1. Introduction

Thermoelectric material can convert waste heat to electricity directly, which causes the material to become a candidate for a green energy harvester. For practical application, a figure of merit (\(ZT = \sigma^2T/k\)) equal to 1 of thermoelectric material is typically required [1]. ZT can be calculated from electrical conductivity (\(\sigma\)), Seebeck coefficients (\(S\)), thermal conductivity (\(k\)), and absolute temperature (\(T\)). For example, the intermetallic compounds: Bi₂Te₃ and PbTe exhibit high thermoelectric performance and ZT close to 1. However, both materials are highly oxidative and toxic [2], which several researchers are avoiding this drawback. For this reason, the metal oxide thermoelectric ceramics are extensively focused because of their good thermoelectric properties and high heat resistance [2].

Among oxide thermoelectric materials, Ca₃Co₄O₉ (CCO) misfit-layered compound is one of the attractive materials, particularly the CCO single crystal has shown high ZT (~0.87 at 973 K) [3]. Nevertheless, it is pretty expensive and difficult to prepare on a large scale. The polycrystalline ceramic of CCO is therefore pointed out, although it still has lower ZT. There have been many attempts to improve ZT of CCO by doping at Ca-site or Co-site [4–6]. The primary enhancement of ZT of CCO ceramics resulted from increased \(\alpha\), \(S\), or decrease in \(k\).

From this aspect, we are interested in the improvement in thermoelectric properties of CCO by doping.

\[ \text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3 \] (BCZT) is a lead-free ferroelectric material, which has exhibited a potential performance to replace PZT material in several electronic devices such as sensors, actuators, and capacitors [7] due to its suitable dielectric and piezoelectric properties. BCZT is quite sensitive with deviation from its stoichiometry and ion doping, which produced phase transition, crystal structure change, and chemical defects [8,9]. The generated defects can affect free mobile charge carriers and enhance electronic and thermal transport in BCZT material [9]. This contribution is expected to influence the thermoelectric properties of CCO ceramic. Hence, the addition of BCZT to CCO ceramic is of great interest for the thermoelectric investigation of CCO-based material.

The thermoelectric properties of CCO ceramic, with BCZT dopant, have not been reported yet. Thus, in this work, we present the effects of BCZT on the thermoelectric properties of CCO ceramics. (1-x)CCO-xBCZT ceramics where \(x\) = 0, 0.003, 0.005, and 0.010 weight fraction were fabricated via solid-state sintering. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques were used to determine the phase of all ceramics. X-ray absorption spectroscopy (XAS) was employed to survey the oxidation state of
elements in these ceramics. The influences of chemical defects, charge concentration, and oxidation state on thermoelectric properties of the doped-CCO ceramics are discussed.

2. Experimental procedures

2.1. Materials

The starting materials were CaCO₃ (99.5%, Riedel-de Haën) and Co₃O₄ (99.5%, Aldrich) for CCO, BaCO₃ (98.5%, Sigma-Aldrich), CaCO₃ (99.95%, Sigma-Aldrich), TiO₂ (99.9%, Riedel-de Haën), and ZrO₂ (98.5%, Sigma-Aldrich) for BCZT.

2.2. Preparation of (1-x)CCO-(x)BCZT powders

The starting oxides were weighed following the chemical formula of Ca₃Co₂O₄ (CCO) and (Ba₀.₈₅Ca₀.₁₅)Zr₀.₇Ti₀.₃O₃ (BCZT). The oxide mixtures were ball milled in ethanol (>99.5%, Merck) for 24 h by using a conventional mixed-oxide method. The mixed powders were dried at 393 K for 24 h and calcined in an alumina crucible at 1,023 K for 24 h (CCO) and at 1,373 K for 3 h (BCZT). After sieving, (1-x)CCO-(x)BCZT binary powders where x = 0, 0.003, 0.005, and 0.010 weight fraction were mixed again in ethanol (>99.5%, Merck) for 6 h and dried at 393 K for 24 h.

2.3. Preparation of (1-x)CCO-(x)BCZT ceramics

A conventional solid-state sintering technique was used to fabricate all samples. After obtaining (1-x)CCO-(x)BCZT powders, one drop of 3 wt% PVA (polyvinyl alcohol, Merck) binder was added to the (1-x)CCO-(x)BCZT powders (~1 g). The mixed powders were pressed into pellets with a diameter of 10 mm and thickness of 2 mm using a uniaxial press with 187.3 MPa. Binder removal was carried out by heating the pellets at 773 K for 1 h in an air atmosphere with a heating/cooling rate of 5 K/min. These pellets were then sintered at 1,223 K, 1,273 K, 1,323 K, and 1,373 K for 24 h of dwell time in an air atmosphere with a heating/cooling rate of 5 K/min on an alumina plate.

2.4. Characterization

The bulk densities of all ceramics were determined using the Archimedes’ method. The relative densities of the ceramics were calculated from the relationship between theoretical and bulk densities. In this study, the theoretical density of CCO and BCZT were 4.68 g/cm³ [10] and 5.77 g/cm³ [11], respectively. The microstructural observation of the samples was carried out using a SEM (JEOL JSM 6335 F). Phase identification of the sintered samples was investigated in a 2-theta range of 20–70° using XRD (MiniFlex, Rigaku). The chemical composition of the ceramics was studied by X-ray absorption near edge structure (XANES) at beamline 5.2:SUT-NANOTEC-SLRI XAS, Synchrotron Light Research Institute (SLRI), Thailand.

2.5. Measurement of thermoelectric properties

The thermoelectric properties from 300 K to 800 K were investigated. The electrical conductivity and the Seebeck coefficients were measured using an instrument designed by Iwanaga et al. [12]. The charge carrier concentration of the samples was investigated by Hall measurement. The laser flash instrument (Netzsch, LFA 457) was employed for measuring thermal conductivity.

3. Results and discussion

The (1-x)CCO-(x)BCZT ceramics with x = 0, 0.003, 0.005, and 0.010 were sintered at temperature range between 1,223 K to 1,373 K for 24 h. The sintering temperatures above 1,223 K produced the melted and deformed pellets, which were quite difficult for studying the phase, charge start of the defect environment, and thermoelectric properties. Thus, the pellets sintered at 1,223 K become representative for all ceramics. Figure 1 shows the microstructure of all the ceramics prepared in this work. The CCO ceramic had a porous microstructure, accompanied by its lowest relative density (~90%), as shown in Table 1. With the addition of BCZT, the porosity of the CCO-BCZT composites decreased. The relative densities of the doped ceramics, which are listed in Table 1, increased gradually with increasing BCZT content, and the maximum value was about 98% for x = 0.010.

Moreover, the SEM images revealed the presence of other phases in the samples in addition to CCO. As seen in Figure 1, the secondary phase was quite small; thus, it was quite tricky for obvious phase identification by energy-dispersive spectroscopy (EDS). However, we could use EDS to identify the phase of CaO (white color) for x = 0.005. The interpretation of different phases will be discussed together with XRD results in the next section.

The XRD patterns of all ceramics are illustrated in Figure 2. All the peaks in sample match well with the standard card (PDF 21–0139) for CCO. The XRD patterns of the doped CCO ceramics with x ≤ 0.005 were not different from that of CCO ceramic. However, from their SEM images, the results confirmed the presence of other phases. The content of these phases might be below the detection limits of...
Figure 1. SEM images for (1-x)CCO-(x)BCZT ceramics: (a) x = 0, (b) x = 0.003, (c) x = 0.005, and (d) x = 0.010.

the instrument used in this work. When BCZT was added (x = 0.010), the XRD pattern revealed additional peaks. The concentration of these phases is much higher; therefore, XRD was able to detect them. These phases were Ca$_3$Co$_2$O$_6$, CoO, Co$_3$O$_4$, and CaO, formed by variation in the ratio of Ca/Co as suggested by Tahashi et al. [13]. The general Ca/Co ratio of single-phase CCO is 3/4. The addition of BCZT might increase the Ca/Co ratio to 3/2 due to enhancement of Ca ions from BCZT. The presence of excess Ca ions resulted in partial decomposition of Ca$_3$Co$_2$O$_6$ to Ca$_3$Co$_2$O$_6$ and other oxide phases [13]. The formation of these phases significantly influenced the electrical conductivity, Seebeck coefficient, and thermal conductivity of these samples, which will be discussed later.

According to XRD results, the additional phases were Ca$_3$Co$_2$O$_6$, CoO, Co$_3$O$_4$, and CaO. The chemical reaction for the formation of these phases is given in Equation (1),

$$\text{Ca}_3\text{Co}_2\text{O}_6 \rightarrow \frac{1}{2}\text{Ca}_3\text{Co}_2\text{O}_6 + \frac{3}{2}\text{CoO} + \frac{1}{2}\text{Co}_3\text{O}_4 + \frac{3}{2}\text{CaO} + \frac{1}{2}\text{O}_2$$

(1)

Both Ca$_3$Co$_2$O$_6$ and Ca$_3$Co$_2$O$_6$ are regarded as the thermoelectric phase. On the contrary, other oxides are in the non-thermoelectric and could produce chemical defects. It is worth mentioning the defect formation for each oxide. In the case of CoO, the vacancy defects of Co$^{2+}$ ions ($V''\text{Co}$) could be produced and explained by Kröger-Vink notation in Equation (2),

$$\text{Co}^{3+}_{\text{Co}} + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{CoO} + V''\text{Co}$$

(2)

where Co$^{3+}_{\text{Co}}$ represent Co atom in Co site and $V''\text{Co}$ is ionized Co vacancy. In the case of Co$_3$O$_4$, it might have two types of cobalt vacancies. They relate to tetrahedral and octahedral coordination geometries of Co$^{2+}$ and Co$^{3+}$ ions, respectively. Equations (3)

| BCZT content (x) | Theoretical density (g/cm$^3$) | Bulk density (g/cm$^3$) | Relative density (%) | $E_g$ (eV) |
|------------------|--------------------------------|-------------------------|----------------------|------------|
| 0                | 4.680                          | 4.22                    | 90.17                | 0.220      |
| 0.003            | 4.683                          | 4.38                    | 93.52                | 0.143      |
| 0.005            | 4.685                          | 4.43                    | 94.55                | 0.106      |
| 0.010            | 4.691                          | 4.63                    | 98.70                | 0.059      |
Figure 2. XRD patterns in the 2-theta range of 20° – 70° for (1-x)CCO-(x)BCZT ceramics: (a) x = 0, (b) x = 0.003, (c) x = 0.005, and (d) x = 0.010.

and (4) present two possible vacancies of Co$^{2+}$ ($V''_{\text{Co}}$) and Co$^{3+}$ ions, i.e. doubly, and triply ionized cation vacancy, respectively.

$$6\text{Co}^2_\text{Ca} + 4\text{O}_2 + 12\text{e}' \rightarrow 2\text{Co}_3\text{O}_4 + 6V''_{\text{Co}}$$ (3)

$$3\text{Co}^2_\text{Ca} + 2\text{O}_2 + 9\text{e}' \rightarrow \text{Co}_3\text{O}_4 + 3V''_{\text{Co}}$$ (4)

In CaO, the vacancy defects of Ca$^{2+}$ ions ($V''_{\text{Ca}}$) could be produced and its Kröger-Vink notation is given in Equation (5) [9]

$$\text{Ca}^2_\text{Ca} + 1/2\text{O}_2 + 2\text{e}' \rightarrow \text{CaO} + V''_{\text{Ca}}$$ (5)

As seen in the equations, the creation of the cation vacancies, i.e. $V''_{\text{Ca}}$, $V''_{\text{Co}}$, and $V''_{\text{Co}}$ also produces excess free electrons due to the requirement of charge neutralist. Both the cation vacancies and free electrons are mobile charge carriers, leading to doping of charge carriers in the ceramics.

Electrical conductivities ($\sigma$) as a function of temperature in the range from 300 K to 800 K for all ceramics are shown in Figure 3(a). At 300 K, the CCO ceramics with BCZT content $x=0.005$ had electrical conductivity values nearly equal to that of the pure CCO ceramic ($\sim 0.002 \times 10^3$ S/m). Interestingly, the addition of BCZT ($x=0.010$) become effective, and the electrical conductivity values of this ceramic were enhanced greatly (from $0.062 \times 10^3$ S/m to $0.52 \times 10^3$ S/m). This enhancement was attributed to the increment of charge carrier concentration ($n$) in the ceramic due to the ionized defects formed in the samples as explained earlier. The measured charge concentration at 300 K for the $x = 0.010$ was $3.15 \times 10^{18}$ /cm$^3$, which is much higher than the value of $x = 0$ ($1.31 \times 10^{15}$ / cm$^3$). The increase in charge concentration is associated with the formation of chemical defects in this ceramic. Upon increasing the temperature, the carrier concentration of all ceramics increased because of the stimulation of thermal energy. The composition at $x = 0.010$ exhibited the greatest increase in $\sigma$ values compared with other ceramics. This is due to the fact that the trend is accompanied well by the increase of mobile charge carrier concentration of $x = 0.010$, as shown in Figure 3(b). The $n$ values at 800 K of the ceramics with $x = 0$, and 0.010 were $1.79 \times 10^{17}$/cm$^3$ and $1.3 \times 10^{21}$/cm$^3$, respectively. Thermal activation leads to interest in carrier concentration at high temperatures. Equation (6) [4] was therefore used to investigate the activation energy ($E_a$) of all ceramics,

$$\sigma = nea^2 (A/T) \exp(-E_a/k_BT)$$ (6)

where $n$ is the carrier concentration, $e$ is the charge of the carrier, and $a$ is the intersite distance of hopping, $A$ is the pre-exponential term, $k_B$ is the Boltzmann’s constant, and $T$ is the absolute temperature. The plots of $\ln \sigma$ as a function of 1000/T for all ceramics are presented in Figure 3(c). The activation energy $E_a$ can be extracted from the slope of linear fitting, and the $E_a$ values of all samples are listed in Table 1. $E_a$ values decreased gradually and became much lower at $x = 0.010$ ($\sim 0.059$ eV). The $E_a$ value means that the charge carriers’ energy barrier needs to be overcome for conducting. Thus, the sample with lower $E_a$ would have a lower energy barrier, resulting in better conduction than the sample with higher $E_a$. This contribution confirmed the significant electrical enhancement of CCO ceramic with the addition of BCZT $x = 0.010$. 
The temperature dependence of the Seebeck coefficients (α) of all ceramics is illustrated in Figure 4(a). All ceramics showed positive values of α, indicating p-type semiconducting behavior. However, there was a difference in the Seebeck coefficient for each ceramic. The CCO and the BCZT-doped CCO (x = 0.010)
showed an increase of $\alpha$ with increasing temperature. Meanwhile, the compositions $x = 0.003$ and 0.005 showed a rise of a value up to 600 K, then decrease up to 800 K. The $\alpha$ value at high temperature could be attributed to the suitability of charge carrier concentration and charge mobility. The excess charge concentration could induce scattering of mobile charges, leading to a reduction; meanwhile, the suitable concentration increased a value. As a result, in Figure 3(b), the $n$ value of the compositions $x = 0.003$ and 0.005 ranged between $3.72 \times 10^{-7}$/cm$^3$ to $8.98 \times 10^{-9}$/cm$^3$ at a temperature above 600 K. This concentration might be excessive and caused charge scattering, which results in a decrease in their Seebeck coefficients. In the case of CCO, the maximum value of $n$ was about $1.79 \times 10^{-7}$/cm$^3$ at 800 K. This concentration might be suitable; thus, the $\alpha$ still increased upon temperature increase.

Interestingly, with the addition of BCZT ($x = 0.010$), the ceramic promoted abrupt enhancement in $\alpha$ ($\sim$400 $\mu$V/K) at 800 K although it had a large charge concentration ($1.3 \times 10^{21}$/cm$^3$). This result was opposite to the others. Hence, this enhancement might result from the additional factor. The possible reason was the presence of Ca$_3$CoO$_6$ in this ceramic (see its XRD pattern in Figure 2). Tahashi et al. [14] had suggested that Ca$_3$CoO$_6$ had a Seebeck coefficient higher than Ca$_3$Co$_2$O$_6$ and this phase required energy for charge transport more than Ca$_3$Co$_2$O$_6$. Thus, at the temperature below 700 K, the thermal energy might not be enough for the Ca$_3$Co$_2$O$_6$ phase. The $\alpha$ value, therefore, increased gradually upon temperature increase. However, at 800 K, the thermal energy might be enough. As a result, the Ca$_3$Co$_2$O$_6$ phase could greatly enhance the Seebeck coefficient of this ceramic. The other contribution might come from the electron system [15] in the CCO misfit-layered materials, suggested by Heikes formula [16] in Equation (7),

$$a = -\frac{k_e}{e} \ln \left( \frac{g_3}{g_4} \frac{1}{1 - y} \right)$$

where $g_3$ and $g_4$ are the number of configurations of Co$^{2+}$ and Co$^{3+}$ ions, respectively. The $y$ is the fraction of Co$^{4+}$ in the CoO$_2$ layer. Equation (7) suggests that a value can be increased by increasing the concentration of Co$^{3+}$ ions, which is attributed to a spin-entropy enhancement.

Figure 4(b) shows XAS $K$-edges spectra of Co ions of all ceramics. The features at A and B peaks are associated with the transition from the Co$^{3+}$ core level to the Co$^{3d-2p}$ hybridized final state and the Co$^{4+}$ core level to the unoccupied $4p$-derived orbitals, respectively [17]. Regarding the B peak, the maximum absorption positions shifted from 7726 eV for $x = 0$ to 7729 eV for $x = 0.010$. In general, the peak at 7726 eV reflects the presence of Co$^{2+}$; meanwhile, the peak at 7729 eV reflects the presence of Co$^{3+}$. These results showed the increase in the concentration of Co$^{3+}$ ions in the ceramic with $x = 0.010$, which led to the enhancement of the Seebeck coefficient.

The temperature dependence of the total thermal conductivity ($k_{total}$) for all ceramics is shown in Figure 5(a). The $k_{total}$ values of the ceramics with $x \leq 0.005$ decreased with increasing temperature; meanwhile, the composition $x = 0.010$ almost had stable values upon increasing temperature. The thermal conductivity of the composition $x = 0.010$ was lowest about 0.5 W/m-K at 300 K and 0.4 W/m-K at 800 K. In general, $k_{total}$ in the materials can be expressed as $k_{total} = k_{ph} + k_e$, where $k_{ph}$ and $k_e$ are a contribution of lattice vibration and electronic thermal conductivity, respectively. In the case of $k_e$, the value could be estimated using Wiedemann-Franz’s law, which is written as

$$k_e = L_0 T$$

Where $L$ is the Lorenz number ($2.45 \times 10^{-8}$ WQK$^{-2}$). The $k_{ph}$ and $k_e$ functions of a temperature of all ceramics are plotted in Figure 5(b). It was seen that the main contribution of thermal conductivity of these ceramics resulted from $k_{ph}$. The decrease in $k_{ph}$, upon temperature increase, was attributed to phonon–phonon solid interaction at high temperature [5]. Conversely, with $k_{ph}$, all ceramics showed a rise of $k_e$ with increasing temperature, particularly the composition $x = 0.010$. This result reflected that mobile charge carriers, i.e. cation vacancies and free electrons, not only participated in electrical conductivity but also governed the thermal conductivity of this ceramic.

The thermoelectric power factors (PF) (calculated from $\alpha \times \sigma^2$) and figure of merit (ZT) as a function of a temperature for all ceramics are shown in Figure 5(c,d), respectively. The CCO with addition $x = 0.003$ and 0.005 did not exhibit significant enhancement compared with CCO. Interestingly, the BCZT addition $x = 0.010$ improved PF and ZT values. Both values increased gradually with increasing temperature up to 700 K; then, the values became much higher at 800 K. The PF and ZT values at 800 K were about 235 $\mu$W/mK$^2$ and 0.5, respectively. The trend of the enhancements was accompanied well with the Seebeck coefficient in Figure 4(a). Therefore, the main reason for a rapid increase of PF and ZT at 800 K in the CCO with BCZT addition ($x = 0.010$) should be attributed to the existence of Ca$_3$Co$_2$O$_6$ phase and the improvement of the spin-entropy effect [15,16].

With these results, we found that the addition of BCZT could enhance the electrical conductivity, Seebeck coefficients, and thermal conductivity of CCO ceramic by forming chemical defects and
introducing the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase. However, the doping at $x \leq 0.005$ did not promote the practical improvement of thermoelectric properties. The results here suggested the addition of BCZT at $x = 0.010$ could promote a high ZT value at 800 K of CCO ceramic, which may be an alternative $p$-type oxide thermoelectric material for high-temperature thermoelectric devices.

4. Conclusions

(1-$x$)CCO-$x$BCZT ceramics where $x = 0$, 0.003, 0.005, and 0.010 were fabricated successfully via solid-state sintering at 1,223 K for 24 h. The addition of BCZT introduced chemical defects in CCO ceramic, which increased charge carrier concentration. This contribution increased the electrical conductivity of the ceramics, particularly for $x = 0.010$. The Seebeck coefficients were enhanced by presence of Co$^{3+}$ ions and the introduction of the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase. The thermal conductivity of these ceramics was mainly attributed to the phonon vibration, and the lowest value was found of composition $x = 0.010$. The CCO ceramic doped BCZT at $x = 0.010$ promoted the highest values of thermoelectric power factor (235 $\mu$W/mK$^2$) and figure of merit (0.5) at 800 K, which might find the applications for high-temperature thermoelectric devices.

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