REVIEW

Nanostructured oxide materials and modules for high-temperature power generation from waste heat

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Abstract

A large amount of thermal energy emitted from many industrial processes is available as waste heat. Thermoelectric (TE) power generators that convert heat directly into electricity can offer a very promising means of waste heat recovery. However, the requirements for this task place in the materials are not easily satisfied by conventional TE materials. Not only must they possess a sufficient TE performance, but they should also be stable at high temperatures, nontoxic and have low-cost comprising elements, and must be also able to be processed and shaped cheaply. Oxides are among the strongest candidate materials for this purpose. In this review, the progress in the development of two representative p- and n-type novel oxide materials based on Ca$_3$Co$_4$O$_9$ and doped-ZnO is presented. TE modules built up from these oxides were fabricated, tested at high temperatures, and compared with other similar oxide modules reported in the literature. A maximum power density of 45.3 mW cm$^{-2}$ was obtained for an oxide module comprising eight p–n couples at a temperature difference of 496 K, an encouraging result in the context of the present high-temperature oxide modules.

Keywords: figure of merit, layered cobalt oxide, zinc oxide, high temperature, thermoelectric generator

Classification numbers: 4.00, 5.01

1. Introduction

In conventional energy conversion/production process, typically 50% or more of the energy used is wasted, mostly as heat. The capability of thermoelectric (TE) materials to convert waste heat into usable electrical energy in a pollution and maintenance-free and all-solid-device has attracted enormous interest over the last two decades [1]. A typical TE generator comprises two semiconductor materials, p- and n-type doped TE elements, connected to each other to form a TE couple. The TE couples are then connected electrically in series and thermally in parallel to form a module. A practical TE module can contain up to hundreds of TE couples depending on the output power needed. The key to realize an efficient TE generator for waste heat recovery lies, however, in finding good materials with high TE performance, a good durability at high temperature and preferably robustness under operation in air. The performance of a TE material is evaluated by the dimensionless figure-of-merit $ZT = S^2T/\rho\kappa$, where $S$, $T$, $\rho$ and $\kappa$ are the Seebeck coefficient, absolute temperature, electrical resistivity and thermal conductivity, respectively). Currently, the most widely used TE materials are alloys, which often suffer
from poor durability at high temperature, low abundance (Bi–Te), toxicity (Pb–Te) and high cost (Si–Ge) of the comprising elements as illustrated in figure 1(a) [2]. The conversion efficiency of TE generator primarily depends on the materials’ TE performance $ZT$, and the operating temperature difference between the cold and the hot side of the generator. With higher operating temperature, both the TE conversion and Carnot efficiencies can be significantly improved [3]. Under these conditions, oxide-based TE generator would be one of the strongest candidates due to the naturally good thermal stability of TE oxide materials used at high temperatures comparing with conventional alloy-based modules.

Oxide thermoelectrics has gained much interest during the last decade since the large TE response was discovered in some metal oxide-based materials [4–7]. We have over the years carried out research on various TE oxide systems to search for high-temperature TE materials [8–25]. In this review, the development of doped ZnO and Ca$_3$Co$_4$O$_9$ novel oxides representative of n-type and p-type materials is presented with highlights on heavily doping and nanostructuring approaches to improve their high-temperature TE properties. The performance of TE modules building up from these oxides is shown and compared with other oxide TE modules reported in the literature.

2. TE oxides

Our materials of p-type and n-type oxide systems based on Ca$_3$Co$_4$O$_9$ and doped-ZnO presented in this paper were prepared by the solid state reaction followed by a hot pressing (HP) or spark plasma sintering (SPS) process. The detailed experimental procedures for producing and characterizing these materials were reported previously [8–25].

2.1. p-type layered Ca$_3$Co$_4$O$_9$-based oxides

Ca$_3$Co$_4$O$_9$-based oxide material has been intensively investigated due to its good TE performance ($ZT = 0.83$ at 973 K for the single crystal) [5] and its highly thermal and chemical stabilities, even up to 1200 K in air [20, 23, 26–29]. Shown in figure 2 is an incommensurate character in the crystal structure of this compound, which can be described as [Ca$_3$Co$_4$O$_9$]$_{1/2}$[Co$_2$O$_3$], where $b1$ and $b2$ are two different periodicities along the $b$-axis for the rock salt-type Ca$_2$Co$_3$ subsystem and the CdI$_2$-type Co$_2$O$_3$ subsystem, respectively [26]. However, single crystals are less likely to be applied for fabricating practical TE devices. It is hence highly desirable to achieve sufficient TE properties in a polycrystalline form of these oxides.

In fact, many attempts have been made over the years to enhance the TE performance of the polycrystalline Ca$_3$Co$_4$O$_9$ by ions doping and improving the fabrication methods, e.g. employing HP or SPS techniques [20–53]. Most research has focused on the doping at Ca-site by e.g. the rare-earth elements such as Pr, Y, Nd, Gd, Nd, Eu, Yb and Lu [21, 23, 27–49], while few reports have performed the substitution on the Co-site [20, 22, 50–53]. The core idea of doping Ln (Ln = rare-earth elements) on Ca-site (Ca$^{2+}$) is to increase the Seebeck coefficient due to the decrease in hole concentration by the substitution of Ln$^{3+}$ for Ca$^{2+}$ and further reduce the thermal conductivity by heavily doping elements. The peculiar structural arrangement of the CoO$_2$ layers, containing cobalt cations with mixed-valence of 3+ and 4+, is the origin of the interesting properties of the layered cobaltite system. Therefore, ions doping on the Co-site, especially Co ion in the CoO$_2$ planes results in pronounced TE effect owing to the fact that charge carrier is transported mostly within these layers. Accordingly, the TE performance was significantly improved using this approach and the maximum $ZT$ values were found to be about 2–2.5 times larger than that of non-doped material [21, 22, 30, 34].

Figure 2. Schematic crystal structure of nanoscale misfit-layered Ca$_3$Co$_4$O$_9$ along $b$-axis (adapted from [2 and 26]).
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Figure 3. SEM images of fracture surface of HP samples for pure \(\text{Ca}_3\text{Co}_4\text{O}_9\) (a), Ga-doped (b), and Lu-doped (c) samples and (d) XRD patterns and Rietveld refinement profile of a typical Ga-doped sample (adapted from [20, 21]).

Figures 3(a)–(c) displays typical SEM images of fracture surface of non-doped, Ga- and Lu-doped \(\text{Ca}_3\text{Co}_4\text{O}_9\) samples consolidated by HP technique, showing a rather dense microstructure. All the HP samples have a relative density of over 94% of the theoretical density (\(\sim\)4.68 g/cm\(^{-3}\) [26]). It can be clearly observed from figures 3(a)–(c) that both the pure and doped samples exhibited a lamella structure, and this lamella-like morphology become more oriented [20, 21] with the doped samples as compared with the pure one, particularly the sample doped with Lu (figure 3(c)). Ga doping was found to act as a sintering aid [20, 22], while Lu, which has larger ionic radius substitution on the Ca-site changed the misfit ratio i.e. \(b_1/b_2\) [21], which may be the reason leading to the different observed microstructure. A characteristic x-ray diffraction (XRD) spectrum of a typical Ga-doped \(\text{Ca}_3\text{Co}_4\text{O}_9\) sample with Rietveld refinement profile is presented in figure 3(d), confirming its isostructure and phase purity.

Figures 4 and 5 show the TE properties of two systems: \(\text{Ca}_{3-x}\text{Lu}_x\text{Co}_4\text{O}_9\) and \(\text{Ca}_{3-x}\text{Ga}_x\text{Co}_4\text{O}_9\), which are representative of two doping approaches i.e. at the Ca- and Co-sites, respectively. Shown in figure 4(a) is the electrical resistivity at 300 and 1100 K as a function of Lu and Ga concentration. The electrical resistivity tends to increase with increasing Lu concentration, while it decreases for the samples with Ga doping at both low and high temperatures. The influence of Lu and Ga doping on the Seebeck coefficient shows two different tendencies: \(S\) increases with increasing Lu content, while \(S\) starts increasing for the sample with low Ga concentration i.e. \(x = 0.05\), then it decreases with higher Ga content. It was evidenced by the Hall measurement that carrier concentration increased for \(x = 0.05\), but it slightly decreased for \(x > 0.05\) [20]. The simultaneous increase in the electrical resistivity and Seebeck coefficient by Lu doping was reported to be due to the decrease in hole concentration by the substitution of Lu\(^{3+}\) for Ca\(^{2+}\) [21]. As for Ga doping, the increasing Seebeck coefficient and decreasing electrical resistivity at high temperature while the carrier concentration increases suggests that this system may have more than one type of independent carrier [20, 22].

The thermal conductivity and the dimensionless figure of merit are presented in figures 5(a) and (b), respectively, for non-doped and selected Ga- and Lu-doped samples. Figure 5(a) reveals that the thermal conductivity is significantly reduced by heavy elements due to the suppression in the lattice thermal conductivity, particularly with Lu doping [21]. The TE performance \(ZT\) is thus remarkably improved by Ga and Lu doping, and the effect is more substantial in the high-temperature region \((T > 650\text{ K})\). The maximum \(ZT\) value at \(\sim 1100\text{ K}\) reached about 0.4, which is about two times higher than the non-doped material (figure 5(b)).

SPS method, which is a pressure-assisted pulsed current fast sintering process, offers an advantageous way to fabricate nanostructured bulk materials. With SPS technique, the microstructure of the material and crystal growth are well controlled while maintaining the original properties of the materials. Employing this fabrication method, we
have successfully synthesized TE nanocomposites with microstructural design consisting of oriented lamellar-like nanostructures doped with heavy ions together with embedded metallic nano-inclusions such as Ag \[23\]. Figures 6(a)–(c) show SEM images of fracture surface (a), high-resolution transmission electron microscopy (HRTEM) (b) and bright field (BF)-TEM images (c), of a typical nanostructured bulk sample Ca\(_{2.8}\)Lu\(_{0.15}\)Ag\(_{0.05}\)Co\(_{4}\)O\(_9\) prepared by SPS. A very homogeneous and dense microstructure exhibiting a pronounced lamella-like morphology can be clearly observed (figure 6(a)). The HRTEM image shows a modulated nano-scale layered structure (figure 6(b)), and the evidence of Ag metallic nano-inclusions was found in the misfit-layered cobalt oxide system, as is clearly shown in figure 6(c). This effective approach has led to a remarkable improvement of \(ZT = 0.6\) at 1100 K) for TE p-type oxide materials. It is more interesting to note that \(ZT\) of this material is further improved by about 6% after a subsequent heat treatment and then this high \(ZT\) value is maintained even after further extreme heating and cooling cycles (figure 6(d)). The excellent chemical and thermal stability of this material as well as the rapid increase in \(ZT\) with increasing temperature strongly suggest this system as a very promising oxide TE material for high-temperature power generation. However, there is still ongoing work in order to avoid using expensive elements such as Lu. These findings demonstrate an effective way (oriented lamella nanostructure + heavily doping + metallic nano-inclusions) to improve the TE performance of polycrystalline materials, and it may be also applied to other TE systems.

2.2. n-type ZnO-based oxides

Zinc oxide is a wide band gap semiconductor with a direct band gap of 3.2–3.5 eV \[2\]. ZnO crystallizes in the wurtzite structure, and non-doped bulk ZnO is an n-type semiconductor i.e. its electrical resistivity decreases with increasing temperature. A small amount of Al doping could result in remarkable decreases in the electrical resistivity and change the conduction behavior from semiconducting to metallic. ZnO is high-temperature stable, non-toxic and low-cost. These properties make it a promising candidate for n-type TE materials \[6, 54–60\]. The extraordinary high-temperature n-type TE properties of Al-doped ZnO were first brought to public attention by Ohtaki \(et\ al\) in 1996 \[58\]. A long history of development through nanostructuring as well as heavily doping on this material for high-temperature TE oxide has recently led to successive progress in \(ZT = 0.47\) at 1000 K and 0.65 at 1247 K for a dual doping of Al and Ga using conventional pressing techniques \[6\]. A recent review by Ohtaki \[2\] provides a deep understanding of the
Figure 6. (a) SEM image of fracture surface of the $\text{Ca}_{2.8}\text{Lu}_{0.15}\text{Ag}_{0.05}\text{Co}_4\text{O}_9$ sample prepared by SPS, (b) high-resolution transmission electron microscopy (HRTEM), (c) BF-TEM images and (d) the TE performance at 1100 K under various heating and cooling cycles in air ((c) and (d) adapted from [23]).

Figure 7. The historical progress in development of two typical oxide TE materials for doped n-type ZnO and p-type $\text{Ca}_3\text{Co}_4\text{O}_9$. ZnO-based oxides system as well as the prospect of how to improve the TE performance of this type of materials. Very recently, Jood et al [54] have reported a figure-of-merit $ZT$ of 0.44 at 1000 K for a nanostructured Al-doped ZnO, again confirming that the ZnO-based oxide is a good candidate n-type high-temperature TE material. At the Department of Energy Conversion, Denmark, single Al-doped as well as Al, Ga dually doped ZnO oxides have been studied and prepared using SPS technique. The influence of SPS conditions on the TE properties and the microstructure evolution were investigated in detail in order to understand the sintering mechanism of this system [25]. However, using this technique

Figure 8. (a) Photo of the actual p–n legs and present oxide module consisting of eight unicouples, (b) TE power generation characteristics of the oxide module at different temperature gradients.
Table 1. Power generation characteristics of present oxide modules as compared with the others reported.

| Reference          | Materials                                   | No. of p–n | Jointing technique | \(T_{\text{hot}}\) (K) | \(\Delta T\) (K) | \(V_{\text{f}}\) (V) | \(P_{\text{max}}\) (mW) | Legs size (mm) | Power density (mW cm\(^{-2}\)) |
|--------------------|---------------------------------------------|------------|--------------------|-------------------------|-----------------|---------------------|------------------------|----------------|---------------------------------|
| Urata et al [61]   | p-Ca\(_2\)Zi\(_2\):Co\(_{0.3}\):O\(_9\)     | 8          | Ag                 | 1273                    | 298             | 1.0                 | 170                    | 5 \times 5      | 42.5                            |
| Souma et al [64]   | p-Ca\(_2\):Mn\(_{0.8}\):O\(_{0.2}\):O\(_9\) | 12         | Diffusion welding  | 934                     | 455             | 0.8                 | 52.5                   | 3 \times 4        | 18.2                            |
| Matsubara et al [63] | p-Ca\(_2\):Gd\(_{0.3}\):Co\(_{0.7}\):O\(_9\) | 8          | Pt paste           | 773                     | 390             | 1.0                 | 63.5                   | 3 \times 3        | 44.1                            |
| Souma et al [62]   | p-Na\(_2\):Co\(_{0.8}\):O\(_{0.2}\):O\(_9\) | 12         | Ag, diffusion      | 839                     | 462             | 0.8                 | 53                    | 3 \times 4        | 20.1                            |
| Shin et al [65]    | p-Li-doped NiO                             | 4          | Sintering          | 1164                    | 539             | 0.4                 | 34.4                   | 3 \times 4        | 35.8                            |
| Ura et al [66]     | p-Ca\(_2\):Bi\(_{0.3}\):Co\(_{0.7}\):O\(_9\) | 8          | Ag paste           | 897                     | 565             | 1.0                 | 170                   | 5 \times 5 \times 4.5 | 42.5                            |
| Noudem et al [67]  | p-Ca\(_2\):Bi\(_{0.3}\):Co\(_{0.7}\):O\(_9\) | 2          | Ag paste           | 990                     | 630             |                     | 31.5                   | 4 \times 4 \times 10 | 49.2                            |
| Funahashi et al [68]| p-Ca\(_2\):Bi\(_{0.3}\):Co\(_{0.7}\):O\(_9\) | 1          | Ag paste           | 1073                    | 500             | 0.1                 | 94                    | 3.7 \times 4-4.5   | 310                             |
| Lim et al [70]     | p-Ca\(_2\):Co\(_{0.8}\):O\(_{0.2}\):O\(_9\) | 1          | Ag paste           | 1175                    | 727             |                     | 95                    | 8.5 \times 6.0     | 93.2                            |
| Han et al [69]     | p-Ca\(_2\):Ni\(_{0.5}\):Co\(_{0.5}\):O\(_9\) | 2          | Ag paste           | 873                     | 523             | 0.3                 | 36.8                   | 3 \times 6        | 49.1                            |
| Funahashi and      | p-Ca\(_2\):Bi\(_{0.3}\):Co\(_{0.7}\):O\(_9\) | 140        | Ag paste +5 wt% CaMnO\(_3\) | 1072                    | 551             | 4.5                 | 150                   | 1.3 \times 1.3 \times 5 | 31.7                            |
| Mikami et al [71]  | p-Ca\(_2\):Bi\(_{0.3}\):Co\(_{0.7}\):O\(_9\) | 44         | Ag paste           | 1100                    | 658             | 1.8                 | 423                   | 15 \times 15      | 2.1                             |
| Choi et al [72]    | p-Ca\(_2\):Co\(_{0.8}\):O\(_{0.2}\):O\(_9\) | 6          | Ag                 | 773                     | 260             | 0.3                 | 3.7                   | 5 \times 5 \times 15 | < 0.1                           |
| Mele et al [73]    | p-Ca\(_2\):Co\(_{0.8}\):O\(_{0.2}\):O\(_9\) | 8          | Ag paste and foil hot-press | 906                     | 496             | 0.7                 | 65.3                  | 3 \times 3 \times 8 | 45.3                            |

at 1173 K, the ZT values are in the range of 0.14–0.17, which is much smaller than that reported so far. A possible reason may be due to the inhomo geneous grains distribution of the samples densified by SPS process [25]. Further investigations are in progress. Figure 7 summarizes a historical development of n-type and p-type based on ZnO and Ca\(_2\):Co\(_{0.3}\):O\(_9\) modules over the years, suggesting that these materials are promising candidates for high-temperature power generation.

3. High-temperature oxide modules

Fabricating modules using oxide materials, is facing some critical issues, on top of their relatively low ZT, such as the mismatch of p- and n-type elements, difficulty in electrodes joining and the instability of interface contacts at high temperatures. These drawbacks make the performance of oxide modules still low as compared with the ones built from alloys. Nevertheless, oxide TE modules are still very attractive due to their capability of operating at high temperatures with low cost of materials processing.

For oxide module fabrication in this work, the Ag foil and paste were used to make electrodes. A set consisting of 16 legs (eight unicouples of p-type Ca\(_2\):Co\(_{0.3}\):O\(_9\) and n-type Al-doped ZnO) were attached using Ag paste onto designed alumina substrates with Ag electrodes on top. The whole module was then placed in a graphite die and hot-pressed in Ar atmosphere at 1073 K under a pressure of about 30 MPa. The power generation testing of the module was examined using a commercial module testing system TEGeta-PANCO in air at high temperature (heater temperature) up to 1300 K. When testing the modules at high temperature in air, boron nitride spray was used to prevent metallic contact layers and n-type elements from oxidizing.

In fact, a considerable number of oxide-based TE modules have been fabricated and examined [61–74]. Most of the previous studies have been focused on modules containing Ca\(_2\):Co\(_{0.3}\):O\(_9\) as p-leg and perovskite n-type legs such as CaMnO\(_3\) and LaNiO\(_3\) [61, 63, 67, 68] or Al-doped ZnO as n-leg with p-leg of Na\(_2\):Co\(_{0.3}\):O\(_9\) [62, 64]. However, the combination of Ca\(_2\):Co\(_{0.3}\):O\(_9\) as p-leg and Al-doped ZnO as n-leg in a practical module has not been broadly investigated. This may be due to the fact that it is challenging to master the fabrication of these two components in a large quantity and reproducibility. Beside the choice of materials, the performance of an oxide module strongly depends on the contact resistance between TE oxide legs and metal electrodes, of which the actual internal resistance could be over 400% higher than the theoretical value [70].

Figures 8(a) and (b) show the photo of the actual p–n legs and a typical oxide module comprising eight p-Ca\(_2\):Co\(_{0.3}\):O\(_9\)/n-ZnO\(_{0.98}\):Al\(_{0.02}\):O unicouples and its TE power generation characteristics at different applied temperature gradients of \(\Delta T = 358\) and 496 K. At the highest applied temperature of \(T_{\text{hot}}/T_{\text{cold}} = 906/410\) K corresponding to \(\Delta T = 496\), the measured open circuit voltage \(V_{\text{ofm}}\) of the module was 0.7 V, and the voltage decreased linearly with increasing current (see figure 8(b)). The measured maximum output power was 38.4 and 65.3 mW at \(\Delta T = 358\) and 496 K, respectively. The measured maximum power density of 45.3 mW cm\(^{-2}\) at \(\Delta T = 496\) is comparable with some oxide modules [61, 63], and about two times higher than the p-Na\(_2\):Co\(_{0.3}\):O\(_9\)/n-ZnAlO modules [62, 64]. The higher power
density of our module could be attributed to a lower internal contact resistance (1.8 Ω) of ours than that reported for p-NaCo$_2$O$_4$/n-ZnAlO (2.97 Ω) [64]. Listed in table 1 are the power generation characteristics of our modules and most of the oxide modules reported so far in the literature.

4. Concluding remarks

We show that oxide TE materials and high-temperature oxide modules are becoming more and more important, both for research and applications, because they can be used for waste heat recovery at high temperatures. Among TE oxides, Ca$_2$Co$_3$O$_6$ and Al-doped ZnO are very promising, and the development in their TE performance has marked an obvious progress by means of the nanostructuring approach. The performance of TE modules built from these oxides is getting encouraging results. However, contact resistance and the long-term stability of oxide modules still need to be further explored.

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