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Research Article

An Optimization of Composition Ratio among Triple-Filled Atoms in $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ System

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Bulk nanostructured materials are important as energy materials. Among thermoelectric materials, the skutterudite system of $CoSb_3$ is a representative material of bulk nanostructured materials. Filling a skutterudite structure with atoms that have different localized frequencies (also known as triple filling) was reported to be effective for lowering thermal conductivity. Among studies representing superior power factors, In-filled skutterudite systems showed higher Seebeck coefficients. This study sought to optimize the composition ratio among the triple-filled atoms in an $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ system. The composition dependence of the thermoelectric properties was investigated for specimens with different ratios among the three kinds of filler atoms in the $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ system. In addition, the process variables were carefully optimized for filled skutterudite systems to obtain a maximum ZT value.

1. Introduction

Bulk nanostructured materials are a key research topic as energy materials. Materials for energy applications should satisfy the needs of both high conversion efficiency and large power output. Nanostructures are required for the high performance of materials, but bulk materials are needed to produce large power output. In thermoelectric materials, the skutterudite system found in $CoSb_3$ is a representative material of bulk nanostructured materials [1, 2]. For example, high-performance bulk nanostructured materials have been manufactured using this system by filling the Sb-dodecahedron voids in the $CoSb_3$ skutterudites with foreign ions such as rare-earth elements, alkalines, and alkaline-earth metals (thereby forming filled skutterudites). These weakly bound filler atoms with their independent vibrational modes were reported to interact with the normal modes of the structure and suppress thermal conductivity dramatically [2]. The efficiency of a thermoelectric material is determined by its dimensionless thermoelectric figure-of-merit $ZT = S^2\sigma T\kappa^{-1}$, where S, σ, κ, and T are the Seebeck coefficient, electrical conductivity, total thermal conductivity, and absolute temperature, respectively. Therefore, good thermoelectric materials should have a high power factor ($\mathrm{PF} = S^2\sigma$) value and a low thermal conductivity value. For this reason, $CoSb_3$-based skutterudites have stimulated much scientific interest.

These filler atoms have been reported to play many roles. When the filler atoms are doped into the skutterudite system, they make chemical bonds with Sb ions. They can act as donor ions in an n-type $CoSb_3$ matrix, increasing carrier concentration [3, 4]. The filler atoms can also serve as a phonon scattering center, suppressing thermal conductivity. Filling a skutterudite structure with atoms that have different localized frequencies (triple filling) has also been reported to be effective for lowering thermal conductivity [2–4]. The filler atoms can also enhance the Seebeck coefficients of filled $CoSb_3$ skutterudite system [5–7], an effect which has been reported many times, especially for the In-filled $CoSb_3$ skutterudite system. Among these studies representing superior power factors, In-filled skutterudite specimens [5–7] showed higher Seebeck coefficients than In-free filled skutterudite systems [8–14].

In this study, we sought to optimize the composition ratio among triple-filled atoms in an $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ system. Shi et al. and Yang et al. [3, 4] reported that multiple filling (filling with many ions that have different localized frequencies) might be effective in further lowering thermal conductivity. This study designed triple-filled compositions in the In-filler system $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$, as Ba and Ce have very different resonance frequencies (54 cm^{-1} for Ce and 93 cm^{-1} for Ba) [6]. In many previous studies, the optimized filling amount was reported to be 0.3 ($R_{0.3}Co_4Sb_{12}$, R = filler atoms) for the filled skutterudite system [6, 13], so the filler amount was fixed at 0.3 ($In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$) and only the ratios among the filler atoms were varied. The composition dependence of the thermoelectric properties was investigated for specimens with different ratios among the three kinds of filler atoms.

In addition, previous studies noted the need for the process variables to be carefully tuned for filled-skutterudite systems, and especially for rare-earth and alkali-earth filled systems [15, 16]. A higher temperature melting and aging process should be used for filled skutterudites than intrinsic skutterudites. The phase-formation reaction (γ-$CoSb_2$ + Sb → δ-$CoSb_3$) may occur at an elevated temperature in filled-skutterudite systems [15–17]. The optimized process conditions were determined for synthesizing the δ-$CoSb_3$ single phase without the γ-$CoSb_2$ phase to acquire samples with a maximum ZT value.

2. Experimental Procedure

Multiple-filled skutterudite samples $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ were synthesized by a combination of induction melting and spark plasma sintering (SPS). The starting materials were high-purity In (99.999% shot), $BaSb_3$ (99.98% ingot), Ce (99.999% powder), Co (99.95% slug), and Sb (99.999% shot), which were weighed according to the required stoichiometric ratio and loaded into carbon-coated quartz ampoules. The quartz ampoules were sealed under a vacuum of 10^{-3} Torr. The encapsulated samples were melted by using a radio frequency induction furnace and quenched during solidification to prevent phase separation. The ingots were then encapsulated in a vacuum again and annealed at 973 K for five days to form a homogeneous skutterudite phase (δ-$CoSb_3$). The obtained ingots were pulverized into fine powders, followed by SPS in a graphite die at 963 K under 50 MPa of pressure for ten minutes in a vacuum. The prepared samples were sliced with a low-speed diamond saw and then polished.

The phases of the powders were analyzed using X-ray diffraction (XRD) over a 2θ range of 10–90° (D/MAX-2500/PC, Rigaku, Japan, CuKα radiation). Microstructure of the bulk specimens was observed by using a scanning electron microscopy (SEM, JSM6700F, JEOL, Japan) and a high-resolution transmission electron microscopy (HRTEM, JEM4010, JEOL, Japan). The electrical conductivity and the Seebeck coefficient were measured by means of the four-point probe method using a thermoelectric property measurement system (RZ2001i, Ozawa Science, Japan).

Thermal conductivity was evaluated from the density, the specific heat, and the thermal diffusivity by use of a laser flash method (Netzsch). The Hall coefficient and the carrier concentration were measured based on the Van der Pauw method at room temperature (Resi Test 8300, Toyo Corporation). All of the aforementioned thermoelectric property measurements except Hall coefficient were performed within the temperature range of 300 to 800 K.

3. Results and Discussion

The composition dependence of the thermoelectric properties was investigated for specimens with different ratios among the three kinds of filler atoms in the $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ system. Figure 1(a) shows a schematic phase diagram of the compositions investigated in this study. Even though low concentration of the Ba and Ce atoms were included in these compositions, the process conditions were appropriately optimized for these rare-earth and alkali-earth filled skutterudites. As a result, the four compositions were indexed as a $CoSb_3$ skutterudite single phase without any secondary phases like the $CoSb_2$ phase as shown in Figure 1(b).

The Seebeck coefficients ($|S|$) for all the compositions manufactured at high temperatures were larger than 200 μV/K as can be seen in Figure 2(a). This large Seebeck coefficient is a characteristic of In-filled skutterudite systems. Three possible explanations were reported for the large Seebeck coefficients in the In-filled skutterudite systems. Li et al. reported that nano-dispersed second phase might enhance the Seebeck coefficient of In-filled skutterudites [5]. They reported that InSb phase was dispersed at the boundaries and that this nano-dispersed phase might reduce the mobility of the charge carriers and thereby enhance the Seebeck coefficient of the thermoelectric material. The Seebeck coefficient is a function of the carrier mobility and concentration as follows [18]:

$$\begin{aligned} S &= \frac{\pi^2}{3}\frac{k_B}{q}k_BT\left\{\frac{d\left[\ln(\sigma(E))\right]}{dE}\right\}_{E=E_F} \\ &= \frac{\pi^2}{3}\frac{k_B}{q}k_BT\left\{\frac{1}{n}\frac{dn(E)}{dE}+\frac{1}{\mu}\frac{d\mu(E)}{dE}\right\}_{E=E_F}, \end{aligned} \tag{1}$$

where, S is the Seebeck coefficient; μ is the mobility of the carrier; and n is the carrier concentration. As shown in (1), the Seebeck coefficient was inversely proportional to the mobility. However, it was hard to find the InSb secondary phase by means of XRD and SEM analyses in this study as shown

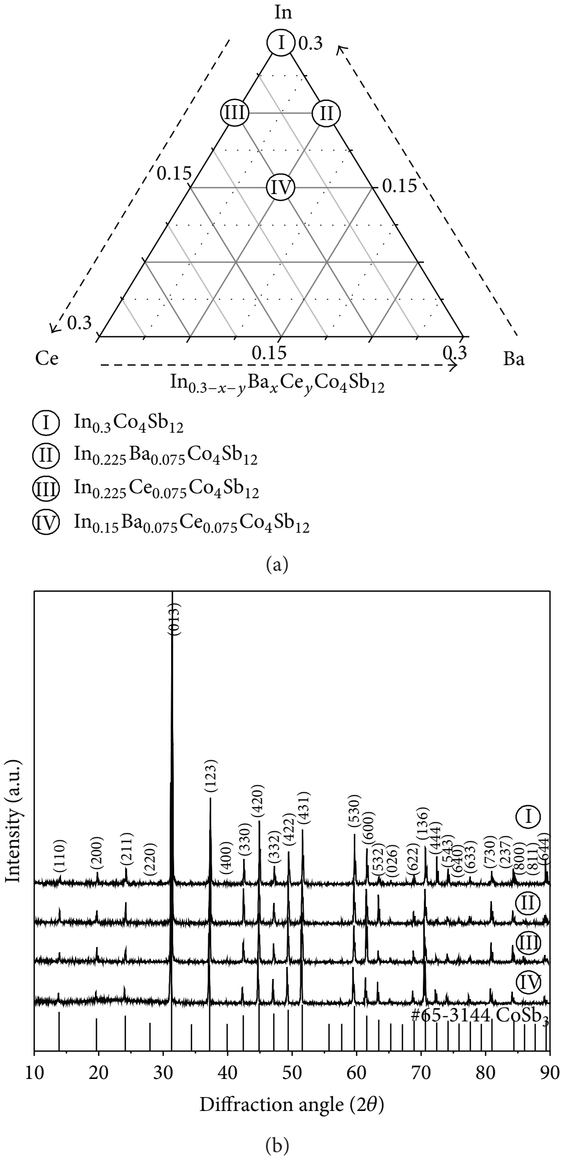


Figure 1: (a) A schematic phase diagram of four compositions investigated in the $In_{0.3-x-y}Ba_xCe_yCo_4Sb_{12}$ filled skutterudite system and (b) X-ray diffraction patterns of the compositions.

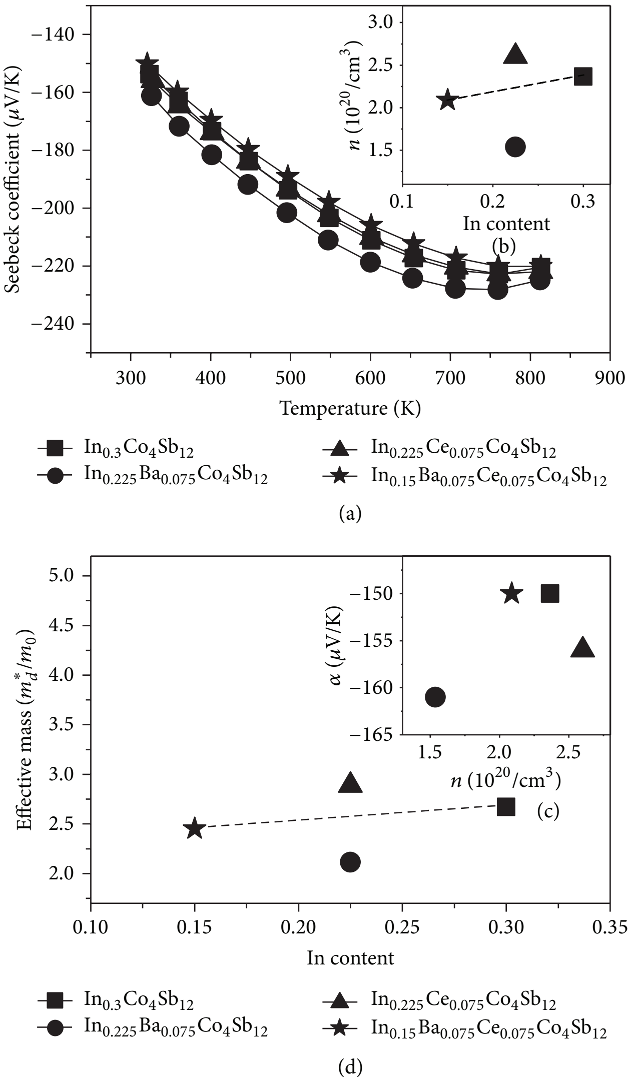
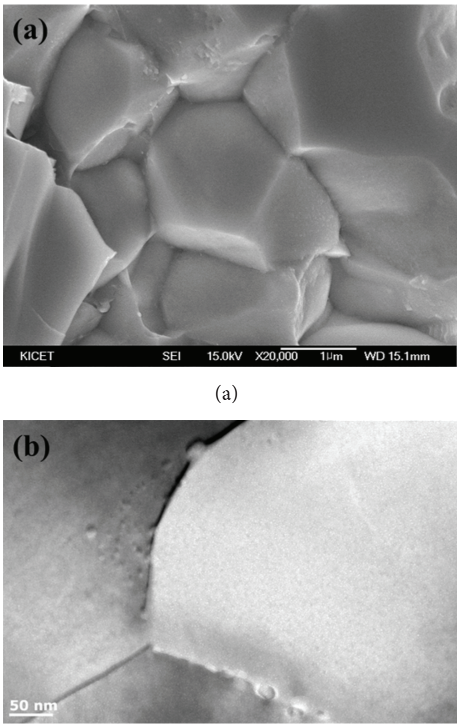


Figure 2: (a) Temperature dependence of the Seebeck coefficients, (b) In-content dependence of a carrier concentration, (c) In-content dependence of the Seebeck coefficient, and (d) In-content dependence of an effective mass value.

in Figure 3(a). The underlimit of detection size or amount of secondary nanoparticles also might be the reason of not observed the nano-dispersed secondary phase. As shown in Figure 3(b), however, a small amount of secondary phase with smaller size than the reported scale [5] was detected from a TEM analysis. This means that the In-filler could be doped into the lattice in this study. The reason for the different results about InSb secondary phase is not clear yet. Different process conditions could be one of the reasons for the difference between this work and other reports [5]. More precise analysis for the relationship between process conditions and amount of the InSb secondary phase in various filled skutterudite systems should be carried out for better understanding the In and InSb effects.

Shi et al. emphasized the electronegativity values (χ) of the filler atoms [19]. They reported that if the difference of electronegativity values is smaller than 0.8 between a filler atom and Sb, the filler atom cannot be doped into the void of $CoSb_3$ skutterudite structure. The electronegativity of an In atom (1.7) is nearly the same as that of an Sb atom (1.9). As a result, they reported that an In-filler atom cannot fill the void of the $CoSb_3$ structure. If the In-filler atoms cannot perform the role as a donor, the low carrier concentration could increase the Seebeck coefficient in the In-filled skutterudite system. This is because the Seebeck coefficient is inversely proportional to the carrier mobility and the carrier concentration as shown in (1). However, the carrier concentration value increased in proportion to the amount of In-filler as shown in Figure 2(b). This result shows



(a)

(b)

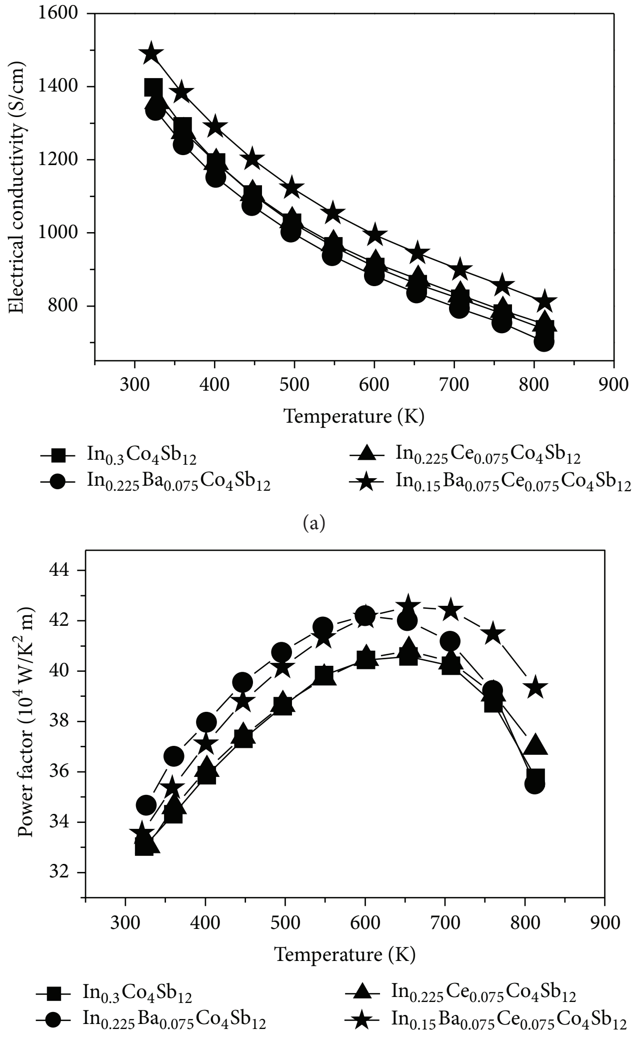
Figure 3: (a) A scanning electron microscopy image and (b) a high-resolution transmission electron microscopy image of the bulk $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ specimens.

that the In-filler (χ = 1.7) in this study can perform the role as a donor just as in the cases of Ba (χ = 0.9) and Ce (χ = 1.1).

Another possibility is that the In-filler can increase the effective mass of electrons in the skutterudite system. In this study, the Seebeck coefficients show no linear relationship to the carrier concentration as shown in Figure 2(c). Even though the carrier concentration was highest in the $In_{0.225}Ce_{0.075}Co_4Sb_{12}$ composition, a large Seebeck coefficient was measured in this composition. This lack of a relationship between the carrier concentration and the Seebeck coefficient suggests that the In-filler has an additional effects on the Seebeck coefficients of this triple-filled system. In general, the Seebeck coefficient is proportional to the effective mass of the carriers [15–18]:

$$S = \frac{8\pi^2 k_B^2 T}{3qh^2} m_d^* \left(\frac{\pi}{3n}\right)^{2/3}, \qquad (2)$$

where, S is the Seebeck coefficient; k_B is Boltzmann's constant; T is the absolute temperature; q is the carrier charge; h is Plank's constant; m_d^* is the effective mass; and n is the carrier concentration. Thus, an increase in the effective mass can cause an increase in the Seebeck coefficient. Figure 2(d) shows that the effective mass was nearly proportional to the amount of In-filler. The increased effective mass can help explaining the large Seebeck coefficients of the In-filled skutterudites system. As a result, it is anticipated that the large Seebeck coefficients of the In-filled system are ascribed to both the effect of the InSb secondary phase and the increased effective mass. More detailed study should follow to determine which of the two is the main factor causing the large Seebeck coefficients in In-filled systems.



(a)

(b)

Figure 4: (a) Temperature dependence of electrical conductivities and (b) power factor values for the $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ filled skutterudite compounds.

The electrical conductivity values were inversely proportional to the Seebeck coefficients of the triple-filled skutterudites as shown in Figure 4(a). As mentioned above, the In-filler can perform the role as a donor in this study. Therefore, the carrier concentration could decrease when In^{3+} was substituted by Ba^{2+}, since the charge state of the donor Ba^{2+} is lower than that of In^{3+}. As a result, the electrical conductivity of the $In_{0.225}Ba_{0.075}Co_4Sb_{12}$ composition was lower than that of the $In_{0.3}Co_4Sb_{12}$ composition. After this, when Ce^{3+} was additionally substituted in for In^{3+}, the electrical conductivity of the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition was higher than that of the $In_{0.225}Ba_{0.075}Co_4Sb_{12}$ composition. This increased electrical conductivity can be explained by the fact that the charge state of the Ce ion was frequently reported to be 4+ [20]. Because of the increased donor effect, the carrier concentration of the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition was higher than that of the $In_{0.225}Ba_{0.075}Co_4Sb_{12}$ composition as shown in Figure 2(b). The lower conductivity of the $In_{0.225}Ce_{0.075}Co_4Sb_{12}$ composition is difficult to explain and may be due to high melting point of Ce atoms. As mentioned in Section 1, the process variables should be carefully tuned for filled-skutterudite systems, especially for rare-earth and alkali-earth filled systems [15, 16]. A higher-temperature melting and aging process should be used for filled-skutterudites than for intrinsic skutterudites, making it difficult to manufacture a $CoSb_3$ skutterudite single phase from a Ce-filled composition. Further study is needed to explain the low electrical conductivity of a Ce-filled system. One more important factor is that the electrical conductivity of the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition was even higher than that of the $In_{0.3}Co_4Sb_{12}$ composition. The effective mass of the $In_{0.3}Co_4Sb_{12}$ composition was larger than that of the other compositions as shown in Figure 2(d). The largest effective mass $In_{0.3}Co_4Sb_{12}$ composition can cause low electrical conductivity in spite of its highest carrier concentration.

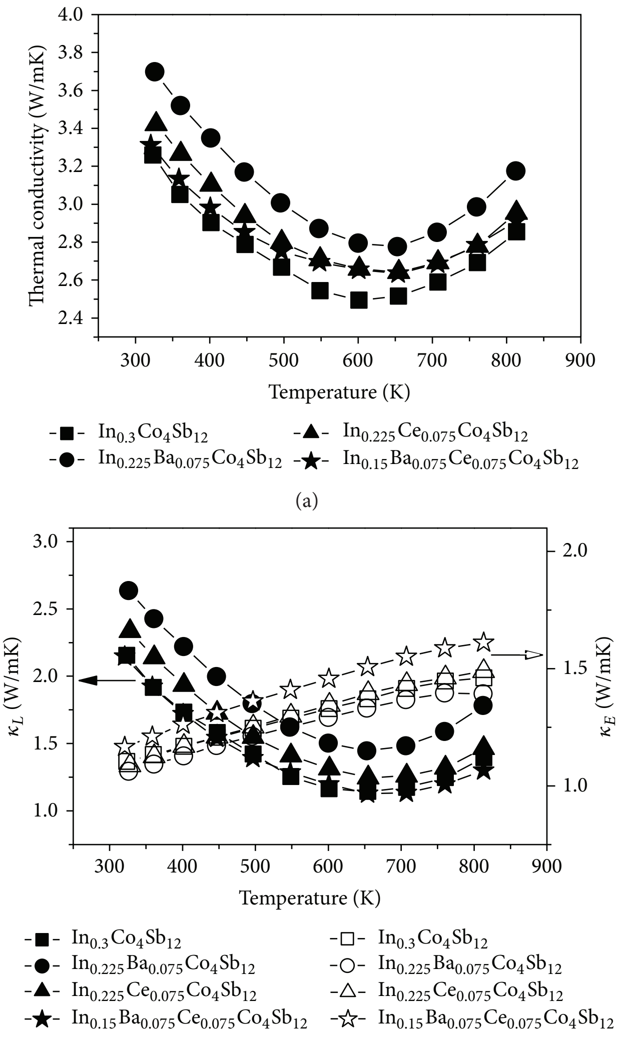
In general, the electrical conductivity of thermoelectric materials is inversely proportional to their Seebeck coefficients. Although electrical conductivity of $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ was higher than other compositions, the Seebeck coefficient was lowest as can be seen in Figure 2(a). However, degree of reduction in the Seebeck coefficient is smaller than increment in electrical conductivity. As a result, the highest value of power factor higher than 42×10^{-4} W/K^2 m was obtained in the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition as shown in Figure 4(b).

Figure 5 shows the temperature dependence of the total thermal conductivity, the electronic thermal conductivity, and the lattice thermal conductivity of the samples. The thermal conductivity is the sum of the lattice thermal conductivity and electronic thermal conductivity as can be seen in the following:

$$\kappa = \kappa_L + \kappa_{el} = \kappa_L + L\sigma T, \qquad (3)$$

where, κ_L, κ_{el}, L, σ, and T are the lattice thermal conductivity, the electronic thermal conductivity, the Lorenz number (2.45×10^{-8} WΩ/K^2), the electrical conductivity, and the absolute temperature, respectively. κ_{el} can be obtained by means of the Wiedemann-Franz Law; $\kappa_{el} = L\sigma T$ [21], and κ_L can be determined by $\kappa_L = \kappa - \kappa_{el}$.

As shown in Figure 5(a), the total thermal conductivity was lowest in the $In_{0.3}Co_4Sb_{12}$ composition. The thermal conductivity of the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition was higher than that of the $In_{0.3}Co_4Sb_{12}$ composition. This was because the electrical conductivity of the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition was the highest among all of the compositions. In spite of its highest electrical conductivity, the lattice thermal conductivity of the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition was the lowest in this study. This low lattice thermal conductivity can be explained by the triple rattlers effect. Each filler atom was reported to represent a phonon resonance scattering center near a particular frequency [3]. Scattering as wide a spectrum of normal phonons as possible could be the crucial factor when seeking to achieve a low κ_L [3]. Accordingly, filling the skutterudite structure with atoms that have different localized frequencies (triple-filling) was considered to be effective for lowering the κ_L value further [3]. Total thermal conductivity of the $In_{0.225}Ba_{0.075}Co_4Sb_{12}$ composition was the highest in this work in spite of the lowest electrical conductivity. In general, rattler atoms with low valence state (2+) and large ionic radius have been reported to show poor rattling effects in single rattler filled cases [22]. Ba^{2+} has a large ionic radius, so it is believed that the high lattice thermal conductivity of the $In_{0.225}Ba_{0.075}Co_4Sb_{12}$ composition is attributed to the Ba-filler. However, it is difficult to explain that the higher total thermal conductivity of the $In_{0.225}Ce_{0.075}Co_4Sb_{12}$ composition than that of the



(b)

Figure 5: (a) Thermal conductivities and (b) both lattice thermal conductivity (κ_L) and electronic-thermal conductivity (κ_E) for the $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ filled skutterudite compounds.

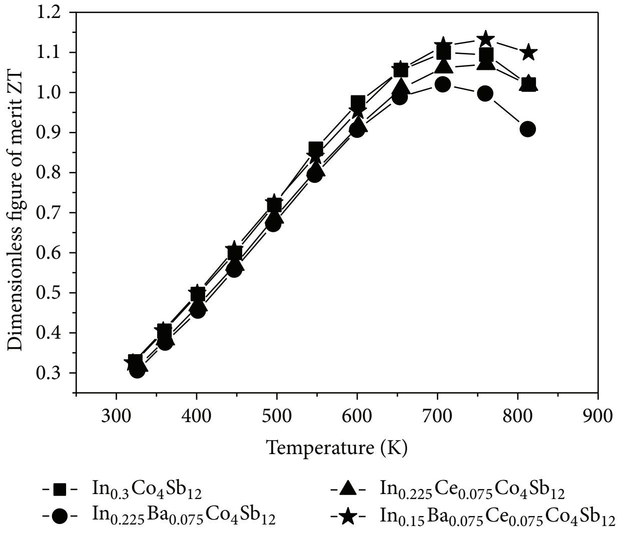


Figure 6: The dimensionless figure of merit (*ZT*) for the $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ filled skutterudite compounds.

$In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ and $In_{0.3}Co_4Sb_{12}$ compositions. Tang et al. reported that the total thermal conductivity increased with increasing Ce-filling amount when Ce-filling content was higher than filling limit [23]. They also found that the filling content limit for Ce-filling case was lower than that of Ba-filling case. Further study is needed to explain the high thermal conductivity of a Ce-filled system.

As a result, a maximum *ZT* value of 1.13 was obtained in the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition as shown in Figure 6. The reasons for this high value seem to be attributable to the large Seebeck coefficient because of the In-filler atoms, high electrical conductivity due to the Ce donor effect, and low thermal conductivity by the triple-filled rattlers.

4. Conclusions

The composition dependence of the thermoelectric properties was investigated for specimens with different ratios among three different filler atoms in the $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ system. The process conditions for the rare-earth and alkali-earth filled skutterudites were appropriately optimized. $CoSb_3$ skutterudite single phase without any secondary phases like $CoSb_2$ phase was obtained for all compositions used in this study.

The Seebeck coefficients ($|S|$) of all the compositions manufactured at high temperatures were larger than $200\,\mu V/K$. Both the effect of the InSb secondary phase and the increased effective mass value could be the causes of the large Seebeck coefficients observed in the In-filled skutterudites systems. The electrical conductivity of the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition was higher than that of the other compositions. This high electrical conductivity can be explained via the donor effect of the Ce ion, as the charge state of the Ce ion was frequently reported to be 4+. In spite of its high electrical conductivity, the lattice thermal conductivity of the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition was lowest in this study owing to the triple rattlers that play a role as a phonon resonance scattering center.

Since the ratio of filler atoms and synthesizing process conditions were optimized in an $In_{0.3\text{-}x\text{-}y}Ba_xCe_yCo_4Sb_{12}$ system, a maximum *ZT* value of 1.13 was obtained in the $In_{0.15}Ba_{0.075}Ce_{0.075}Co_4Sb_{12}$ composition. Accordingly, it seems that the In and Ce increases the Seebeck coefficient and electrical conductivity, respectively, and the triple filled rattlers lower the thermal conductivity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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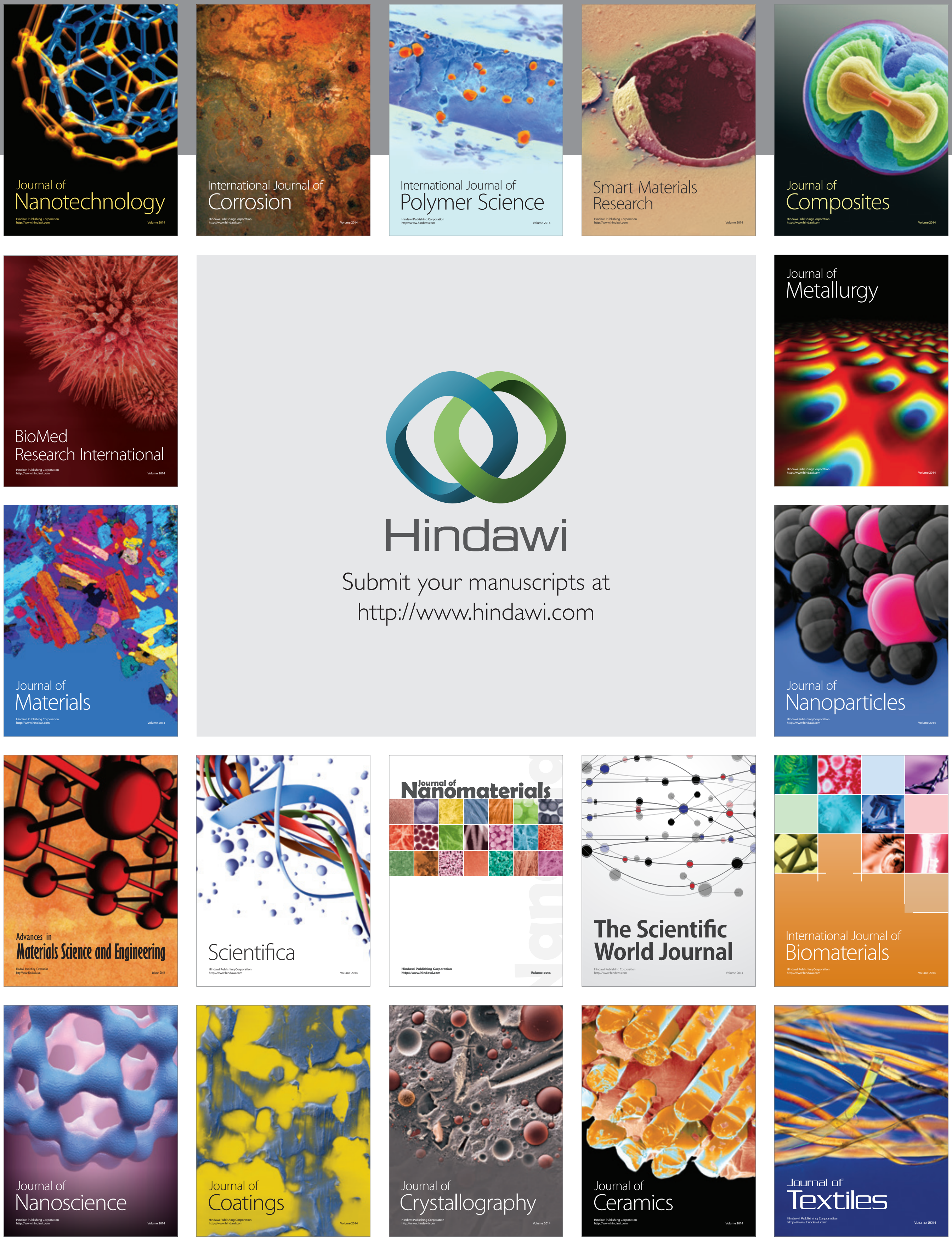
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