]
$\text{Ce}_{0.45}\text{Co}_{2.5}\text{Fe}_{1.5}\text{Sb}_{12}$	$\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12}/\text{Yb}_2\text{O}_3$	2 pairs	Mo–Cu	Cu	Mo	210	0.14	6.4	47–540	[242]
$\text{Ce}_{0.9}\text{Fe}_3\text{CoSb}_{12}$	$\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}/\text{MWCNTs}$	8 pairs	Mo–Cu	Cu	Ag–Cu–Zn	1480	0.46	9.3	41–499	[243]
$\text{DD}_3\text{Fe}_3\text{CoSb}_{12}$	$(\text{Mm}, \text{Sm})_3\text{Co}_4\text{Sb}_{12}$	8 pairs	Metallic	Metallic	Fe–Ni alloy	—	0.806	—	30–600	[237]
$\text{CeFe}_3\text{CoSb}_{12}$	$\text{Yb}_{0.15}\text{Co}_4\text{Sb}_{12}$	14 pairs	Ag	Ag	Ag–Pd	~520	0.48	—	20–300	[244]
$(\text{La}, \text{Ba}, \text{Ga}, \text{Ti})_{0.9}\text{Fe}_3\text{CoSb}_{12}$	$(\text{Yb}, \text{Ca}, \text{Al}, \text{Ga}, \text{In})_{0.7}\text{Fe}_{0.25}\text{Co}_{3.75}\text{Sb}_{12}$	32 pairs	AlN	AlN	—	~400	25	8.5	50–600	[245]
$\text{Yb}_{0.72}\text{Co}_4\text{Sb}_{12}/1.4\text{vol}\% \text{rGO}$	$\text{Ce}_{0.85}\text{Fe}_3\text{CoSb}_{12}/0.72\text{vol}\% \text{rGO}$	8 pairs	Mo–Cu	Cu	Ag–Cu–Zn	—	3.8	8.4	23–600	[246]
$\text{La}_{0.8}\text{Ba}_{0.01}\text{Ga}_{0.1}\text{Ti}_{0.1}\text{Fe}_3\text{CoSb}_{12}$	$\text{La}_{0.3}\text{Ca}_{0.1}\text{Al}_{0.1}\text{Ga}_{0.1}\text{In}_{0.2}\text{Co}_{3.75}\text{Fe}_{0.25}\text{Sb}_{12}$	32 pairs	—	—	—	4920	32	8	50–600	[248]
$\text{Mm}_{0.30}\text{Fe}_{1.46}\text{Co}_{2.54}\text{Sb}_{12.05}$	$\text{Yb}_{0.09}\text{Ba}_{0.05}\text{La}_{0.05}\text{Co}_4\text{Sb}_{12}$	32 pairs	Metallic	Metallic	Mo	2.73	10.5	7	40–500	[249]

research of CoSb₃-based TE materials, such as the optimization and decoupling of thermal and electrical transport properties, and the development of preparation technology, need to be further studied.

(i) For CoSb₃-based materials with the filling atom, although there have been a lot of reports on the optimization of the number of filling atoms, the filling fraction, and the type of filling atoms. However, it is still possible to reduce the thermal conductivity of the CoSb₃ material by further optimizing these parameters to improve the TE performance. (ii) The TE properties of CoSb₃-based materials can be significantly improved by forming solid solution alloy or the filling of the foreign atoms in the Sb₁₂ icosahedron void. It is expected to further improve the TE properties of CoSb₃-based materials by doping and filling with foreign atoms simultaneously. (iii) The introduction of nanoparticles, special structures, and low-dimensional nanocrystallization in CoSb₃-based materials can obviously increase their TE properties and even mechanical properties. We may further screen the types of the introduced nanoparticles and special structures, and study the effects of these nanoparticles and special structures on the TE properties and mechanical properties of CoSb₃-based materials in order to further improve their TE and mechanical performance. Besides, miniaturization of devices is the trend of development; therefore, it is very important to prepare high-performance low-dimensional CoSb₃-based materials. (v) It is a challenge to decouple the electrical and thermal transport properties of CoSb₃-based materials because the TE parameters are closely related to each other and mutually constrained. The decoupling and synergistic optimizations of the electrical and thermal transport properties for CoSb₃-based materials have been achieved through some new effects. However, the physical mechanisms resulting from these new effects still need to be studied further. (vi) For the preparation of CoSb₃-based materials, researchers have reported some advanced preparation techniques, which provide the possibility for large-scale preparation of CoSb₃-based materials. More advanced preparation techniques can still be explored to further shorten the preparation time and reduce the preparation cost of the materials, improving the properties of the prepared materials. (vii) The conversion efficiency of CoSb₃-based TE devices needs to be further improved, and the module manufacturing cost needs to be further reduced by scaling up and process optimization; the service behavior of CoSb₃-based TE devices under complex operating conditions should be

further studied in detail.

In short, there is still much work to be done to further improve the TE properties of both CoSb₃-based materials and devices. Although the challenges are pervasive, the research of CoSb₃-based TE materials is becoming an intense and worldwide activity. More and more researchers are attracted to the field of TE materials. Interdisciplinary communication between physicists, chemists, materials scientists, and device engineers is also deepening. The interdisciplinary research of TE materials and other subjects is more and more extensive. It is expected to promote the sustained and rapid growth of TE research and future large-scale application.

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