Ce Filling Limit and Its Influence on Thermoelectric Performance of Fe₃CoSb₁₂-Based Skutterudite Grown by a Temperature Gradient Zone Melting Method

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Abstract: CoSb₃-based skutterudite is a promising mid-temperature thermoelectric material. However, the high lattice thermal conductivity limits its further application. Filling is one of the most effective methods to reduce the lattice thermal conductivity. In this study, we investigate the Ce filling limit and its influence on thermoelectric properties of p-type Fe₃CoSb₁₂-based skutterudites grown by a temperature gradient zone melting (TGZM) method. Crystal structure and composition characterization suggests that a maximum filling fraction of Ce reaches 0.73 in a composition of Ce₀.₇₃Fe₂₇Co₁₀.₈₃Sb₁₂ prepared by the TGZM method. The Ce filling reduces the carrier concentration to 1.03 × 10²⁰ cm⁻³ in the Ce₁2₅Fe₃CoSb₁₂, leading to an increased Seebeck coefficient. Density functional theory (DFT) calculation indicates that the Ce-filling introduces an impurity level near the Fermi level. Moreover, the rattling effect of the Ce fillers strengthens the short-wavelength phonon scattering and reduces the lattice thermal conductivity to 0.91 W m⁻¹ K⁻¹. These effects induce a maximum Seebeck coefficient of 168 μV K⁻¹ and a lowest κ of 1.52 W m⁻¹ K⁻¹ at 693 K in the Ce₁2₅Fe₃CoSb₁₂, leading to a peak zT value of 0.65, which is 9 times higher than that of the unfilled Fe₃CoSb₁₂.

Keywords: skutterudite; CoSb₃; Ce-filling; thermoelectric

1. Introduction

With the consumption of traditional fossil fuels and the aggravation of environment pollution, exploring new and effective energy utilization techniques has experienced increasing significance [1–3]. Thermoelectric technology, enabling the direct energy conversion between heat and electricity, has provided a promising and eco-friendly energy solution [4–6]. The thermoelectric performance is fundamentally characterized by the material dimensionless figure-of-merit (zT), defined as zT = S²σT/κ, where S, σ, κ, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity (comprised of electronic contribution κₑ and lattice contribution κₗ), and temperature in Kelvin, respectively [7–9]. High power factor (S²σ) and low κ are necessary for high zT [8,9]. S, σ, and κₑ are related to each other as a function of other fundamental parameters, such as carrier concentration (n) [10–12]. These fundamental parameters need to be optimized. Typically, the n of thermoelectric materials can be optimized by valence electron counts engineering [13,14].
modulation doping [15], and band gap engineering [16]. Other than the interrelated parameters, reducing $k_f$ can achieve a low $\kappa$ and high $zT$ [17]. The reduced $k_f$ can be achieved by introducing additional structure defects, such as point defects [18], dense grain boundaries [19], and nanoprecipitates [20, 21] for strengthening phonon scattering.

Among thermoelectric materials, skutterudites, especially CoSb$_3$-based skutterudites, are promising application prospect in the field of mid-temperature power generation [22–24]. Binary CoSb$_3$ is an intermetallic compound formed by a peritectic reaction [25]. CoSb$_3$ is a body-centered cubic cage-like crystal structure (Im-3 space group) with two void positions at the 2a sites (0, 0, 0) and (1/2, 1/2, 1/2) in the unit cell [26, 27]. Intrinsic CoSb$_3$ is a p-type semiconductor with high $S$ and high carrier mobility ($\mu$) [28]. However, the strong Co-Sb covalent bonding induces high $k_f$ (~7.5 W m$^{-1}$ K$^{-1}$ at room temperature) of intrinsic CoSb$_3$, limiting its thermoelectric performance [29, 30].

To reduce the $k_f$ of intrinsic CoSb$_3$, filling the void position at the 2a site with small atom can tune CoSb$_3$ into filled-CoSb$_3$ ($R_x$Co$_{4}$Sb$_{12}$, $R$ is the filling elements and $x$ is the filling fraction), which possesses a feature of phonon glass and electron crystal (PGEC) [31]. The fillers are loosely bounded and rattle near the equilibrium positions and significantly scatter the low-frequency phonons, leading to decreased $k_f$ and improved $zT$ [32, 33]. The fillers can be rare-earth atoms [18, 34], alkaline-earth atoms [35], alkaline metals atoms [36]. Pei et al. [36] found that n-type Na$_{0.48}$Co$_{0.51}$Sb$_{12}$ had a reduced room-temperature $k_f$ of ~0.73 W m$^{-1}$ K$^{-1}$ in accordance with a peak $zT$ of 1.25. Alkaline-earth Ba can be filled into the void position at the 2a site of CoSb$_3$ to form n-type filled-CoSb$_3$ and approach a decreased $k_f$ of 0.73 W m$^{-1}$ K$^{-1}$ and a peak $zT$ of ~1.0 in Ba$_{0.51}$Co$_{4}$Sb$_{12}$ [35]. Yb is another utilized rare-earth filler since the relatively high atomic mass and small ionic radius [18, 37], which can lead to a low $k_f$ of 0.62 W m$^{-1}$ K$^{-1}$ in n-type Yb$_{0.47}$Co$_{0.53}$Sb$_{12}$ [38]. However, rare-earth Ce has a low filling fraction in CoSb$_3$ comparing with Yb. Morelli et al. [39] prepared n-type Ce-filled CoSb$_3$ by arc melting and found a low filling fraction of ~0.1. Even though with a low Ce filling fraction, the $k_f$ was strongly depressed and a low $k_f$ of ~4 W m$^{-1}$ K$^{-1}$ was obtained, which is only half of the unfilled CoSb$_3$. To improve the Ce filling fraction in undoped CoSb$_3$, Tang et al. [40] used phase diagram method to increase this value up to 0.2. Due to the increased filling fraction, a further reduced $k_f$ of ~2 W m$^{-1}$ K$^{-1}$ and a $zT$ value of 1.3 at 850 K were obtained in n-type Ce$_{0.14}$Co$_{4}$Sb$_{12}$ prepared by melting-quenching-annealed-sintering. Besides, the thin film CoSb$_3$ sample prepared by deposition experienced increased Ce-filling fraction. Smalley et al. [41] reported a high Ce-filling fraction of ~0.55 in deposited CoSb$_3$ film.

Although heavy filling in the void position remarkably reduces the $k_f$ of CoSb$_3$-based thermoelectric materials, heavily filled CoSb$_3$-based materials are generally n-type semiconductors because the fillers function as electron donors [20, 34, 41]. In term of the assembly of thermoelectric devices, both p-type and n-type materials are required. Hence, p-type CoSb$_3$-based thermoelectric materials are necessary. To achieve low $k_f$ of p-type CoSb$_3$-based thermoelectric materials, Fe has been partially used to substitute Co [6, 18, 40], behaving as the electron acceptor to tune into p-type. Particularly, after Fe substitution at the Co site, CaFe$_{3.5}$Co$_{0.5}$Sb$_{12}$ has a high $S^2\sigma$ of 33 $\mu$W cm$^{-1}$ K$^{-2}$ with a positive $S$ of 170 $\mu$V K$^{-1}$ and a low $k_f$ of ~0.9 W m$^{-1}$ K$^{-1}$ at 773 K [42]. Furthermore, charge-compensational doping by the substitution at Co or Sb sites has been widely applied to increase the filling faction of Ce in bulk CoSb$_3$-based skutterudites, which can simultaneously tune n-type CoSb$_3$ skutterudites into p-type ones [43, 44]. Tanahashi et al. [45] found a Ce filling fraction of ~0.9 in p-type CoSb$_3$-based skutterudites with the nominal composition of CeFe$_2$CoSb$_{12}$, which is prepared by gas-phase atomization and sintering and approached a $zT$ of 0.63 at 700 K. Chen et al. [46] reported a p-type Ce$_{0.95}$Fe$_2$CoSb$_{12.1}$ grown by scanning laser melting method combined with spark plasma sintering and achieved the Ce filling fraction of 0.85 and the $zT$ of ~0.79 at 750 K.

As suggested in Figure 1a–f, crystal structures of the unfilled and Ce-filled Fe$_2$CoSb$_{12}$ and corresponding density functional theory (DFT)-calculated band structures and density of states (DOS) were firstly investigated. As can be seen, Ce-filling introduces an impurity
level near the Fermi energy \( (E_F) \), which is mainly contributed by the \( f \) orbital of Ce atom. Besides, Ce-filling also increases the slope of DOS near \( E_F \) and correspondingly contributes to increased \( S \) \([47,48]\). Additionally, filled CoSb\(_3\)-based thermoelectric materials can be fabricated by various methods, such as traditional melting-quenching-annealing-sintering \([49]\), melt-spinning combined with spark plasma sintering technique (MS-SPS) \([50]\), high-energy ball-milling combined with hot pressing (BM-HP) technique \([51]\), and temperature gradient zone melting (TGZM) method \([52,53]\). Among them, TGZM is a novel material preparation method, which can synthesize CoSb\(_3\)-based skutterudites with faster speed and higher purity by avoiding the complex peritectic solidification process. Effects of Ce fillers and its filling fraction in TGZM-prepared Fe\(_3\)CoSb\(_{12}\) might be different from that prepared by other methods. In this study, we employed the novel TGZM method to investigate the influence and filling fraction of Ce in Fe\(_3\)CoSb\(_{12}\). A series of Ce-filled p-type CexFe3CoSb12 (x = 0 to 1.5) samples were prepared. We found that the maximum filling level of Ce is 0.73 in the TGZM-prepared Ce\(_{1.25}\)Fe3CoSb\(_{12}\) with a measured composition of Ce0.73Fe2.73Co1.18Sb\(_{12}\). The synergistic effect on Fe substitution at the Co and Ce-filling result in reduced \( n_H \) to \( 1.03 \times 10^{20} \) cm\(^{-3}\) in Ce\(_{1.25}\)Fe3CoSb\(_{12}\). A low \( \kappa_l \) of 0.91 W m\(^{-1}\) K\(^{-1}\) at 693 K can be obtained in the Ce\(_{1.25}\)Fe3CoSb\(_{12}\), significantly contributing to an increased \( zT \) of 0.65 at 693 K.

Figure 1. Band structures and density of states (DOS) of the unfilled and Ce-filled Fe\(_3\)CoSb\(_{12}\)-based skutterudites: The conventional unit cell of unfilled (a) and Ce-filled (b) Fe\(_3\)CoSb\(_{12}\)-based skutterudites. Calculated band structures of unfilled (c) and Ce-filled (d) Fe\(_3\)CoSb\(_{12}\)-based skutterudites and Calculated DOS of unfilled (e) and Ce-filled (f) Fe\(_3\)CoSb\(_{12}\)-based skutterudites.
2. Materials and Methods

2.1. Samples Preparation

Initial ingots of (Fe₃Co)-95 at. % Sb filled with x at. % Ce (x = 0, 0.25, 0.5, 0.75, 1, 1.25, 1.5) were prepared by induction melting at 1473 K for 30 min in a vacuum induction furnace (Xi’an, China) (~10⁻³ Pa) followed by a furnace cooling. Elements Fe (99.95 at. %), Co (99.95 at. %), Sb (99.995 at. %), and Ce (99.9%), purchased from CNBM (Chengdu, China) Optoelectronic Materials Com., Ltd., were properly weighed as raw materials according to the nominal compositions. Extra Sb was added to obtain the samples of nominal composition CeₓFe₃CoSb₁₂ after the TGZM process. Besides, extra Ce was introduced to compensate the Ce loss during TGZM process. The as-cast ingots were cut into cylinder samples with a diameter of 12.8 mm, and the oxide layer on the surface was cleaned before being put into a high-purity alumina tube with an inner diameter of 13 mm to execute the TGZM process, which was described in detail in previous reports [54,55]. The TGZM process was then conducted in a homemade directional solidification furnace of a thermal stabilization time of 48 h with an estimated temperature gradient of 40 K/mm. The TGZM-grown samples were obtained from the mushy zone formed during the TGZM process. The obtained samples were cleaned, polished, and carried out microstructure characterization and performance tests. Samples throughout the manuscript are described as their nominal compositions after the TGZM process.

2.2. Microstructure Characterization

The crystal structures of as-fabricated samples were determined by powder X-ray diffraction (XRD-7000, Shimadzu, Japan) with Cu-Kα radiation. The lattice parameters were obtained by Rietveld analysis. Scanning electron microscopy (SEM, Verios G4, FEI, equipped with EDS, Hillsboro, OR, USA) was used to acquire the morphologies of the sample’s surface and a Double Cs Corrector Transmission Electron Microscope (Cs-TEM, Themis Z, FEI, Hillsboro, OR, USA) was used to characterize their microstructure and chemical features. The actual chemical content was obtained by taking the average of fifteen different positions of each sample. Electron backscattered diffraction (EBSD, Thermo QuasOr type, Waltham, MA, USA) attached to FEI Helios G4 CX type SEM (Hillsboro, OR, USA) was used to determine the crystal orientation relationship.

2.3. Properties Measurements

The samples with 12.7 mm in diameter and 1.5 mm in thickness were used to measure their thermoelectric properties from 303 K to 813 K. In our measurements, σ and S were measured simultaneously using the LSR-3 system (Linseis, Zelb, Bavaria, Germany) under the helium atmosphere. κ was calculated by κ = D·Cₚ·ρ, where D is the thermal diffusivity measured by LFA-1000 (Linseis, Zelb, Bavaria, Germany), Cₚ the specific heat obtained by DSC (STA-449C, Netzsch, Germany), and ρ the density obtained by the Archimedes method. The Hall coefficient (R_H), measured on the PPMS system (CFMS-14T, London, UK) with a magnetic field of ±2T, was used to calculate the room-temperature Hall carrier concentration (n_H), determined by the formula [18]:

\[ n_H = 1/\epsilon R_H, \]

where \( \epsilon \) represents the electron charge.

2.4. Density Functional Theory (DFT) Calculations

The physical properties of Fe₃CoSb₁₂, CeFe₃CoSb₁₂ were calculated using the Cambridge Serial Total Energy Package (CASTEP) [56]. The exchange-correlation interactions were described using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) type [57]. The plane wave cutoff energy was 450 eV for geometry optimization, band structures, and density of states calculations. The Monkhorst-Pack grid parameters were set to 8 × 8 × 8 (34 Irreducible k-points) for calculations. The Convergence tolerances were set to 1.0 × 10⁻⁵ eV/atom, 0.03 eV/Å, 0.05 GPa and 0.001 Å for energy, maximum force, maximum stress and maximum displacement, respectively.
3. Results and Discussion

3.1. Microstructure and Phase Composition

To understand crystal structures of the as-prepared Ce$_x$Fe$_3$CoSb$_{12}$ (x = 0 to 1.5), we firstly investigated powder X-ray diffraction (XRD) patterns and the results are shown in Figure 2a. Main diffraction peaks of samples can be identified as the body-centered cubic CoSb$_3$ with a lattice parameter $a$ of 9.034 Å and a space group of Im-3 (JCPDS 19-0336). Due to the characteristic of eutectic reaction, a small number of Sb impurities are observed. Figure 2b plots the corresponding $a$ of the as-prepared Ce$_x$Fe$_3$CoSb$_{12}$ (x = 0 to 1.5). The calculated $a$ increases with increasing the Ce-filling content and stabilizes at the x of 1.25. The increased $a$ should be attributed to Ce-filling induced lattice expansion.

TEM investigations were carried out to further understand the crystal structure of the as-fabricated Ce$_x$Fe$_3$CoSb$_{12}$. Figure 2c is an atomic-resolution TEM high-angle annular dark-field (HAADF) image of CeFe$_3$CoSb$_{12}$. The inset of Figure 2c is superimposed a $2 \times 2 \times 2$ supper cell model for the CeFe$_3$CoSb$_{12}$ along the [100] direction, well-matched with the observed lattice. Figure 2d is a selected area electron diffraction (SAED) pattern and can be indexed along the [100] zone-axis. Figure 2e presents the corresponding inverse Fast Fourier transform (IFFT) image along with the (011) planes. The observed $d$ spacing between (011) planes is ~6.64 Å, which is larger than that of CoSb$_3$ (~6.39 Å). Besides, no obvious lattice distortion can be observed from Figure 2e, indicating that the as-fabricated samples have a high crystallinity. Figure 2f–h show the EBSD inverse pole figure (IPF) maps of the Ce$_x$Fe$_3$CoSb$_{12}$. As can be seen, no obvious texture information can be observed, indicating the isotropic thermoelectric performance of the as-fabricated Ce$_x$Fe$_3$CoSb$_{12}$.

Figure 2. Cont.
To understand the composition of the as-fabricated Ce\textsubscript{x}Fe\textsubscript{3}CoSb\textsubscript{12}, we conducted SEM image and the corresponding EDS maps of the Ce\textsubscript{1.25}Fe\textsubscript{3}CoSb\textsubscript{12} and the results are shown in Figure 3a–e. As can be seen, Fe, Co, Sb, and Ce are evenly distributed in the as-fabricated Ce\textsubscript{1.25}Fe\textsubscript{3}CoSb\textsubscript{12}. A typical high-resolution TEM (HRTEM) HAADF image of the Ce\textsubscript{Fe}CoSb\textsubscript{12} is shown in Figure 3f. Figure 3g–i are the corresponding elemental maps in atomic scale. Figure 3j is a magnified overlap of elemental maps where the dark green balls represent Ce fillers. As can be seen, Ce filler sits at the 2a sites in the cage among the Sb-icosahedron (pink ball).

![Figure 2](image-url)  
*Figure 2. (a) XRD diffraction patterns and (b) Lattice parameter a of the as-prepared Ce\textsubscript{x}Fe\textsubscript{3}CoSb\textsubscript{12} (x = 0 to 1.5), (c) HAADF image with an inserted 2 × 2 × 2 supper cell model, (d) SAED pattern in (c) and (e) Inverse pole figure (IPF) maps in CeFe\textsubscript{3}CoSb\textsubscript{12}. The EBSD IPF maps in (f) normal direction, (g) rolling direction and (h) transverse direction of the Ce\textsubscript{1.25}Fe\textsubscript{3}CoSb\textsubscript{12}.*

![Figure 3](image-url)  
*Figure 3. SEM image (a), the corresponding elemental maps of Fe (b), Co (c), Sb (d), Ce (e) of the Ce\textsubscript{1.25}Fe\textsubscript{3}CoSb\textsubscript{12} sample. The HRTEM HAADF image (f) of the CeFe\textsubscript{3}CoSb\textsubscript{12} and the corresponding atomic scale elemental map of Sb (g), overlay elemental map of Fe, Co and Sb (h), overlay elemental map of Sb and Ce (i), the magnified overlap of elemental maps superimposed with the crystal structure (j), where the dark green ball, the pink ball and dull-red ball represent Ce, Sb, and Fe/Co.*
Figure 4a shows typical EDS spectra of the Ce<sub>x</sub>Fe<sub>3</sub>CoSb<sub>12</sub>. All samples are composed of Ce, Fe, Co, and Sb without other impurity elements. Figure 4b shows the average atomic ratios of Fe, Co, Sb, and Ce elements in each sample based on the statistic EDS results. As can be seen, the Ce-filling level in the samples increases at first and then tends to be stabilized at the x of 1.25, which is consistent with the peak shift from XRD. Figure 4c compares the Ce-filling fraction of Fe-doped CoSb<sub>3</sub> prepared by different methods. The Ce filling fraction varies with the preparation method and Fe/Co ratio. The Fe/Co ratio in the actual composition of the samples shown in the red dotted box in Figure 4c is close to ~2.5. Under the similar Fe/Co ratio, a relative high filling fraction of 0.73 is achieved in a composition of Ce<sub>0.73</sub>Fe<sub>2.73</sub>Co<sub>1.18</sub>Sb<sub>12</sub> prepared by the TGZM method in this study. Figure 4d shows the TEM-EDS spectrum and maps of the Ce<sub>x</sub>Fe<sub>3</sub>CoSb<sub>12</sub>. As can be seen, Fe, Co, Sb, and Ce elements are homogeneously distributed on a micro-scale, indicating successful Fe substitution at the Co site and Ce-filling.
3.2. Thermoelectric Transport Properties

To understand the thermoelectric properties of the as-fabricated CeₙFe₃CoSb₁₂ (x = 0 to 1.5), σ, S, S²σ, and κ were measured at the temperature range between 303 and 813 K. Figure 5a depicts temperature-dependent σ of the CeₙFe₃CoSb₁₂. The Fe₃CoSb₁₂ has a higher σ (1302 S cm⁻¹) comparing with the Ce-filled samples in the entire measured temperature. With increasing the Ce-filling level, the σ of the CeₙFe₃CoSb₁₂ decreases from 1302 S cm⁻¹ of the Fe₃CoSb₁₂ to 638 S cm⁻¹ of the Ce₁.₂₅Fe₃CoSb₁₂ at 303 K. The slight increase of σ from x = 1.25 to 1.5 might be attributed to the slightly increased Sb content (as evidenced by the XRD peak intensity in Figure 2a). Besides, the nearly linear decrease of σ with increasing the temperature indicates that the as-fabricated CeₙFe₃CoSb₁₂ is a degenerated semiconductor. With increasing the Ce content, S increases from 62 µV K⁻¹ of the Fe₃CoSb₁₂ to 117 µV K⁻¹ of the Ce₁.₂₅Fe₃CoSb₁₂ at 303 K (Figure 5b). The maximum S value of 168 µV K⁻¹ at 693 K can be obtained in the Ce₁.₂₅Fe₃CoSb₁₂. The positive S indicates that the CeₙFe₃CoSb₁₂ is p-type, which is consistent with the calculation of the band structures. A classic single parabolic band (SPB) model was used to evaluate the effective mass m* as described by Equations (1)–(4) [18,60]:

\[
S = \pm \frac{k_B}{e} \left( \frac{2F_1(\eta)}{F_0(\eta)} - \eta \right) \quad (1)
\]

\[
m^* = \frac{\hbar^2}{2k_BT} \left[ \frac{nr_H}{4\pi F_{1/2}(\eta)} \right] \quad (2)
\]

\[
r_H = \frac{3}{2} \frac{F_{1/2}(\eta)F_{-1/2}(\eta)}{2F_0(\eta)} \quad (3)
\]

\[
F_n(\eta) = \int_0^{\infty} \frac{x^n}{1 + e^{x - \eta}} \, dx \quad (4)
\]

where e is the electron charge, η the reduced Fermi energy, \( \eta = E_F/k_BT \), \( F_n(\eta) \) the Fermi integral and \( r_H \) the Hall factor. Figure 5c shows the Pisarenko plot of Fe₃CoSb₁₂ with the measured room-temperature \( n_H \) and corresponding S of Ce-filled Fe₃CoSb₁₂ samples. With increasing Ce-filling level, the experimental S values corresponding to the \( n_H \) deviates from the Pisarenko plot to a higher level, indicating that Ce-filling led to an increase of the \( m^* \). This should be attributed to the increased DOS near the edge of the band structure (Figure 1e,f) induced by Ce-filling. The maximum \( S^2\sigma \) (Figure 5d) significantly increases from 6.7 µW cm⁻¹ K⁻² of the Fe₃CoSb₁₂ to 14.4 µW cm⁻¹ K⁻² of the Ce₁.₂₅Fe₃CoSb₁₂ at 693 K.

![Figure 5. Cont.](image-url)
Figure 5. Thermoelectric properties of Ce$_x$Fe$_3$CoSb$_{12}$ (x = 0 to 1.5). Temperature-dependent (a) $\sigma$; (b) $S$. (c) The experimental $S$ values corresponding to the $n_{Hi}$, where the red line represents the Psarenko plot for Fe$_2$CoSb$_{12}$. Temperature-dependent (d) $S^2$; (e) $\kappa$; (f) $\sigma$; (g) $\kappa_l$; (h) $zT$. (i) Comparison of the room-temperature $\kappa$ for nominal Ce$_{1.25}$Fe$_3$CoSb$_{12}$ with the reported values for CeFe$_2$CoSb$_{12}$ prepared by AM, [59] CeFe$_3$Sb$_{12}$ [61] and CeFe$_{0.4}$Fe$_{2}$CoSb$_{12}$ [62] prepared by TM, CeFe$_3$CoSb$_{12}$ prepared by GS, [45] Ce$_{0.95}$Fe$_3$CoSb$_{12.1}$ prepared by SS, [46] and Ce$_{0.86}$Fe$_3$CoSb$_{12.09}$ prepared by melt spinning and spark plasma sintering (MS) [63].

Figure 5e plots temperature-dependent $\kappa$ of the as-fabricated Ce$_x$Fe$_3$CoSb$_{12}$ (x = 0 to 1.5). With increasing the Ce-filling level, the $\kappa$ gradually decreases and approaches 1.52 W m$^{-1}$ K$^{-1}$ of Ce$_{1.25}$Fe$_3$CoSb$_{12}$ at 693 K. The $\kappa_l$ can be calculated as $\kappa_l = L\sigma T$ (Figure 5f), where $L$ is the Lorenz number calculated based on SPB model. With increasing the Ce-filling level, the $\kappa_l$ significantly reduces due to reduced $\sigma$. Figure 5g presents temperature-dependent $\kappa_l$, calculated by $\kappa - \kappa_l$. The $\kappa_l$ of the Ce-filled Fe$_3$CoSb$_{12}$ is much lower than that of the unfilled Fe$_3$CoSb$_{12}$. The $\kappa_l$ reduces with increasing the Ce-filling level and approaches a lowest $\kappa_l$ of 0.91 W m$^{-1}$ K$^{-1}$ at 693 K in the Ce$_{1.25}$Fe$_3$CoSb$_{12}$. This should be primarily attributed to the rattling effect for strengthening short-wavelength phonon scattering, induced by Ce-filling [64]. Figure 5h displays temperature-dependent $zT$ of the as-fabricated Ce$_x$Fe$_3$CoSb$_{12}$ (x = 0 to 1.5). Benefitting from the enhanced $S^2\sigma$ and significantly reduced $\kappa$, a peak $zT$ value of 0.65 can be achieved in the Ce$_{1.25}$Fe$_3$CoSb$_{12}$ at 693 K, which is 9 times higher than that of the unfilled Fe$_3$CoSb$_{12}$. Figure 5i compares the room-temperature $\kappa$ of nominal Ce$_{1.25}$Fe$_3$CoSb$_{12}$ in this study prepared by TGZM with the reported $\kappa$ of p-type Ce-filled and Fe-doped CoSb$_3$ prepared by other methods. As can be seen, a relatively lower $\kappa$ is obtained in TGZM prepared Ce$_{1.25}$Fe$_3$CoSb$_{12}$, which is due to the higher Ce filling fraction with an optimized Fe/Co ratio. Besides, the maximum $zT$ values of different Ce-filled and Fe-doped CoSb$_3$ prepared by various methods are compared and shown in Figure S1 of the Supplementary Material, indicating a higher $zT$ value can be obtained by optimizing Ce-filling fraction and Fe/Co ratio.
4. Conclusions

In this study, under the guidance of the DFT calculation, where Ce-filling can introduce an impurity level near the $E_F$ and increase the thermoelectric performance of the Fe$_3$CoSb$_{12}$, we have designed and prepared the p-type Ce$_{1.25}$Fe$_3$CoSb$_{12}$ ($x = 0$ to 1.5) by a facile TGZM method. The Ce-filling limit in TGZM-prepared Fe$_3$CoSb$_{12}$ was found to be 0.73 with a measured composition of Ce$_{0.73}$Fe$_{2.73}$Co$_{1.18}$Sb$_{12}$. The filling limit is approached at the nominal composition of Ce$_{1.25}$Fe$_3$CoSb$_{12}$. Under the synergistic effect, Fe substitution at the Co site and Ce-filling, an optimal $n_H$ of 1.03 $\times$ $10^{20}$ cm$^{-3}$ is approached. The high $S$ of 168 $\mu$V K$^{-1}$ at 693 K due to the increase of the Ce filling level induces a high $S^2\sigma$ of 14.4 $\mu$W cm$^{-1}$ K$^{-2}$ at 693 K in the Ce$_{1.25}$Fe$_3$CoSb$_{12}$, which is increased by 100% comparing with that of the Fe$_3$CoSb$_{12}$. The rattling effect of Ce fillers strongly strengthens phonon scattering, leading to reduced $\kappa_l$ as low as 0.91 W m$^{-1}$ K$^{-1}$ at 693 K in the Ce$_{1.25}$Fe$_3$CoSb$_{12}$. Benefitting from the low $\kappa$ of 1.52 W m$^{-1}$ K$^{-1}$ induced by both optimized $n_H$ and reduced $\kappa_l$, a peak $zT$ value of 0.65 at 693 K can be achieved in the Ce$_{1.25}$Fe$_3$CoSb$_{12}$, which is 9 times higher than the Fe$_3$CoSb$_{12}$.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/ma14226810/s1, Comparison of the maximum $zT$ value of nominal Ce$_{1.25}$Fe$_3$CoSb$_{12}$ in this study prepared by TGZM with the reported $zT$ of p-type Ce-filled and Fe-doped CoSb$_3$ prepared by other methods.

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