Calcium cobaltite, a promising oxide for energy harvesting: effective strategies toward enhanced thermoelectric performance

Jincheng Yu and Robert Freer*

Department of Materials, University of Manchester, Manchester M13 9PL, United Kingdom
* Author to whom any correspondence should be addressed.
E-mail: Robert.Freer@manchester.ac.uk

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Abstract
Thermoelectric (TE) materials are able to generate power from waste heat and thereby provide an alternative source of sustainable energy. Calcium cobaltite is a promising p-type TE oxide because of its intrinsically low thermal conductivity arising from the misfit-layered structure. Its structural framework contains two sub-layers with different incommensurate periodicities, offering different sites for substituting elements; the plate-like grain structure contributes to texture development, thereby providing opportunities to modulate the TE response. In this topical review, we briefly introduce the misfit crystal structure of calcium cobaltite and summarize three efficient strategies to enhance the TE performance, namely (a) elemental doping, (b) optimization of fabrication route, and (c) composite design. For each strategy, examples are presented and enhancing mechanisms are discussed. The roles of dopants, processing routes and phase composition are identified to provide insights into processing-microstructure-property relationships for calcium cobaltite based materials. We outline some of the challenges that still need to be addressed and hope that the proposed strategies can be exploited in other TE systems.

1. Introduction

The supply of energy, and its usage in industrial, transportation and domestic environments, is closely related to the development of human society. Up to now, carbon-based fuels have been the primary energy resources because of extensive reserves and advanced mining technologies [1]. However, these non-renewable resources are diminishing and are responsible for excessive emissions of carbon dioxide, accelerating global warming [2]. Consequently, interest has turned to alternative energy sources, including nuclear [3], solar [4] and wind, although their use has been limited for different reasons.

Thermoelectric (TE) materials, enabling the conversion of heat into electricity, are a promising sustainable energy source. By coupling n-type and p-type materials in TE modules, power generation or active cooling can be realized [5]. With no moving parts, minimal vibrations, no direct pollutants, existing commercial TE systems usually have a small size, good stability but limited working temperature range [6, 7]. Due to their reliable performance in applications from radioisotope TE generators for space missions, to waste heat recovery modules for automotive, aerospace and industrial environments [8, 9], TE materials have attracted increasing attention in recent years. Furthermore, the energy harvesting provided by TE materials can be utilized to power the Internet of Things (IoT) sensors, providing considerable opportunities to replace traditional wires and batteries [10, 11]. The dimensionless figure of merit ZT (defined as $\sigma S^2 T/\kappa$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $\kappa$ is the thermal conductivity and $T$ is the absolute temperature) is one of the primary criteria to select TE materials for module fabrication [12, 13]. A high ZT value, reflecting high conversion efficiency, is therefore expected on the basis of high electrical conductivity, large thermopower and low thermal conductivity.

Traditional TE materials are based on antimony, lead, and bismuth tellurides [14, 15]. As a result of the toxic and expensive components, and their low resistance to atmospheric oxidation at high temperatures, their exploitation is limited. However, such disadvantages are not encountered in metal-oxide-based materials.
compounds. In the past two decades, there has been growing interest in oxide TE materials because of their high chemical and thermal stability and the relative abundance of their starting materials [8]. Whilst the performance of most oxides is limited by their high thermal conductivity and modest electrical conductivity [16, 17], several show outstanding TE properties. Among oxide-based TE materials, the layer-structured, p-type calcium cobaltite has long been of interest because of its intrinsically low thermal conductivity and good high temperature stability [18]. For single crystal Ca$_3$Co$_4$O$_9$, a high ZT value of 0.87 at 973 K, was reported by Shikano et al [19]. In contrast, polycrystalline ceramics of similar compositions exhibit lower TE performance because of modest densification caused by the layered structure [20]. Nevertheless, there is scope for further improvement and optimization because the layered structure of the cobaltites provides an excellent framework to accommodate substituting elements and opportunities to regulate defects by controlling processing conditions [21].

In this topical review, we briefly introduce the crystal structure of calcium cobaltite and summarize effective strategies to enhance TE properties of calcium cobaltite based materials, including the use of elemental doping, optimization of fabrication route and composite design. These strategies work on the basis of controlling different TE parameters (electrical conductivity, thermopower and thermal conductivity) by optimizing the dopant species, band structure, grain boundary density, point defect scattering and phase assemblages. We believe these strategies can be exploited more widely and help to guide the development of other types of TE materials.

2. Crystal structure

The crystal structure of single crystal Ca$_3$Co$_4$O$_9$ (prepared by the flux method) was first reported by Masset et al [22], and subsequently determined by Miyazaki et al [23] as [Ca$_2$CoO$_3$]$_{0.62}$CoO$_2$. Figure 1 shows the monoclinic structure of calcium cobaltite, which is built upon the alternate stacking of rock salt [Ca$_2$CoO$_3$] and two-dimensional [CoO$_2$] layers (composed of edge-sharing CoO$_6$ octahedra) along the c axis [24]. This leads to incommensurate periodicities between different sublattices along the b axis, thereby yielding two different lattice constants for b ($b_1 = 4.56$ Å; $b_2 = 2.82$ Å) along with the same parameter values for a and c ($a = 4.83$ Å; $c = 10.84$ Å) [25, 26]. In fact, the misfit ratio between the [CoO$_2$] layer and the [Ca$_2$CoO$_3$] layer is not exactly a rational number but approaches the golden ratio $\tau \approx (1 : 0.618)$ [25]. It was reported that mixed cobalt valence states occur in the calcium cobaltite lattice, where Co$^{2+}$ exists in the rock salt layers, while Co$^{3+}$ and Co$^{4+}$ coexist in the [CoO$_2$] layers [27]. By preserving charge neutrality in the different layers, electrons are transferred from the negatively charged [CoO$_2$] layers to the positively charged

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**Figure 1.** The crystal structure of pristine Ca$_3$Co$_4$O$_9$ with an approximate 5/3 unit cell along the (a) [100] and (b) [010] zone axes ($X_3$ represents the rock salt sublayer; the grey, red and dark red balls represent Ca, Co and O atoms, respectively). Reprinted from [26], with the permission of AIP Publishing.
[Ca₃CoO₃] layers, thereby generating hole carriers in the [CoO₂] layers [28]. Therefore, the carrier concentration in calcium cobalite is reflected by the ratio of Co⁴⁺/(Co³⁺+Co⁴⁺) [29]. At the same time, the low spin Co³⁺ ions are chiefly responsible for maintaining the large thermopower; the presence of intermediate spin and high spin Co³⁺ will lead to higher g₃/g₄ values, thereby degrading the thermopower (g₃ and g₄ represent the numbers of the configurations of Co³⁺ and Co⁴⁺ ions) [30]. In addition to acting as the carrier reservoir, the insulating rock salt layer contributes to inhibiting phonon transport, thereby reducing lattice thermal conductivity [31]. Essentially, this layered structure is very much in line with the concept of Phonon-Glass Electron-Crystal [32].

Figure 2(a) shows a high-resolution transmission electron microscope image of calcium cobalite; the interplanar distance between the AO layers (highlighted by dark arrows) is estimated to be 10.7 Å [22], in good agreement with (001) crystal planes of Ca₃CoO₃. The simulated transmission electron microscope image for Ca₃CoO₃ along the [100] zone axis (figure 2(b)) confirms that the structure is made up of an alternating sequence of [CoO₂] and [Ca₃CoO₃] layers, which can be described by the formula [CoO₃, CaO₁.₅₋ₓ]₂[CoO₂]₁.₆₂ [22]. Based on selected area electron diffraction patterns from the [001] zone axis (figure 2(c)) Seo et al [33] determined the lattice parameter b for the rock salt layer and the [CoO₂] layer to be 4.56 Å and 2.82 Å respectively, matching well with the results of Masset et al [22] and Miyazaki et al [23]. This complex layered structure provides opportunities to modify the TE properties by regulating the degree of mismatch of the sublattices [34] or by elemental substitution at the calcium or cobalt sites in the different layers [35, 36].

3. Elemental doping

Tuning the TE properties of Ca₃CoO₃ by single or dual doping is a popular strategy. By appropriate elemental substitution at the calcium or cobalt sites in the crystal lattice, the electrical conductivity, thermopower and thermal conductivity can be modulated by optimized carrier concentration and mobility [37, 38], plus point defect scattering effects [39, 40], band structure changes [36, 41] and elemental segregation [42, 43].

Essentially, there can only be substitution at the Ca-site in the rock salt layer, whilst substitution at the Co-site can occur in either the [Ca₂CoO₃] or the [CoO₂] layers. As the carrier concentration (n) is regulated by the concentration of Co⁴⁺ ions in the [CoO₂] layer, a commonly adopted approach to enhance carrier concentration is by increasing the average Co valence to achieve hole-doping. Therefore, univalent ions, e.g. Ag⁺, K⁺ and Na⁺, are substituted for Ca²⁺ in the rock salt layer [44–46], thereby elevating the Co⁴⁺ fraction in the [CoO₂] layer, whilst maintaining charge neutrality. By introducing 3.3 at.% Ag at the Ca sites in calcium cobalite Zhang et al [46] achieved a competitive ZT value of 0.21 at 1223 K. Similarly, Constantinescu et al [45] found that the power factor of Ca₃CoO₃ could be increased from 0.18 to 0.33 mWm⁻¹ K⁻² at 1073 K by 2.3 at.% Na⁺ substitution for Ca²⁺; the enhanced electrical conductivity originates mainly from the increased carrier concentration. The carrier mobility can be improved by introducing divalent ions, such as Sr²⁺ and Mg²⁺, at Ca²⁺ sites in the rock salt layer [47–49]. Although the
charge-balanced substitution does not affect carrier concentration, an earlier density of function theory study of Baran et al [40] showed that the lattice expansion could induce a strain field in the [CoO$_2$] layer, thereby decreasing the electronic density of state and reducing the effective mass (m$^*$).

As the substitution of Ca$^{2+}$ by higher valence ions (e.g. Cr$^{6+}$, La$^{3+}$, Eu$^{3+}$, Bi$^{3+}$) [27, 39, 50] generates electrons, the hole concentration is expected to be reduced. However, these substituting ions have larger atomic mass or size than Ca$^{2+}$ ions, which gives rise to obvious strain and mass variations. A further effect is pronounced point defect scattering, which significantly reduces the lattice thermal conductivity. In terms of the Debye–Callaway model [52], there is a large disorder scattering parameter ($\Gamma$) and short relaxation time ($\tau_D$), as described by equations (1)–(4) [53]:

$$\tau_D^{-1} = A\omega^4 = \left[ V/(4\pi^{3/2}) \right] \Gamma \omega^4$$  \hspace{1cm} (1)

$$\Gamma = \Gamma_{MF} + \Gamma_{SF}$$  \hspace{1cm} (2)

$$\Gamma_{MF} = \sum_{i=1}^{n} C_i \left( \frac{M_i}{M} \right)^2 f_i^2 f_i' \left( \frac{M_i - M}{M} \right)^2$$  \hspace{1cm} (3)

$$\Gamma_{SF} = \sum_{i=1}^{n} C_i \left( \frac{M_i^2}{M^2} \right) f_i^2 f_i' \epsilon_i \left( \frac{\epsilon_i - \epsilon_f}{\beta} \right)^2$$  \hspace{1cm} (4)

where $\tau_D$ is the relaxation time for point defect scattering, $A$ is a constant independent of temperature and frequency, $\omega$ is the phonon frequency, $V$ is the volume per atom, $v$ is the velocity of sound, $\Gamma$ is the disorder scattering parameter, $\Gamma_{MF}$ and $\Gamma_{SF}$ are scattering parameters related to mass variation and strain field, $C_i$ is the relative degeneracy of the site, $M_i$ and $f_i$ are the average mass and radii of dopants, $f_i$ is the fractional occupation and $\epsilon_i$ is the amplitude of thermal vibration of the atoms. It was reported that by substituting 1.7 at.% Cr$^{6+}$ or 10.0 at.% Eu$^{3+}$ at the Ca$^{2+}$ site, the thermal conductivity at 300 K reduced by 35% [27, 39]. In addition to lowering thermal conductivity, Bi$^{3+}$ doping at the Ca$^{2+}$ site also increases carrier mobility, through enlarging the inter-site hopping distance, and enhances the preferred grain orientation, thereby leading to a high ZT; for example a value of 0.25 at 973 K was reported by Liu et al [54].

Similar to the case for Ca-site substitution, the thermal conductivity and carrier concentration can be further optimized by inserting ‘heavy’ ions (e.g. Cu$^{2+}$, Fe$^{3+}$, Cr$^{3+}$) at the cobalt site in the [CoO$_2$] layer [55, 56]; they have larger atomic mass than the cobalt ion, and have a lower valence than the average for cobalt (between +3 and +4). In addition, the carrier mobility can be efficiently enhanced by regulating the degree of structural order in the [CoO$_2$] layer through Co-site substitution in the [Ca$_2$CoO$_3$] layer. Based on x-ray absorption fine-structure analysis, Wu et al found that 5 at.% Fe$^{3+}$ substitution for Co$^{3+}$ disordered the local structure, relative to cobalt at the same site, but increased order in the CoO$_3$ octahedra [38]. As a result, the carrier mobility and thermopower were enhanced by the reduced carrier scattering in the [CoO$_2$] layer and the electron-doping in the [Ca$_2$CoO$_3$] layer, respectively. As a further option, Co-site substitution in the [CoO$_2$] layer provides opportunities to enhance electronic transport properties by modifying the band structure [57].

Turning to the Seebeck coefficients, it was found they could be significantly enhanced by substituting Fe$^{3+}$, Mn$^{4+}$ or Ir$^{4+}$ for Co$^{3+}$ in the [CoO$_2$] layers [36, 41, 58]. Wang et al [36, 41] examined the variation in effective mass (m$^*$) when 2.5 at.% Fe$^{3+}$ and Mn$^{4+}$ were substituted into calcium cobaltite, and fitted relevant specific heat capacity data using equation (5) [59]:

$$C/T \sim \gamma + \beta T^2$$  \hspace{1cm} (5)

where $C$ is specific heat, $T$ the absolute temperature, $\gamma$ is the electronic specific heat coefficient (large $\gamma$ reflects large effective mass) and $\beta$ is the phonon specific heat coefficient. The magnetic contributions to specific heat were ignored because there was negligible difference in $\gamma$ values under magnetic fields of 0–9 T [60]. As the $\gamma$ value increases, after successful Fe/Mn doping, it was inferred that the effective mass was increased via enhanced electronic correlations, which results in large Seebeck coefficients, thereby supporting the degenerate Fermi gas model [61]. The increased effective mass essentially stems from a paramagnetic drag effect via strong coupling between the carriers and doped magnetic ions [62–64]. In particular, the power factor for the 2.5 at.% Fe$^{3+}$ substituted material (0.7 mWm$^{-1}$ K$^{-2}$ at 1000 K) is nearly triple that for undoped calcium cobaltite. Huang et al [58] proposed that Ir$^{4+}$ substitution for Co$^{3+}$ enhances the thermopower because Ir doping helps to extend the electronic band in the vicinity of the Fermi level; the band structure is renormalized by enhanced carrier localization. Consequently, the maximum valence band
is decreased whilst the band gap is increased, leading to enhanced Seebeck coefficients according to equation (6) [65]:

\[ S \sim \frac{k}{e} \left[ \frac{E_g}{(kT)} \right] \]  

where \( S \) is the Seebeck coefficient, \( k \) is the Boltzmann constant, \( e \) is the electronic charge, \( E_g \) is the band gap and \( T \) the absolute temperature.

The target elemental doping outlined above is usually designed with stoichiometric ratios of raw materials to form a substitutional solid solution, whereas the non-stoichiometric addition of ‘oversized’ dopants, such as \( K^+ \), \( Ba^{2+} \) and \( Bi^{3+} \), is able to induce elemental segregation at grain boundaries of calcium cobaltite without the generation of secondary phases [42, 43, 66]. The mismatch caused by large differences in ionic size between the dopants and host ions is more likely to give rise to elemental segregation (namely the development of high concentrations of dopants near the grain boundaries without secondary phase formation) because there are more open sites available to accommodating the dopants [42]. The enhanced TE performance arising from grain boundary segregation can be explained by figure 3. Whilst segregation lowers the grain boundary energy and helps to realize the steady-state distribution of low-energy boundaries, thereby controlling the porosity of the polycrystalline samples and enhancing the texture development [43], it can also act as a carrier filtering barrier layer at the grain boundaries, thus reducing carrier concentration and increasing thermopower [42]. By inducing K segregation at the grain boundaries in K doped \( Ca_3Co_4O_9 \), Romo-De-La-Cruz et al. [42] achieved a power factor of 0.93 mWm\(^{-1}\)K\(^{-2}\) at 320 K, about twice that for pristine calcium cobaltite. Similarly, Carvillo et al. [43] found that the combination of high densification, induced by high-pressure synthesis and low thermal conductivity caused by ‘heavy’ elemental doping, plus Ba segregation at grain boundaries facilitated texture development and filtered low-energy carriers, thereby increasing the ZT values of Ba doped \( Ca_3Co_4O_9 \) ceramics to 0.52 at 1023 K.

4. Optimization of fabrication route

From the initial powder preparation to the final sintering process, the synthesis methods, sintering techniques and heat-treatment conditions play vital roles in determining the TE properties of calcium cobaltite based ceramics through controlling the phase composition [67], texture development [68], grain growth [69] and oxygen vacancies [29].

To date, a variety of fabrication routes including solid state reaction [70–72], sol-gel synthesis [69, 73, 74], coprecipitation [31, 75] and polymer solution [76, 77] have been employed to synthesize...
calcium cobaltite powders; their advantages and disadvantages are easily distinguished. The solid-state reaction route is frequently used as it is simple and low cost, but purity of the final products may be a problem and the grain sizes are usually micron-sized. Although wet chemical routes enable synthesis of ultrafine powders, they are time-consuming and low-yield. Sotelo et al [75, 77] discussed the effects of synthesis methods (solid state reaction, sol-gel, polymer solution and coprecipitation) for precursor powders on electronic transport properties of Ca$_3$Co$_4$O$_9$ ceramics (figure 4). For a given sintering condition (1173 K for 24 h in air), samples prepared by wet chemical routes exhibit superior TE performance than the solid state synthesized samples, mainly due to enhanced electrical conductivity. Samples prepared by the coprecipitation method show the highest power factor of 0.43 mW m$^{-2}$ K$^{-2}$ at 1073 K, which was ascribed to the increased volume fractions of primary conducting phase (calcium cobaltite) and increased carrier mobility, enabled by the cleaner grain boundaries resulting from the higher reactivity of as-prepared powders.

Due to the naturally high aspect ratio of ($a$-$b$/$c$) planes in calcium cobaltite [78], it is easier for grains to develop texture along the $c$ axis with the assistance of seed crystals, external pressure and magnetic field. Highly textured samples usually exhibit strong anisotropy of TE properties. Essentially, along the $ab$ plane, electrical conductivity and thermal conductivity will be maximized while the Seebeck coefficient will be minimized [79, 80], because of the reduced grain boundary barriers; in contrast, properties across the $ab$ plane are the opposite. Therefore, different sintering techniques, including template, seed-assisted molten salt process [78], hot pressing (HP) [81, 82], spark plasma sintering (SPS) [83–85], laser floating zone process [76], tape casting [86, 87] and high-magnetic-field sintering [88], have been utilized to enhance the preferred grain orientation. As figure 5 shows, for (Ca$_{0.87}$La$_{0.03}$Ag$_{0.1}$)$_3$Co$_4$O$_9$ ceramic sintered at 1373 K, the ZT value at 1073 K, in the direction parallel to the $ab$ plane, is nearly quadruple the value in the direction perpendicular to the $ab$ plane, due to the strong texture induced by tape casting [87]. Furthermore, Lim et al [68] found that for textured calcium cobaltite prepared by the SPS method, the power factor and thermal conductivity at 1200 K measured parallel to the $ab$ plane could reach 500.0 $\mu$W m$^{-1}$ K$^{-2}$ and 3.1 W m$^{-1}$ K$^{-1}$

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**Figure 4.** Temperature dependence of: (a) electrical conductivity, (b) Seebeck coefficient and (c) power factor for Ca$_3$Co$_4$O$_9$ ceramics prepared from different types of precursor powders (green: solid-state reaction, blue: sol-gel method, red: polymer solution method, black: coprecipitation method). Reprinted from [75], Copyright (2015), with permission from Elsevier. Reprinted from [77], Copyright (2012), with permission from Elsevier.
respectively, representing about 400% and 200% increase compared to the values measured perpendicular to the $ab$ plane. In a related investigation Wu et al. [79] found that for SPS-processed calcium cobaltite, the ZT values at 823 K parallel to the $ab$ plane were 50% higher than those in the perpendicular direction. Kenfau et al. [82] compared the electrical transport properties of Ca$_3$Co$_4$O$_9$ ceramics prepared by solid state reaction, HP and SPS route. Although Seebeck coefficients were similar (170 $\mu$V K$^{-1}$ at 800 K), the hot-pressed samples exhibited the lowest electrical resistivity (8.0 m$\Omega$ cm at 850 K) and highest power factor (550 $\mu$Wm$^{-1}$ K$^{-2}$ at 850 K) because of the improved carrier mobility arising from the enhanced preferred grain orientation.

Finally in this section, the effects of calcination and sintering processes need to be taken into account. For example, by optimizing the calcination temperature of sol-gel synthesized calcium cobaltite precursor at 923 K, Chen et al. [73] obtained nano-crystalline grains (about 100 nm), which enabled vigorous grain growth during sintering. Based on work on the sintering mechanics of single grain boundaries [89], Chen et al. [73] showed that torque arising from anisotropic grain boundary energies, caused nano-sized grains to rotate, reducing the degree of misorientation during sintering, thereby enhancing the texture development in calcium cobaltite ceramics. In turn, the reduction of grain boundary density led to an increase in electrical conductivity. More generally, the presence of poorly conducting secondary phases in calcium cobaltite based materials can be efficiently suppressed during sintering by promoting reactions that form the primary phase by optimizing the sintering conditions [67, 90]; this also helps to increase electrical conductivity. For instance, Yu et al. [67] prepared single-phase Ca$_{2.7}$Bi$_{0.3}$Co$_{3.92}$O$_{9+\delta}$ thick films by sintering at 1203 K and adjusting the dwell time; in this way a maximum power factor of 55.5 $\mu$Wm$^{-1}$ K$^{-2}$ was achieved at 673 K. Furthermore, an additional annealing step in air or oxygen atmosphere for as-sintered calcium cobaltite based ceramics can be beneficial, enhancing grain growth, texture development, the fraction of the main phase, and the concentration of Co$^{4+}$ by reducing oxygen vacancies in the lattice [18, 29], thereby enhancing both the carrier concentration and mobility.

5. Composite design

By integrating calcium cobaltite with other types of thermoelectric, the transport properties of the composite can be efficiently enhanced. For example, Vengust et al. [91] and Chen et al. [92] prepared calcium cobaltite based materials with increasing volume fractions of sodium cobaltite. They showed that the electrical conductivity of the composite increased significantly with addition of sodium cobaltite; the former ascribed this to the higher intrinsic electrical conductivity of sodium cobaltite, whilst the latter found that sodium cobaltite enhanced preferred grain orientation, leading to improved carrier mobility. Vengust et al. [91] also
reported that the Seebeck coefficients of the composite increased because of compressive strain originating from the mismatch of thermal expansion coefficients between the sodium cobaltite and the host phase, thereby resulting in a high $ZT$ of 0.35 at 973 K when 70 vol.% sodium cobaltite was incorporated. A similar strategy was adopted by Rasekh et al. [93] who used bismuth calcium cobaltite as the reinforcement phase; the composites were prepared by an electrically assisted laser floating zone process. As well as improving texture, they found that the Seebeck coefficients were higher than those obtained for the single-crystalline samples because of oxygen vacancies formed during the composite fabrication process. Collectively, the studies demonstrated that TE performance can be enhanced by controlling the phase content of the assemblage.

Recently, it was shown that dispersions of nano-sized inclusions of additives, such as $\text{In}_2\text{O}_3$, $\text{Ta}_2\text{O}_5$, and $\text{TiC}$ [94–96], into the calcium cobaltite matrix is an efficient way to reduce thermal conductivity. As these nano-sized additives do not react with the matrix phase, they become embedded in the grain boundaries and interfaces, and act as scattering centers, reducing the mean free path of phonons via Rayleigh-type and geometrical phonon scattering mechanisms (figure 6) [97]. For example, calcium cobaltite ceramics containing 4.0 vol.% nanoparticles of $\text{Ta}_2\text{O}_5$ (about 9.25 nm in size) or 0.25 wt.% $\text{TiC}$ (< 200 nm in size) showed about 30% reduction in thermal conductivity at 372 K, compared to the pristine calcium cobaltite [95, 96]. Conversely, Ag particles (<1000 nm in size) are frequently used to increase electrical conductivity, as the highly conductive Ag is able to create new carrier transport routes inside the composite [98, 99]. As a result of the coupled effects of enhanced electrical conductivity and reduced thermal conductivity, solid state synthesized calcium cobaltite with 3.0 wt.% Ag exhibited a maximum $ZT$ value of 0.14 at 873 K, approximately 75% increase over the Ag-free samples [100]. Indeed, Nong et al. [101] reported a maximum $ZT$ value of 0.61 at 1118 K for $\text{Ca}_{2.8}\text{Ag}_{0.05}\text{Lu}_{0.15}\text{Co}_4\text{O}_9$ ceramic, the highest value for SPS-processed calcium cobaltite. They attributed the exceptional performance to the formation of a fine-scale distribution of nano-sized Ag precipitates (about 300 nm in size) which modified scattering processes and raised the Seebeck coefficient to 238.0 $\mu$V K$^{-1}$ at 1118 K. Therefore, the presence of suitable nano-inclusions in the calcium cobaltite matrix can both control and enhance the TE parameters.

6. Conclusions and challenges

TE devices for harvesting energy from waste heat can help to alleviate the current energy crisis. P-type calcium cobaltite shows advantages over traditional TE alloys, in terms of its low toxicity, high-temperature stability and the rich elemental abundance of the raw materials. As calcium cobaltite exhibits a misfit layered crystal structure composed of a rock salt [$\text{Ca}_2\text{CoO}_3$] layer and a two-dimensional [$\text{Co}_2\text{O}_3$] layer, elemental doping at different sites provides many opportunities to modulate the TE response:
(a) The carrier concentration can be modified by hole or electron doping through inserting ions with different valences at Ca or Co sites in both sublayers. The range of carriers introduced depends on the differences in valence between the dopants and host ions.

(b) The carrier mobility can be enhanced by inserting ions of larger atomic radius at Ca site in the rock salt layer and by elemental segregation to grain boundaries. The former induces strain fields in the [CoO₂] layer, thereby reducing the effective mass. The latter helps to develop strong texture, which helps to lower energy barriers at grain boundaries.

(c) The Seebeck coefficient can be enhanced by modifying the band structure. Substitution of ions, such as Fe³⁺, Mn⁴⁺ and Ir⁴⁺, for Co³⁺ in the [CoO₂] layer can increase the effective mass and broadens the band gap. Elemental segregation to grain boundaries also helps to reduce the concentration of low-energy carriers, thereby enhancing the thermopower.

(d) Thermal conductivity can be efficiently reduced by inserting ions with large atomic mass and radius at Ca or Co sites in both sublayers. The size and mass variations caused by doping enhances the scattering disordering parameter, thereby reducing the phonon mean free path.

By optimizing the fabrication route, including the calcination and sintering processes, the overall electrical conductivity can be increased by increasing the volume fractions of highly conducting main phase (calcium cobaltite). Carrier mobility can be improved by wet chemical synthesis, through forming cleaner grain boundaries and facilitating texture development. The carrier concentration can also be enhanced by annealing in air, which helps to introduce lattice oxygen, thereby raising the Co⁴⁺ concentration and hence more holes.

By forming composites between calcium cobaltite and other thermoelectrics, the electrical conductivity can be increased synergistically. The Seebeck coefficient can be enhanced through the mismatch of thermal expansion coefficients between the matrix and reinforcement phase, and by oxygen vacancies generated during fabrication. Nano-sized inclusions can act as scattering centers to enhance phonon scattering, thereby reducing lattice thermal conductivity.

Although the strategies outlined above have led to encouraging progress in enhancing TE performance of calcium cobaltite, there are still several challenges to be addressed. Firstly, the level of elemental doping needs to be carefully controlled, especially when secondary phases are present. As elemental solubility in the crystal lattice may be limited, the addition of excess levels of dopant may lead to the generation of poorly conducting secondary phases, which can degrade electrical conductivity, and also move away from the target chemical composition through leaching effects [75, 102]. Indeed, for a given chemical composition, elemental segregation is sensitive to the processing conditions. For example, Yu et al [18] and Boyle et al [66] examined the effects of bismuth substitution on microstructural evolution in calcium cobaltite ceramics. The former reported the formation of Bi-rich secondary phases for 10.0 at.% Bi substituted calcium cobaltite prepared by SPS, whilst the latter only observed Bi segregation at grain boundaries without any impurity phase in high-pressure synthesized calcium cobaltite with the Bi substitution up to 13.3 at.%: Consequently, the Bi dopants played different roles in these two cases with different effects on TE performance.

Secondly, texture development is certainly helpful in reducing in-plane grain boundary density, and thereby increasing the in-plane carrier mobility, but the reduced in-plane energy barriers also result in longer relaxation times for phonons, which in turn increases thermal conductivity. Srivastava et al [80] found that for textured SrTiO₃/graphene composites, the ZT values, both parallel and perpendicular to the pressing direction, were quite similar, owing to compensating changes in the TE parameters. Therefore, it is necessary to address the problem of elevated, in-plane thermal conductivity, while taking advantage of the anisotropy, with the aim of improving TE properties.

Finally, significant reduction in thermal conductivity can be achieved by the addition of nanoparticles to enhance phonon scattering. However, efficient methods need to be developed to guarantee the uniform distribution of nano-sized inclusions. Undesirable aggregation will occur if the particles are not well dispersed in the matrix; locally-concentrated particles fail to perform as efficient scattering centers. Therefore, further work is necessary on the dispersion of reinforcement particles.

In this topical review, we have summarized popular strategies towards enhanced TE performance of calcium cobaltite. Whilst there is still room for future development exploitation, we have sought to provide useful insights into calcium cobaltite based systems and expect by utilizing the approaches described, breakthroughs will also come in other TE systems.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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ORCID iD

Robert Freer Ⓢ https://orcid.org/0000-0003-1100-8975

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