Sains Malaysiana 47(1)(2018): 181–187
http://dx.doi.org/10.17576/jsm-2018-4701-21

Enhancement of Thermoelectric Properties of $Yb_{0.25}Co_4Sb_{12}$ Skutterudites through Ni Substitution

(Peningkatan Sifat Termoelektrik bagi Bahan Skuterudit $Yb_{0.25}Co_4Sb_{12}$ melalui Penggantian Ni)

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ABSTRACT

In this work, we investigate the effects of Ni doping on the thermoelectric (TE) properties of $Yb_{0.25}Co_4Sb_{12}$ sample. $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0 \leq x \leq 0.5$) samples were prepared by mechanical alloying and subsequently consolidated by spark plasma sintering. The morphology of consolidated samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS). The thermoelectric properties of bulk samples were measured from room temperature to 800 K. The XRD analysis confirmed that, the successful formation of the Co_4Sb_{12} skutterudite phase and Ni is substituted into Co site of the skutterudite crystal lattice. Moreover, the electrical resistivity decreased to 14.6 μΩm at 785 K for $Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$ sample, due to increase of the electron concentration by Ni-addition. The absolute Seebeck coefficient reached the highest value of 223 μV/K at 592 K for $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$ sample, thus yielding a maximum value of power factor of 2.41×10^{-3} W/mK^2 at 592 K. The highest dimensionless thermoelectric figure of merit value ZT of 0.49 at 692 K has been achieved for the $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$ sample, compared to ZT=0.06 for the $Yb_{0.25}Co_4Sb_{12}$ sample at same temperature. This work indicates a strategy to improve the thermoelectric performance by Ni substitution of Co sites in the $Yb_{0.25}Co_4Sb_{12}$ skutterudite through simultaneous improvement of its electrical conductivity, Seebeck coefficient and reduction of its thermal conductivity.

Keywords: Mechanical alloying; Ni-doping; skutterudite; thermoelectric

ABSTRAK

Dalam kajian ini, kesan pendopan Ni ke atas sifat $Yb_{0.25}Co_4Sb_{12}$ telah dikaji. Sampel $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0 \leq x \leq 0.5$) telah disediakan dengan kaedah pengaloian mekanikal dan seterusnya digabungkan dengan pensinteran pencucuh plasma. Morfologi untuk sampel gabungan telah dicirikan oleh pembelauan sinar-X (XRD) dan imbasan mikroskop elektron berserta tenaga serakan X-ray spektroskopi (SEM-EDS). Ciri termoelektrik sampel telah diukur daripada suhu bilik ke 800 K. Analisis XRD mengesahkan bahawa Ni berjaya didopkan ke dalam $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ $CoSb_3$ dalam fasa skutterudite, dengan Ni menggantikan beberapa lokasi Co dalam kekisi kristal skuterudit. Selain itu, kerintangan elektrik menurun kepada 14.6 μΩm di 785 K bagi sampel $Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$, disebabkan oleh peningkatan bilangan pembawa cas elektron oleh Ni. Pekali Seebeck mutlak mencapai nilai tertinggi 223 μV/K pada 592 K bagi sampel $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$, lalu menghasilkan nilai maksimum faktor kuasa 2.41×10^{-3} W/MK^2 pada 592 K. Angka merit, ZT yang optimum adalah 0.49 pada 692 K telah dicapai untuk sampel $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$. Kajian ini menunjukkan strategi untuk meningkatkan prestasi termoelektrik melalui penggantian Ni pada bahagian Co dalam bahan skutterudite $Yb_{0.25}Co_4Sb_{12}$, sekaligus menambahbaik kekonduksian elektrik, pekali Seebeck dan pengurangan kekonduksian haba.

Kata kunci: Ni-dop; pengaloian mekanikal; skuterudit; termoelektrik

INTRODUCTION

Thermoelectric (TE) systems become as energy harvesting, which can recover the wasted heat energy and converted into useful electricity (Bashir et al. 2014; Elsheikh et al. 2014). Skutterudite materials system is considered a promising candidate for thermoelectric application. However, the basic binary skutterudite $CoSb_3$ structure is undesirable as a thermoelectric material due to its very low electrical conductivity and very high thermal conductivity (Il-Ho et al. 2010). For example, in 2001, Kawaharada et al. studied the $CoSb_3$ skutterudite which was prepared by arc melting followed by the sintering method. The result of thermal conductivity was very high about 7 W/mK at room temperature, mainly due to phonon conduction at low temperature. The maximum figure of merit, *ZT* for this formulation was 0.051 at 723 K. Zhang et al. (2004) studied the preparation process of $CoSb_3$ compounds through mechanical alloying and spark plasma sintering methods. The thermal conductivity achieved was in the range of (3 to 8 W/mK) at room temperature, whilst attaining a maximum figure of merit of 0.095 at 673 K. From the results obtained, we confirm that, the basic binary skutterudite $CoSb_3$ materials are not favorable for thermoelectric applications.

On the other hand, recent formulations of filled-skutterudite thermoelectric materials have the advantage that they generally possess low lattice thermal conductivity, due to the filling of the skutterudite 'cages' with 'rattler' atoms (Takizawa et al. 1999; Tritt et al. 1996). Several studies have been carried out on doped/filled-skutterudite materials and illustrated that, the filler atoms have advantage of reducing the lattice thermal conductivity and electrical resistivity as well. This contributes to enhance the overall performance of TE materials (Elsheikh et al. 2017, 2016; Truong et al. 2014). In 2006, Yang et al. synthesized Co_4Sb_{12} with substitution of Ni on the Co site of the skutterudite crystal lattice by mechanical alloying and hot pressing technique. The result of the electrical resistivity was significantly decreased through the Co site substitution with Ni, where the resistivity decreased from 350 μΩm for the binary Co_4Sb_{12} sample to 50 μΩm for the $Co_{3.6}Ni_{0.4}Sb_{12}$ sample at room temperature. On the other hand, the thermal conductivity reduced from 11 to 5.5 W/mK at room temperature for the same samples. The highest ZT value was 0.035 for $Co_{3.6}Ni_{0.4}Sb_{12}$ sample at room temperature. In the same year, research carried out by Peng et al. (2006) on the Co_4Sb_{12} skutterudite with Fe substitution on the Co site through the mechanical alloying and hot pressing method. The electrical resistivity was decreased by Fe substitution, from 24 to 7.5 μΩm for the $Co_{3.35}Fe_{0.65}Sb_{12}$ sample at room temperature due to increased carrier concentration. The lattice thermal conductivity was significantly reduced from 4.6 to 0.75 W/mK for Co_3FeSb_{12} sample and lead to an improve ZT value to 0.32 was achieved for the $Co_{3.35}Fe_{0.65}Sb_{12}$ sample at 773 K. In 2007, Geng et al. (2007) studied the Yb-filled on Co_4Sb_{12} skutterudite with high ZT of 0.7 at 673 K for $Yb_{0.15}Co_4Sb_{12}$ sample.

In addition, Ni-doping has a potential to enhance the thermoelectric performance of skutterudite materials by the substitution of the Co site. In this work, we study the substitution of the transition metal of Ni on the Co site for the $Yb_{0.25}Co_4Sb_{12}$ skutterudite system. Ni-doping is expected to improve the electrical conductivity, which is expected to enhance the power factor and moderate increase of ZT.

EXPERIMENTAL METHODS

MATERIALS PREPARATION

The starting elements powder with high purity; Co (99.8%, 1.6 μm), Sb (99.5%, 200 mesh), Yb (99.9%, 200 mesh) and Ni (99.999%, 200 mesh) were purchased from Alfa Aesar. The stoichiometric materials where loaded into Zirconia Jar (50 mL) with Zirconia balls (5 mm in diameter) and the weight ratio of balls to powders were 20:1. The jar was placed into a ball mill (GOKIN Ltd., PLANET) were discussed in detail elsewhere (Said et al. 2017). The samples were cut and polished for measurement of the thermoelectric properties.

STRUCTURAL CHARACTERIZATION ANALYSIS

X-ray diffraction (XRD) measurements were carried out for compact samples, using X-ray diffraction (Bruker AXS D8 Advance) system, The diffraction patterns were obtained with Cu k_α radiation (λ = 1.5406 Å) and generator settings (40 kV and 40 mA) with a step size of 0.020406° and scan speed of 1 s per step. XRD was used to identify the phases and estimate the corresponding lattice parameters. The microstructure characterizations of compacted specimens were obtained by using FEI Helios 450HP dual beam with energy-dispersive X-ray spectroscopy (EDS).

THERMOELECTRIC PROPERTIES MEASUREMENTS

The electrical resistivity and the Seebeck coefficient were measured simultaneously with a commercial testing instrument (ZEM-3-Ulvac-Riko) in He atmosphere by a standard four-probe direct current technique. Thermal diffusivity, D, and specific heat, C_p were measured by using a laser flash technique on TC-7000H (Ulvac-Riko) apparatus, then the thermal conductivity was estimated from the equation $k = D \times C_p \times d$, where d is the density of sample. The density (d) of the sintered materials was measured by using Archimedes method. All the TE properties measurements were performed from room temperature to 800 K, the dimensionless figure of merit, ZT, was then evaluated.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of $Yb_{0.25}Co_4Sb_{12}$ bulk samples with different Ni-additions at room temperature. The result found that, the main phase of skutterudite $CoSb_3$ (PDF 03-065-1791) structure (space group Im-3) was observed, with minor amount of secondary phases such as; $CoSb_2$ (PDF 03-065-4102) and Ni (PDF 00-001-1258) have been detected in all doped samples. However, $Yb_{0.25}Co_4Sb_{12}$ bulk sample shows only a single phase of skutterudite structure mainly due to the limited of Yb-filler in the void ($0.2 \le x \le 0.3$) according to Park et al. (2014). Moreover, the Rietveld refinement analysis of XRD pattern implemented for all bulk samples, the structure showed in Figure 2. Table 1 shows the results of the refinement including nominal compositions, actual compositions, lattice parameters and density of $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0 \le x \le 0.5$) SPSed samples. Furthermore, the lattice parameters were found to decrease after the Ni-doping. The shrinking of the lattice parameters indicated that the Ni-atoms were substituted the Co-atoms, this was observed to occur due to the smaller atomic radius of Ni as compared to Co.

Figures (3(a)-5(a)) display SEM micrographs of different Ni-additions into $Yb_{0.25}Co_4Sb_{12}$ bulk samples. It can be seen that, the microstructures clearly showed the dominated phase of skutterudite structure, with slight amount of $CoSb_2$ has been observed as secondary phase were present in all SPSed samples. The elemental mapping shows agglomeration of Yb-rich in some regions, which is presented as white grains for most samples.

The agglomeration of Yb increased with Ni-addition. Ni-addition was fairly distributed in the grains and grain boundaries for $Yb_{0.25}Ni_{0.1}Co_{3.9}Sb_{12}$ sample has been detected by elemental mapping as seen in Figure 3(e).

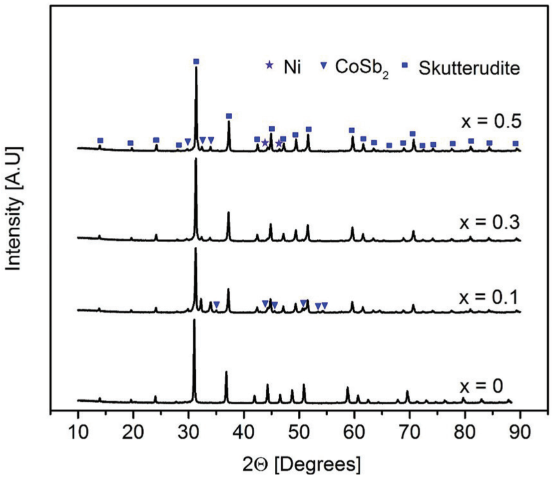

FIGURE 1. The XRD pattern of $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0 \leq x \leq 0.5$) bulk samples

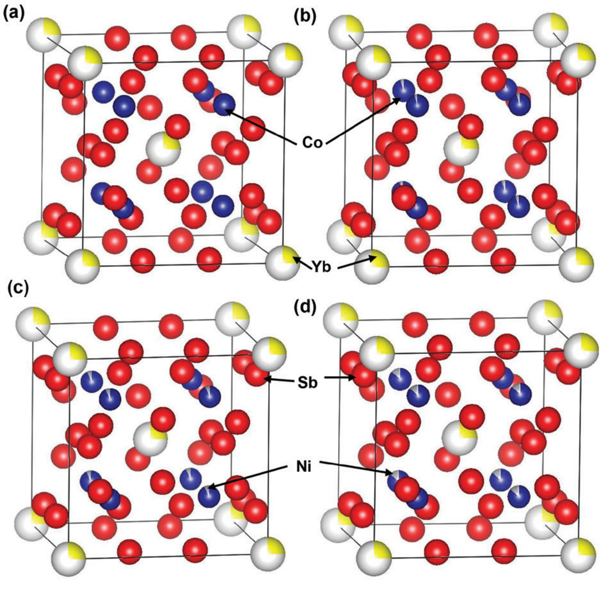

FIGURE 2. The Jana refinement images of (a) $Yb_{0.25}Co_4Sb_{12}$, (b) $Yb_{0.25}Co_{3.9}Ni_{0.1}Sb_{12}$ (c) $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$ and (d) $Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$ bulk sample

However, the elemental mapping for $Yb_{0.25}Ni_{0.3}Co_{3.7}Sb_{12}$ sample identified some agglomeration of Ni in the matrix. Moreover, Figure 5(e) clearly observed a random distribution of Ni-element was determined by elemental mapping. The results of EDS points of $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0.1 \leq x \leq 0.5$) SPSed samples tabulated in Table 2. In addition, SEM and EDS shown an agreement with the XRD analysis results, it can be seen that the Ni-doped and Yb-element is partially filled skutterudite bulk material with trace Yb has been detected.

Figure 6 displays the temperature dependences of electrical resistivity of $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ bulk samples. The electrical resistivity reduced with increasing Ni-doping content and temperature, indicating a typical semiconductor behavior for all samples. This is due to

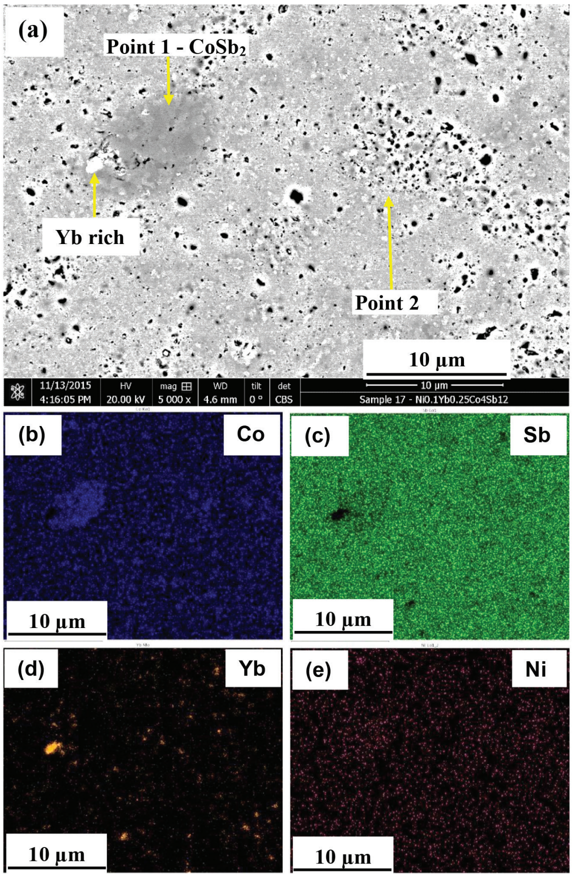

FIGURE 3. The SEM-EDS images of $Yb_{0.25}Co_{3.9}Ni_{0.1}Sb_{12}$; (a) micrograph and (b-e) the elemental mapping of bulk sample

TABLE 1. The nominal compositions, actual compositions, lattice parameters and density of $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0 \leq x \leq 0.5$) bulk samples

Nominal composition	Actual composition	Lattice parameter (Å)	Density (%)
$CoSb_3$ (Wee et al. 2010)		9.0350	
$Yb_{0.25}Co_4Sb_{12}$	$Yb_{0.25}Co_4Sb_{12}$	9.0412 (2)	99 %
$Yb_{0.25}Co_{3.9}Ni_{0.1}Sb_{12}$	$Yb_{0.25}Co_{3.9}Ni_{0.1}Sb_{12}$	9.0349 (8)	96 %
$Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$	$Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$	9.0443 (4)	96 %
$Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$	$Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$	9.0404 (4)	99 %

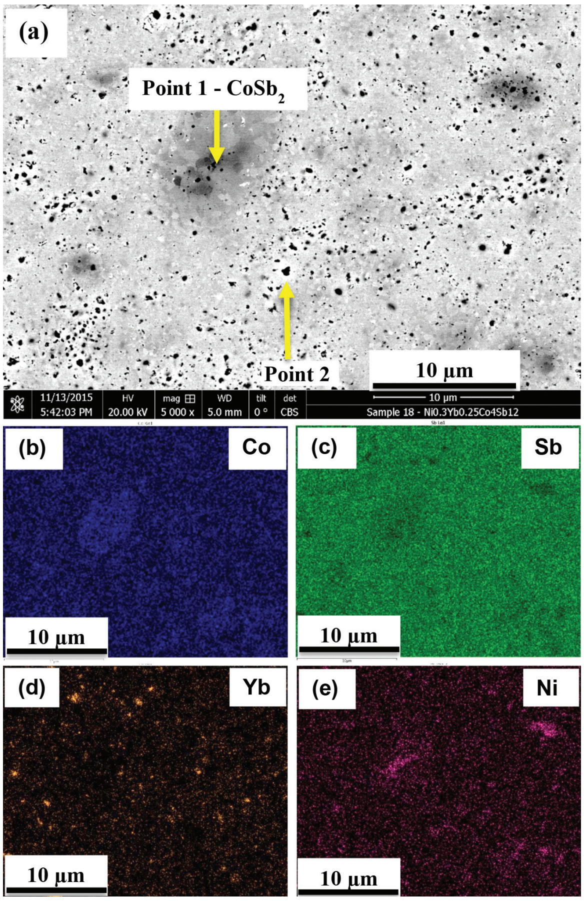

FIGURE 4. The SEM-EDS images of $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$; (a) micrograph and (b-e) the elemental mapping of bulk sample

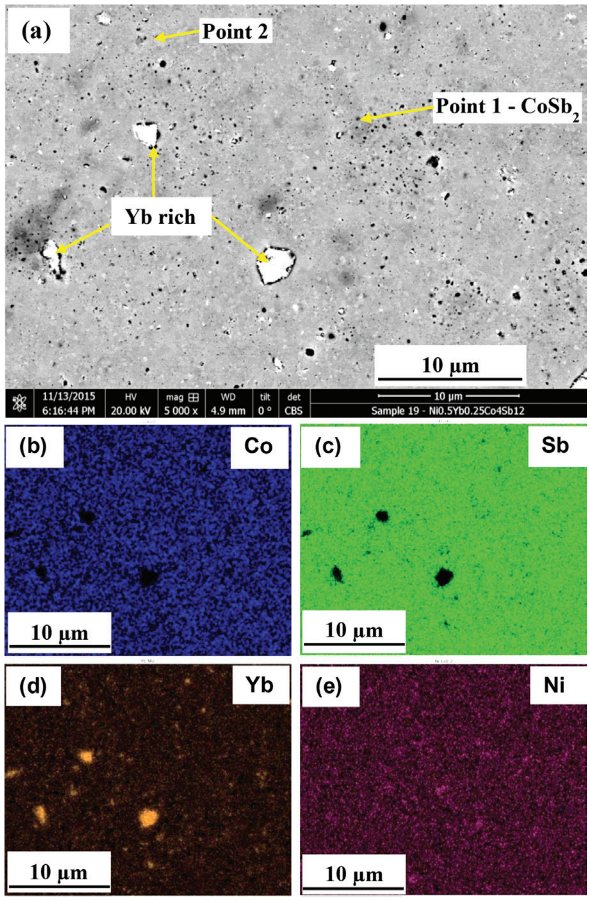

FIGURE 5. The SEM-EDS images of $Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$; (a) micrograph and (b-e) the elemental mapping of bulk sample

TABLE 2. EDS points of $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0.1 \le x \le 0.5$) bulk samples

Compound	Atomic percent (%)					
	$Yb_{0.25}Co_{3.9}Ni_{0.1}Sb_{12}$		$Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$		$Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$	
Element/Point	1	2	1	2	1	2
Co	28.83	21.69	24.5	22.61	32.97	21.86
Sb	64.61	71.87	56.61	74.27	62.93	71.7
Yb	0.4	2.38	0	1.07	1.33	4
Ni	6.16	4.06	11.74	2.05	2.77	2.44

more carriers are generated with increasing temperature. $Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$ sample showed the lowest electrical resistivity of 14.6 µΩm at 785 K, which is lower than Ni-free sample of 36.1 µΩm at same temperature. This is mainly due to the excess electrons supplied by Ni-doping and also due to increasing the carrier concentrations. In comparison of another research study, where Yang et al. (2006) obtained electrical resistivity of 40 µΩm for $La_{0.4}Co_{3.6}Ni_{0.4}Sb_{12}$ sample at room temperature, which is higher than the present result. Thus, Ni-substitution of Yb-filled skutterudite improved the electrical resistivity of Co_4Sb_{12} bulk sample.

The temperature dependences of Seebeck coefficient of $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ balk samples are shown in Figure 7. The absolute Seebeck coefficient values improved with increasing Ni-doped content and temperature. The highest absolute Seebeck coefficient value reached 223 µV/K at 592 K for $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$ sample, which is higher than undoped $Yb_{0.25}Co_4Sb_{12}$ sample of 153 µV/K at same temperature. This is mainly due to the electrons supplied by Ni-substitution. The present result is systematically higher when compared with the previous reports, where Yang et al. (2006) obtained ~ 165µV/K for $Co_{3.6}Ni_{0.4}Sb_{12}$ compound at 592 K and Park et al. (2012) obtained 144 µV/K and 130 µV/K at 823 K for $Yb_{0.3}FeCo_3Sb_{12}$ and $Yb_{0.9}Fe_3CoSb_{12}$ skutterudite, respectively.

The temperature dependences of the power factor for $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ bulk samples are exhibited in Figure

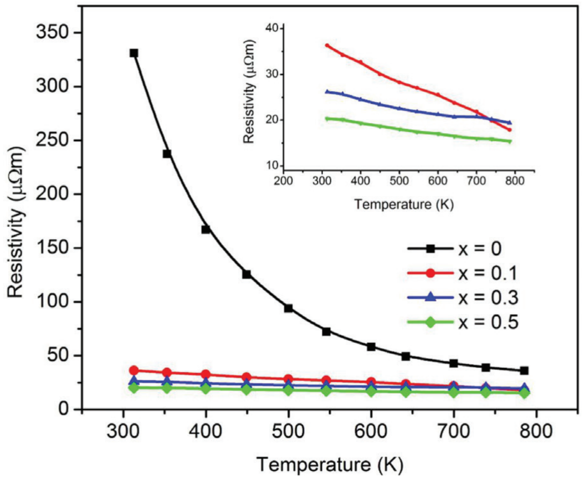

FIGURE 6. The electrical resistivity for $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0 \leq x \leq 0.5$) bulk samples; The insert enlarges the section of electrical resistivity at low values (10 to 40 μΩm)

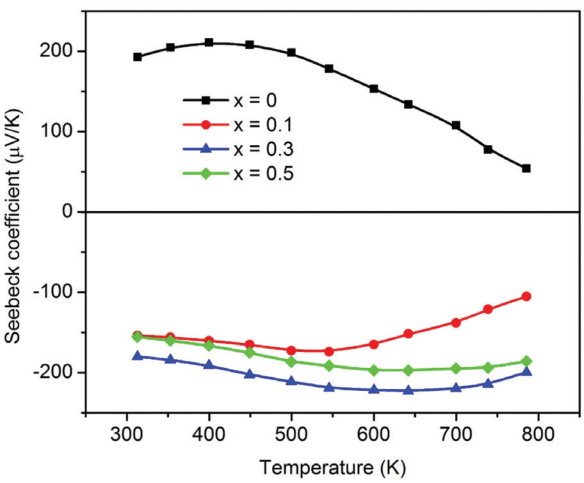

FIGURE 7. The Seebeck coefficient for $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0 \leq x \leq 0.5$) bulk samples

8. The power factor can be calculated from the Seebeck coefficient (S) and electrical resistivity (ρ) values according to the equation PF = S^2/ρ. The power factor improved with Ni-doping content and temperature. $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$ sample reached the maximum value of power factor of 2.41×10^{-3} W/mK^2 at 592 K, this is due to the increase in Seebeck coefficient which is higher at x = 0.3 than decreasing the electrical resistivity. In comparison, this result is much higher than that of Ni-free sample of 0.40 $\times 10^{-3}$ W/mK^2 at same temperature and slightly higher compared to Park et al. (2012) report of ~ 2.2×10^{-3} W/mK^2 which been achieved for $Yb_{0.9}Fe_3CoSb_{12}$ compound at same temperature.

Figure 9(a) illustrates the temperature dependence of thermal conductivity (K) of $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ bulk samples. The total thermal conductivity is the sum of electronic (k_e) and lattice (k_L) thermal conductivities $k_{tot} = k_e + k_L$. It was found that, the thermal conductivity increased with increasing Ni-doped content at room temperature. For

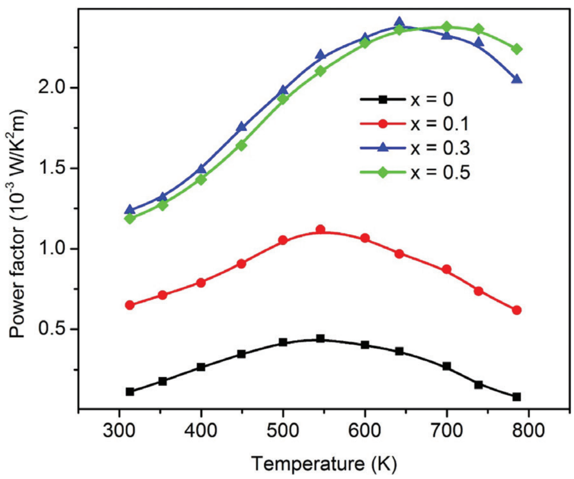

FIGURE 8. The power factor for $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0 \leq x \leq 0.5$) bulk samples

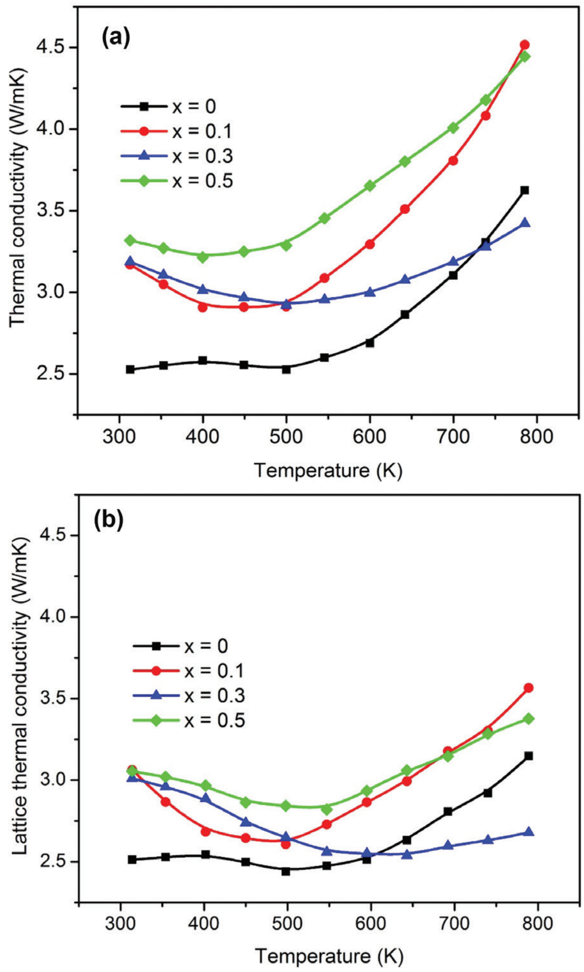

FIGURE 9. Temperature dependence of (a) thermal conductivity and (b) lattice thermal conductivity of $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0 \leq x \leq 0.5$) bulk samples

the doped samples, $Yb_{0.25}Co_{3.9}Ni_{0.1}Sb_{12}$ sample show the lowest value of thermal conductivity of 2.91 W/mK at 500 K. This result is lower than that obtained by Yang

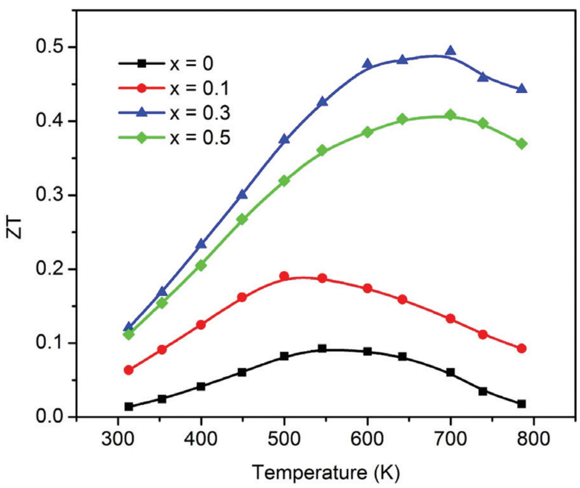

FIGURE 10. The figure of merit for $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ ($0 \leq x \leq 0.5$) bulk samples

et al. (2006) was ~ 3.8 W/mK for $Co_{3.6}Ni_{0.4}Sb_{12}$ sample at same temperature, and that obtained by Da Ros et al. (2007) for the $Yb_{0.17}Co_{3.97}Ni_{0.03}Sb_{12}$ sample which 3.7 W/mK at the same temperature. This is due to the effect of electron concentrations by Ni substitution. Figure 9(b) presents the variation of lattice thermal conductivity (k_L) for $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ samples as a function of temperature. The lattice thermal conductivity which was evaluated from subtracting the electronic contribution from the total thermal conductivity through the Wiedemann–Franz law ($k_e = L\sigma T$, where $L = 2.44 \times 10^{-8}\ V^2/K^2$ and σ is electrical conductivity). The results exhibited a reduction with Ni-doped content at room temperature. The lowest lattice thermal conductivity of 2.30 W/mK has been achieved for $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$ sample at 643 K, mainly due to phonon scattering by the rattling of filler in the voids of skutterudite.

The dimensionless figure of merit, *ZT* for $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ bulk samples as a function of temperature are displayed in Figure 10. It can be seen that the *ZT* values improved via increasing Ni-doped content and temperature. The maximum *ZT* value of 0.49 has been attained for $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$ sample at 692 K, which is 88% bigger than undoped $Yb_{0.25}Co_4Sb_{12}$ sample at same temperature. And also it is higher than that obtained by Yang et al. (2006) of ~ 0.15 and 0.31 for $Co_{3.6}Ni_{0.4}Sb_{12}$ and $La_{0.6}Co_{3.6}Ni_{0.4}Sb_{12}$ samples, respectively, at same temperature. The main reason of *ZT* enhancement is due to increasing of power factor.

CONCLUSION

N-type $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ skutterudite samples were successfully prepared via mechanical allying combined with spark plasma sintering. The effects of Ni-doped on the microstructure and TE properties of the $Yb_{0.25}Co_{4-x}Ni_xSb_{12}$ skutterudites were investigated. The XRD patterns for all bulk samples have identified the major phase of $CoSb_3$ skutterudite structure. Ni-addition resulted in an increased of carrier concentration, which decreased the electrical resistivity down to 14.6 μΩm at 785 K for $Yb_{0.25}Co_{3.5}Ni_{0.5}Sb_{12}$ sample. The absolute Seebeck coefficient increased with Ni-doped content fraction, reaching the highest value of 223 μV/K at 592 K has been obtained for $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$ sample. On the contrary, the lattice thermal conductivity was 2.54 W/mK has been attained for $Yb_{0.25}Co_{3.7}Ni_{0.3}Sb_{12}$ sample at 592 K. The same sample achieved the highest dimensionless figure of merit value *ZT* of 0.49 at 692 K, due to decreasing in electrical resistivity and moderate increased in Seebeck coefficient. Thus, this work was identified the contribution of Ni dopant for quaternary Yb filled skutterudite is improving its thermoelectric properties.

ACKNOWLEDGMENTS

This work has been supported by the IPPP Grant (Grant No. PG080/2014A), University of Malaya Research Grant (Grant No. RP023B/13AET and RP023C/13AET) and the Fundamental Research Grant Scheme (Grant No. FP022-2014B).

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Received: 28 November 2016
Accepted: 9 June 2017