Solvothermal synthesis of nano-sized skutterudite $Co_{1-x}Ni_xSb_3$ powders

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Nanostructuring is one of the effective approaches to lower the thermal conductivity of thermoelectric materials for improving its figure of merit. The nano-sized uniform skutterudite $Co_{1-x}Ni_xSb_3$ ($x = 0$, 0.05, 0.075, 0.125, 0.15, and 0.25) thermoelectric powders were synthesized in triethylene glycol solution by using $CoCl_2$, $NiCl_2$, and $SbCl_3$ as precursors and $NaBH_4$ as the reductant. Different synthesis conditions were studied to pursue pure and uniform skutterudite $CoSb_3$ powders. The powders were characterized by X-ray diffraction, field emission scanning electron microscope, and energy-dispersive X-ray analysis. Experimental results show that a Ni-doped skutterudite $Co_{1-x}Ni_xSb_3$ single phase was obtained at 290 °C for 12 h. The powders are spherical, small, and uniform. As x increases from 0 to 0.25, the unit-cell parameter a increases from 0.9044 to 0.9065 nm and the particle size increases from 10 to 30 nm. © *2013 International Centre for Diffraction Data*.
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Key words: Nano-particles, Solvothermal synthesis, Skutterudite, Substitution

I. INTRODUCTION

The thermoelectric material is a function material that can transfer thermal energy into electric energy or electric energy into thermal energy directly. The applications of thermoelectric materials in electricity generators or refrigeration devices have many advantages: small, cheap, lightweight, and quiet. The transfer efficiency is proportional to the value of figure of merit $ZT = \sigma S^2/\kappa$ (where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity of the material, and T is the temperature (K)) (Disalvo, 1999; Tritt, 1999). Binary skutterudite compound $CoSb_3$ has a cobalt cubic structure with antimony rings occupying six of the cells with two remaining empty. It possesses a large Seebeck coefficient and good electrical conductivity. However, its thermal conductivity is too high to make it an efficient thermoelectric material (Caillat *et al.*, 1996). Two approaches are used to reduce the thermal conductivity of skutterudites. One is to form filled skutterudites by filling the open 'cage' with rare earth and/or other metallic atoms (Sales *et al.*, 1996; Viennois *et al.*, 2005; Mi *et al.*, 2007a, b). The "rattling" motion of the filled atoms can effectively scatter phonons and hence cause a significant decrease of the lattice's thermal conductivity (Sales *et al.*, 1997). Another approach is nanostructuring of the thermoelectric material (Alboni *et al.*, 2007). The incorporated nanoparticles within the $CoSb_3$ bulk material add scattering centers to affect the phonons (Hicks *et al.*, 1993).

A wet-chemical route is a simple and effective way for preparation of nanostructure materials. Using a hydrothermal method, nanostructured $NaFe_4P_{12}$ skutterudite was synthesized (Liu *et al.*, 2002). Toprak *et al.* (2004) reported a novel chemical-alloying route for synthesis of nano-engineered skutterudite $CoSb_3$ by obtaining the highest ZT value of 0.17 at 611 K. Mi *et al.* synthesized $CoSb_3$ by a solvothermal route, in ethanol solution, at 250 °C for 72 h (Mi *et al.*, 2006). Here, we report the synthesis of uniform and nano-sized skutterudite $Co_{1-x}Ni_xSb_3$ thermoelectric powders of spherical shape (10–20 nm) in triethylene glycol solution at 290 °C with a reaction time of 12 h. The substitution of Ni for Co in $CoSb_3$ is expected to further reduce the thermal conductivity of skutterudite (Viennois *et al.*, 2005; Zhang *et al.*, 2008).

II. EXPERIMENTAL

$SbCl_3$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $NaBH_4$, and triethylene glycol of commercial grade were used without further purification as the starting materials. Stock solutions of $SbCl_3$ (0.6 mol/dm^3), $CoCl_2{\cdot}6H_2O$ (0.2 mol/dm^3), and $NiCl_2{\cdot}6H_2O$ (0.2 mol/dm^3) were separately prepared, by dissolving the reagents in triethylene glycol. Typically, 100 ml of $SbCl_3$ stock solution and various quantities of $CoCl_2$ and $NiCl_2$ stock solutions were taken, according to the designed formula $Co_{1-x}Ni_xSb_3$ ($x = 0$, 0.05, 0.075, 0.125, 0.15, and 0.25), and were mixed. To this mixed solution, $NaBH_4$ in excess dissolved in 160 ml of triethylene glycol was added under vigorous stirring for complete reduction of the metal ions. The reaction lasted for 20 min and within a few minutes the color of the solution turned dark. This suspension was transferred to an autoclave and heated to 290 °C, at a heating rate of 10 °C/min, and maintained at 290 °C for some time. After cooling down to room temperature, the resulting product was centrifuged and washed with distilled water, ethanol, and acetone, sequentially, and finally vacuum dried at 60 °C overnight.

The phase structures of the powders were analyzed by X-ray diffraction (XRD) using a Bruker D8 Advance 18 kW X-ray diffractometer with Cu$K\alpha$ radiation ($\lambda = 0.154178$

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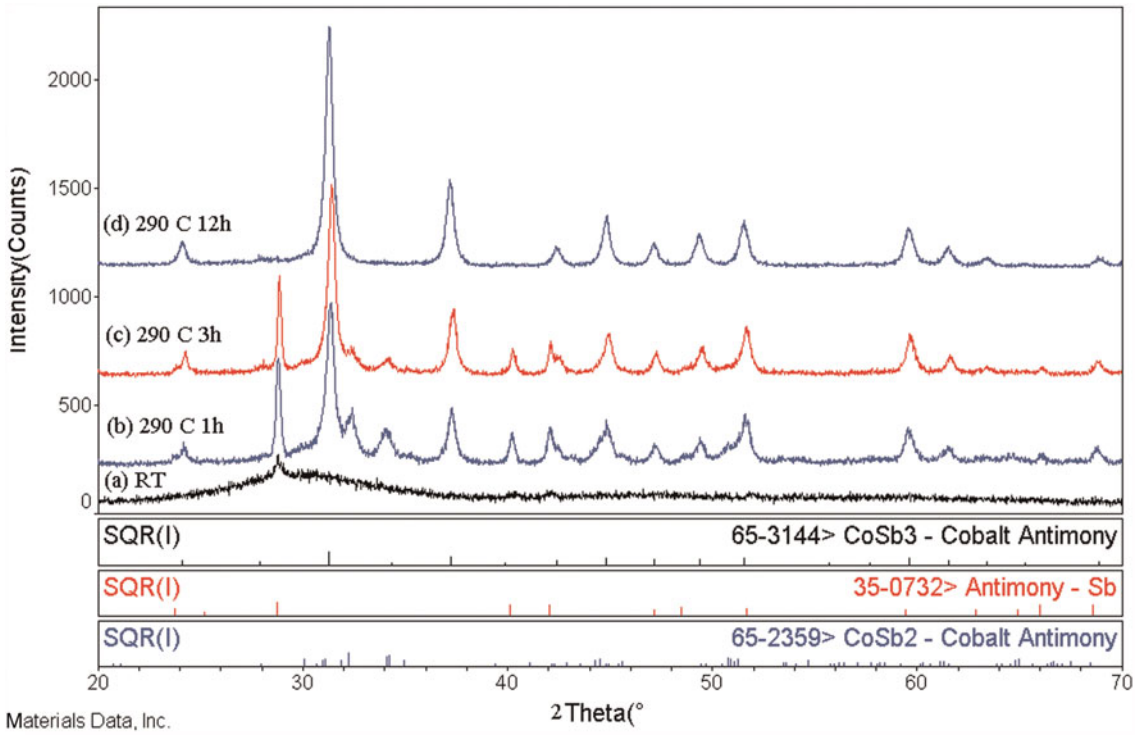

Figure 1. XRD patterns for solvothermal synthesis powders of $CoSb_3$ before heat treatment (a), synthesized at 290 °C for 1 h (b), 3 h (c), and 12 h (d).

nm). Topas 3.0 software was used for Rietveld refinement. The particle size, morphology, and composition of the powders were analyzed using a Hitachi S-4700 field emission scanning electron microscope (FESEM) with an energy-dispersive X-ray (EDX) spectrometer.

III. RESULTS AND DISCUSSION

A. Synthesis of $CoSb_3$

Figures 1(a–d) show the XRD patterns for $CoSb_3$ samples with a proper ratio before heating (a), synthesized at 290 °C for

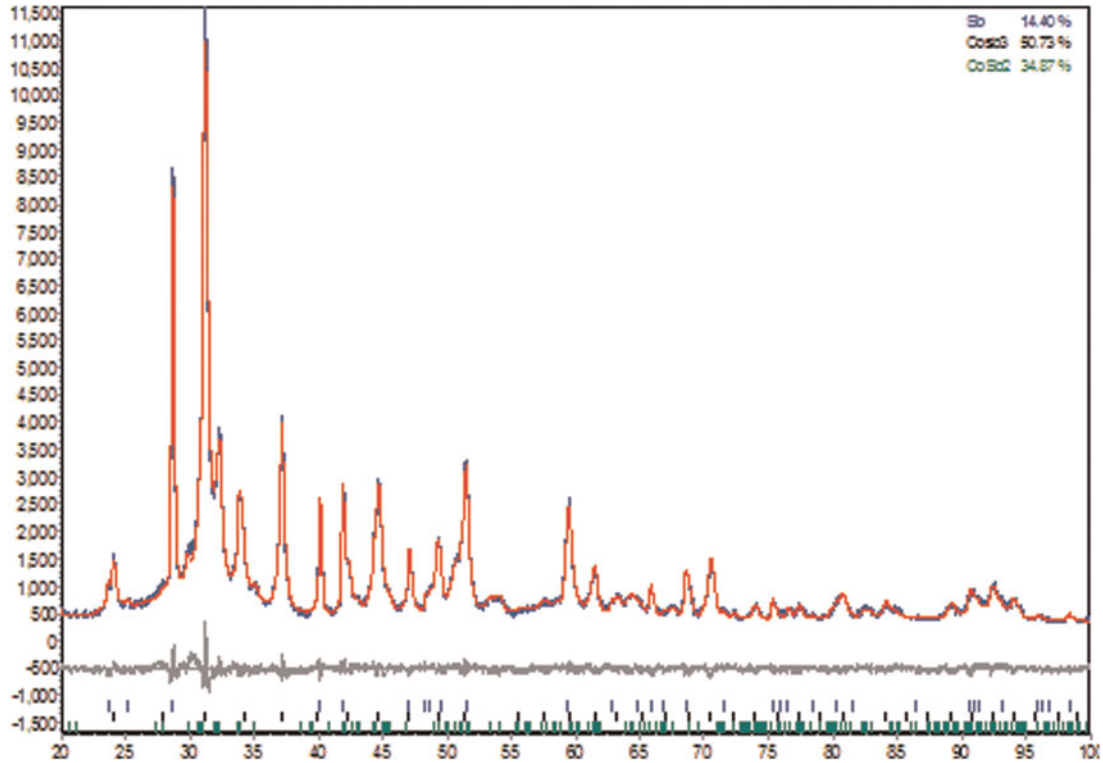

Figure 2. Observed, calculated, and differential profiles by Rietveld refinement for the XRD pattern of the sample of $CoSb_3$ powders synthesized at 290 °C for 1 h.

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TABLE I. Rietveld structural refinement results for solvothermal synthesis powders of $CoSb_3$ synthesized at 290 °C for 1 h.

Compound	$CoSb_3$	$CoSb_2$	Sb
Wt% (at.%)	50.7(2) (33.8)	34.9(3) (32.8)	14.4(1) (33.5)
Space group	$Im\bar{3}$	$P2_1/c$	$R\bar{3}m$
Unit-cell parameters			
a (nm)	0.90551(5)	0.65521(1)	0.430724(3)
b (nm)		0.63920(6)	
c (nm)		0.65124(1)	1.12754(6)
		β (°) = 117.37 (1)	
Volume of unit cell (nm^3)	0.74248(1)	0.24221(7)	0.18116(1)
Calculated density (g/cm^3)	7.5894(1)	8.2940(2)	6.6960(4)
Reliability factors (R-factor)	R_p = 3.95, R_{wp} = 4.96, R_{exp} = 3.29, GOF = 1.51		

1 h (b), 3 h (c), and 12 h (d) respectively. From these four figures, we can see that the sample before heating shows traces of the Sb phase and perhaps the Co phase without any intermetallic compound being formed. The chemical composition of this sample as determined by X-ray fluorescence spectrometer (XRF) is Co-84.92 wt.% Sb (Co-73.2 at.% Sb), very close to the prepared composition of $CoSb_3$. It means that all the Sb^{3+} and Co^{2+} in the mixed solution were reduced after the addition of reductant $NaBH_4$, under vigorous stirring for 20 min at room temperature. The particles of these two phases are very small hence their peaks are very low and wide. The temperature is too low for formation of Co–Sb intermetallic compounds.

For the sample which was synthesized at 290 °C for 1 h, the skutterudite $CoSb_3$ becomes the main phase, together with some amount of Sb and $CoSb_2$ phases [see Figure 1(b)] without any CoSb or Co phases. The quantitative Rietveld analysis by Topas 3.0 software, shown in Figure 2 and Table I, indicated that the percentages of $CoSb_3$, $CoSb_2$, and Sb phases in the sample are 50.7, 34.9, and 14.4 (in wt%) or 33.8, 32.8, and 33.5 (in at.%), respectively. The agreement factors for this Rietveld refinement are R_{wp} = 4.96%, R_p = 3.95%, and R_{exp} = 3.29%, respectively, with the goodness-of-fit (GOF) of 1.51, indicating that the Rietveld refinement is satisfactory. The molar ratio of $CoSb_2$ and Sb phases is about 1:1. The pure $CoSb_3$ phase should be obtained on completion of the synthesis reaction between $CoSb_2$ and Sb. As the reaction time increases, the amount of skutterudite $CoSb_3$ increases and reaches 71 wt% for the reaction time of 3 h due to the growth of $CoSb_3$ in the reaction between $CoSb_2$ and Sb. A single-phase skutterudite $CoSb_3$ was obtained by solvothermal synthesis at 290 °C in 12 h [(Figure 1(d)], a much shorter time as compared with that required for the solvothermal synthesis of $CoSb_3$ in ethanol, as reported by Mi *et al.* (2007a) (250 °C for 72 h).

B. Synthesis of $Co_{1-x}Ni_xSb_3$

Based on the work of the preparation of single-phase $CoSb_3$, we have further synthesized the single-phase Ni-doped $Co_{1-x}Ni_xSb_3$ skutterudites. Figure 3 shows the XRD patterns for the Ni-doped $Co_{1-x}Ni_xSb_3$ skutterudites with x = 0, 0.05, 0.075, 0.125, 0.15, and 0.25, synthesized at 290 °C for 12 h. They are all patterns of pure skutterudites,

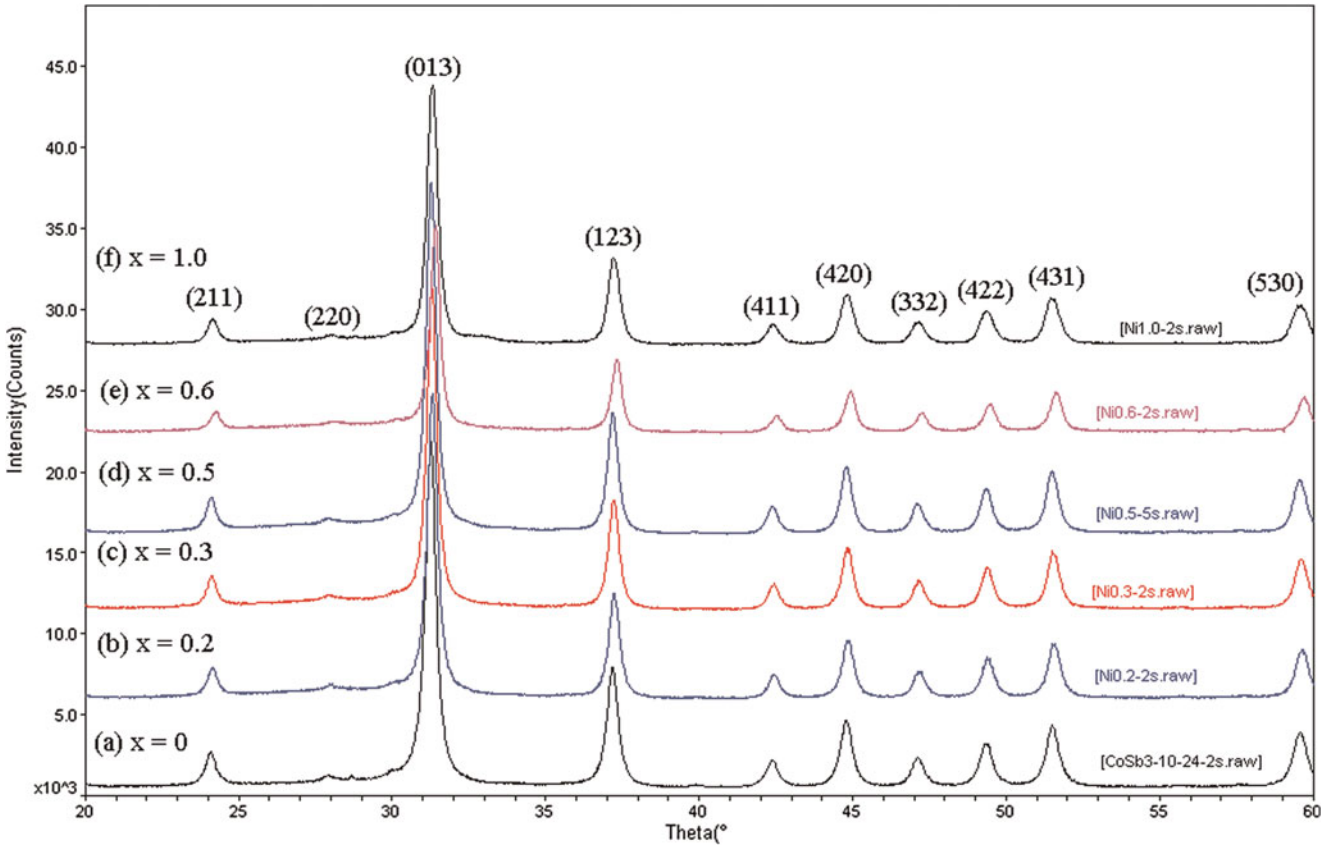

Figure 3. XRD patterns for $Co_{1-x}Ni_xSb_{12}$ powders with x = 0, 0.05, 0.075, 0.125, 0.15, and 0.25 synthesized at 290 °C for 12 h.

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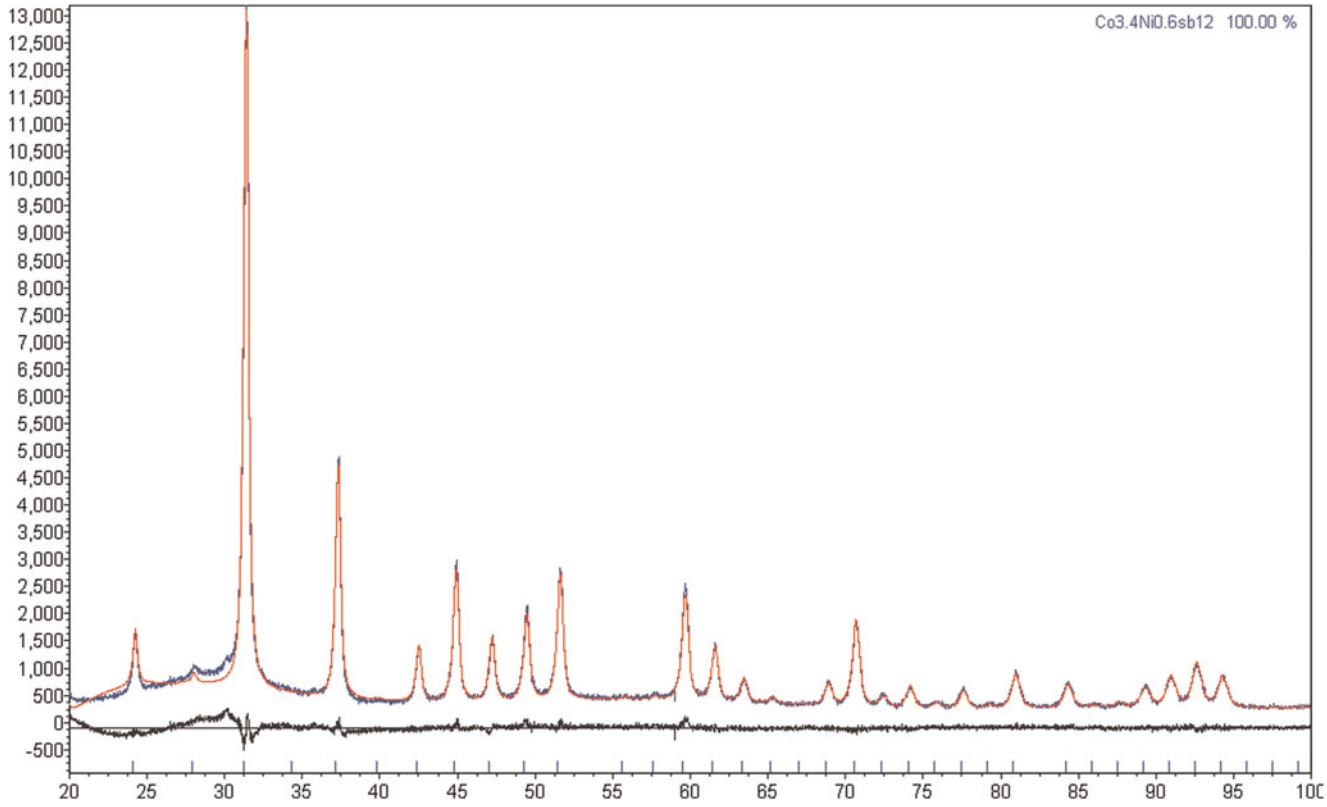

Figure 4. Observed, calculated, and differential profiles by Rietveld refinement for the XRD pattern of $Co_{0.85}Ni_{0.15}Sb_3$ powders synthesized at 290 °C for 12 h.

indicating the Ni atoms are already doped into the $CoSb_3$ lattice, forming a solid solution up to $x = 0.25$. The unit-cell parameters for $Co_{1-x}Ni_xSb_3$ were refined by Topas 3.0 software. A representative refinement of results ($x = 0.15$) is shown in Figure 4 and Table II, indicating the refinement is satisfactory. The unit-cell parameters for $Co_{1-x}Ni_xSb_3$ increase linearly from $a = 0.90440$ to 0.90650 nm as x increases from 0 to 0.25. It is an evidence of the substitution or filling of Ni atom into the $CoSb_3$ lattice.

C. SEM observation

Figures 5(a) and 5(b) show the representative FESEM morphologies for the Ni-doped $Co_{1-x}Ni_xSb_3$ powders with $x = 0$ and 0.15, solvothermally synthesized in triethylene glycol solvent at 290 °C for 12 h. The SEM figures reveal that the skutterudite powder consists of small and homogeneous particles size of 10 nm. The spherical shape of the particles suggests an isotropic crystal growth of skutterudite grains due to its cubic structure. The average particle size for undoped sample $CoSb_3$ is about 10 nm. As the Ni content in $Co_{1-x}Ni_xSb_3$ increases, the average particle size of skutterudite powders increases, and reaches about 30 nm for $x = 0.25$.

The solvothermal syntheses in an ethanol medium for preparation of nano-sized skutterudite $CoSb_3$ (Mi *et al.*, 2006) and $CoSb_{3-x}Te_x$ (Mi *et al.*, 2007b) were reported. To synthesize nano-sized skutterudite $CoSb_3$ and $CoSb_{3-x}Te_x$, reaction performed at 250 °C required a long reaction time of 72 h. The average particle size of $CoSb_3$ and $CoSb_{3-x}Te_x$ were about 80 and 40 nm, respectively. In this work, the high boiling point of triethylene glycol enables the synthesis at a higher temperature of 290 °C. A much shorter reaction time of 12 h was needed for preparation of the nano-sized Ni-doped $Co_{1-x}Ni_xSb_3$ skutterudite powders. From the kinetics point of view, higher reaction temperature is beneficial for both reaction and diffusion. The much smaller and more uniform particles synthesized in triethylene glycol, which is expected to be beneficial to the thermoelectric properties of the material, might not be only due to the shorter reaction time. Triethylene glycol may act as a surface active agent and/or promote nucleation, which leads to fine, uniform, and homogeneous $Co_{1-x}Ni_xSb_3$ skutterudite particles.

TABLE II. Rietveld structural refinement results for the $Co_{0.85}Ni_{0.15}Sb_3$ compound.

Compound	$Co_{0.85}Ni_{0.15}Sb_3$	Site		
Space group	$Im\bar{3}$		8c	24 g
Unit-cell parameters a (nm)	0.90510(3)	x	0.25000	0.00000
Volume of unit cell (nm^{-3})	0.7415(8)	y	0.25000	0.3346(2)
Calculated density (g/cm^3)	7.599(8)	z	0.25000	0.1584(2)
Crystallite size	34.0(6)	atom	$Co_{0.85}Ni_{0.15}$	Sb
Reliability factors (R-factor)	$R_p = 7.20$, $R_{wp} = 9.66$, $R_{exp} = 3.82$, GOF = 2.53			

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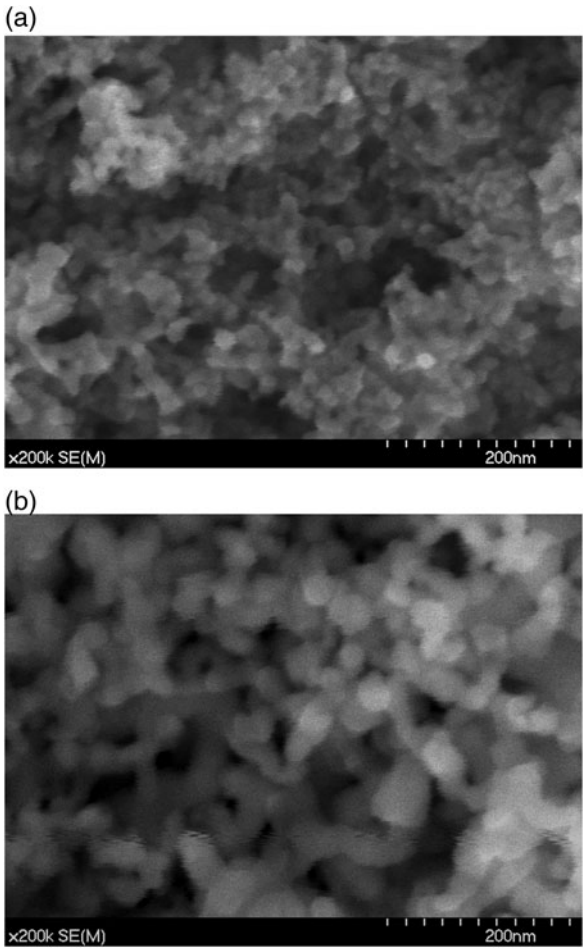

Figure 5. FESEM image for the $Co_{1-x}Ni_xSb_3$ powders with (a) $x = 0$ and (b) 0.15 synthesized at 290 °C for 12 h.

IV. CONCLUSION

Nano-sized thermoelectric skutterudite $Co_{1-x}Ni_xSb_3$ ($x = 0$, 0.05, 0.075, 0.125, 0.15, and 0.25) with a single phase was synthesized by the solvothermal method in triethylene glycol solution, performed at 290 °C for 12 h. High reaction temperature is an important factor to promote the kinetic process and reduce synthesis duration. The $Co_{1-x}Ni_xSb_3$ powders synthesized in triethylene glycol solution in this work are small (10–30 nm), uniform, and homogeneous. As the replacement content of Co by Ni increases in $Co_{1-x}Ni_xSb_3$, the lattice parameter *a* increases from 0.9044 to 0.9065 nm and the particle size increases from 10 to 20 nm.

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