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Effect of La filling on thermoelectric properties of $La_xCo_{3.6}Ni_{0.4}Sb_{12}$-filled skutterudite prepared by MA–HP method

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Abstract

Starting from elemental powder mixtures, single-phase $La_xCo_{3.6}Ni_{0.4}Sb_{12}$($x = 0$, 0.1, 0.4, 0.6)-filled skutterudites were synthesized via the route of mechanical alloying–hot pressing (MA–HP) in this paper. With increasing of La fraction, the lattice spacing of filled skutterudite phase increases and its variation follows the Vegard's law. The magnitude of the Seebeck coefficient and electrical resistivity show slight increases with increasing of La filling fraction; thermal conductivity of the filled skutterudite decreases and the resultant figure of merit increases with increase of La filling fraction. The as-HPed filled skutterudite has a composite nanocrystalline microstructure, which includes some coral-like clusters with relatively large spoke-like grains about 300 nm in length and a superfine equiaxial nanocrystalline matrix with an average grain size of about 50 nm. The coral-like cluster corresponds to the prime filled skutterudite formed directly by MA, while the filled skutterudite formed during hot pressing, which has the same nucleation condition and experiences less grain growth, develops equiaxially into the superfine nanocrystalline matrix.

Keywords: Thermoelectric properties; Filled skutterudite; Nanocrystalline; Mechanical alloying

1. Introduction

Skutterudite compound, which derives its name from a small Norwegian town Skutterud where it was first found, attracts much attention for its promising thermoelectric application in recent years [1–3]. Binary skutterudite, which has an AB_3 formula, where A is Co, Rh or Ir and B is a pnicogen such as P, As or Sb, is not suitable for thermoelectric application owing to its high thermal conductivity. Fortunately, there are two large cage-like voids in a unit cell of the skutterudite compound ($Im\bar{3}$ space group). Undersized heavy atoms such as rare-earth atoms could be filled into the voids to form a filled skutterudite. These filling atoms are weakly bound in the voids and rattle about their equilibrium sites more than other atoms in the structure. Heat-carrying phonons are scattered strongly by this movement, therefore thermal conductivity could be decreased substantially [4–7].

Currently, the most popular filled skutterudites for thermoelectric application are based on $CoSb_3$. Owing to its peritectic nature, a long time annealing (about a week or two) at a somewhat lower temperature (550–600 °C) after arc melting is necessary to get a single-phase filled skutterudite compound [8]. When solid-state reaction (SSR) method [9] is used to prepare filled skutterudite, the whole process can be shortened to about 1 day; however, there are always some impurities such as Sb, MSb_2 ($M =$ Co, Fe or Ni), and some extra procedures such as grinding, acid washing and consolidation are indispensable. Mechanical alloying–hot pressing (MA–HP) method, which includes mechanical alloying (MA) pretreatment and subsequent hot pressing (HP) consolidation, was developed by the authors [10–12], by which single-phase bulk $CoSb_3$, Fe- and Ni-substituted skutterudite were obtained successfully and the whole process was

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greatly simplified and shortened to a time less than 12 h. Dyck et al. [13,14] explored the beneficial influence of Ni on the thermoelectric properties of both unfilled and filled skutterudites prepared by arc melting and SSR methods for the first time; however, to our knowledge, less work has been reported on the unfilled and filled Ni-substituted skutterudite prepared by the method of MA–HP. Recently, effect of hot pressing temperature on phase transformation and thermoelectric properties of La-filled skutterudite prepared by MA–HP method has been reported by us [15]. As a successive work, La-filled and Ni-substituted skutterudite compound will be synthesized by MA–HP method in this paper. Effect of La filling on thermoelectric properties and microstructure characterization of the filled skutterudite compound will be reported.

2. Experiments

Elemental powders of Co (200 mesh, >99.9wt.%), La (200 mesh, >99.9wt.%), Ni (200 mesh, >99.9wt.%) and Sb (200 mesh, >99.9wt.%) were blended in an atomic ratio of La:Ni:Co:Sb = x:0.4:3.6:12, where $x = 0$, 0.1, 0.4 and 0.6, respectively, then subjected to mechanical alloying in a QM-4F planetary ball mill under a purified Ar atmosphere. Hardened stainless steel vessels and balls were used, and ball-to-powder weight ratio was kept at 15:1. The rotation speed was fixed at 400 rpm. All powders' weighing, loading and unloading were operated in a glove box filled with purified argon to minimize oxygen contamination. After mechanical alloying for 10 h, powders were extracted for XRD analysis and preformed by cold pressing. Then the preformed billets were consolidated by hot pressing in Ar atmosphere under 50 MPa at 600 °C for 2 h.

X-ray diffraction was performed with a Rigaku DMAX III powder diffractometer by using Cu Kα radiation. Thermal conductivity was measured with a TC-7000 laser flash apparatus, and Seebeck coefficient α was measured by applying a 10 K temperature difference between the two ends of a bar sample ($3 \times 3 \times 15$ mm) and measuring the output voltage ΔV between them and then calculating the value by $\alpha = \Delta V/\Delta T$. A standard two-probe method was engaged for electrical resistivity measurement. Microstructure observation and EDAX composition analysis of the hot pressed sample were performed with a Sirion 200 field emission scanning electron microscope (FE-SEM).

3. Results and discussion

Fig. 1 shows the XRD patterns of the as mechanically alloyed and the as hot pressed $La_{0.6}Co_{3.6}Ni_{0.4}Sb_{12}$ samples, respectively. It can be seen that the as-MAed powders had a mixed structure with strong elemental peaks observed, along with some tiny peaks of filled skutterudite compound, indicating that small amount of filled skutterudite compound was synthesized during the MA process. These MAed powders were strongly deformed by repeatedly ball milling and quite a lot of mechanical energy was accumulated in them in the form of defects and strain energy, and they were thermodynamically metastable. During the process of hot pressing, with the assistance of heat activation, SSR for filled skutterudite compound was triggered and the remnant metallic elements were reacted into the filled skutterudite phase completely; therefore, single filled skutterudite phase was obtained and presented in the as-HPed XRD pattern.

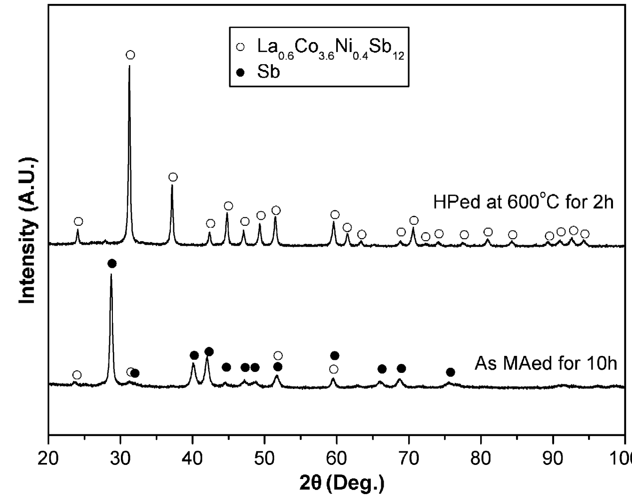

Fig. 1. XRD patterns of the as-MAed and as-HPed $La_{0.6}Co_{3.6}Ni_{0.4}Sb_{12}$ sample.

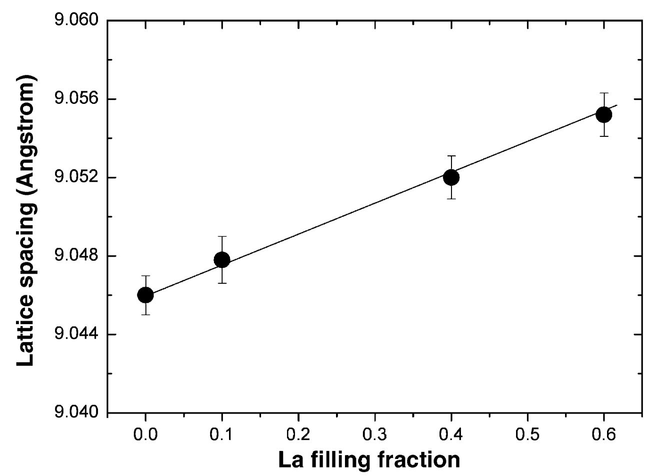

Fig. 2. Variation of lattice spacing of the filled skutterudite with La filling fraction.

The lattice spacing of the as-HPed filled skutterudites with different filling fraction was calculated from their XRD patterns and shown in Fig. 2. With increasing of La filling fraction, the lattice spacing increases linearly, it agrees very well with the Vegard's law.

Fig. 3 shows the Seebeck coefficients of the filled skutterudite with different La filling content. It can be seen that pure $CoSb_3$ skutterudite compound shows p-type conduction, and it changes to n-type when substituting Ni for Co partially. In comparison with the $Co_{3.6}Ni_{0.4}Sb_{12}$ skutterudite, the magnitude of Seebeck coefficient of the filled skutterudite shows some decrease. The filling La

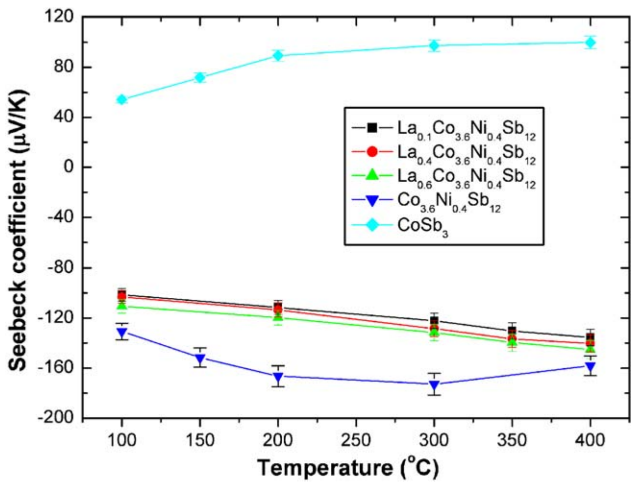

Fig. 3. Seebeck coefficient of the filled skutterudites versus La filling content and temperature.

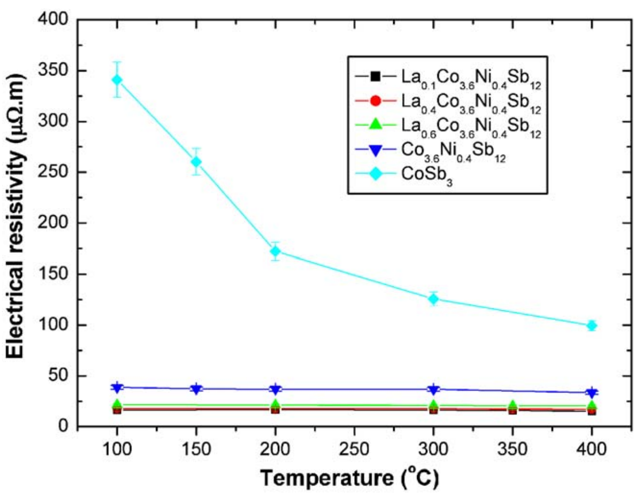

Fig. 4. Variation of electrical resistivity of the filled skutterudites with La filling content and temperature.

atoms may contribute some electrons to the conduction band, and the Seebeck coefficient of the filled skutterudite is lower than that of the $Co_{3.6}Ni_{0.4}Sb_{12}$ skutterudite without filling.

The electrical resistivity of the filled skutterudite compound was shown in Fig. 4. The electrical resistivity decreased greatly by Co site substitution with Ni. Furthermore, the electrical resistivity was further lowered with La filling into the $Co_{3.6}Ni_{0.4}Sb_{12}$ skutterudite. As mentioned above, La filling atoms contribute some electrons to the conduction band and the carrier concentration increases; therefore, the electrical resistivity and the magnitude of Seebeck coefficient of the filled skutterudite are lower than that of $Co_{3.6}Ni_{0.4}Sb_{12}$ skutterudite. On the other hand, the magnitude of electrical resistivity (Fig. 4) and Seebeck coefficient (Fig. 3) of the filled skutterudite shows a slight increase with increasing La filling content; its contribution to electrical conduction is not as obvious as Ni substitution.

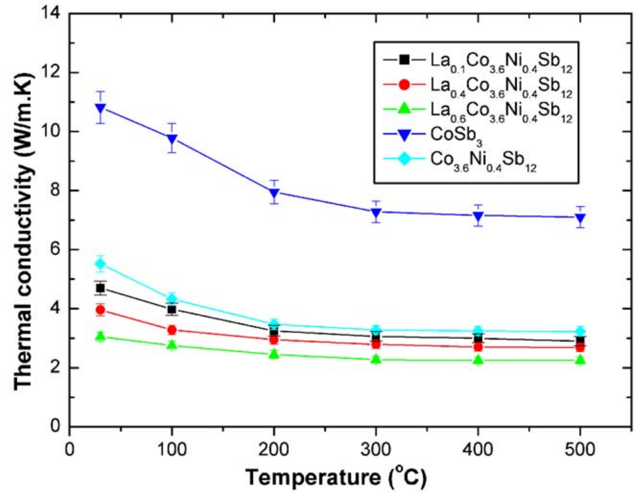

Fig. 5. Thermal conductivity of the filled skutterudite versus temperature and La filling content.

Fig. 5 shows the variation of the thermal conductivity of the filled skutterudite as a function of temperature and La filling. Obviously, pure $CoSb_3$ skutterudite has very large thermal conductivity, and the thermal conductivity of $Co_{3.6}Ni_{0.4}Sb_{12}$ skutterudite is about a half that of the pure $CoSb_3$ skutterudite at room temperature. With La filling into the voids of the skutterudite lattice, it rattles in the voids and scatters the phonons and decreases the phonon thermal conductivity substantially. As we know, thermal conductivity (κ) of semiconductor can be expressed as $\kappa = \kappa_{el} + \kappa_{ph}$, where κ_{el} and κ_{ph} correspond to carrier and phonon thermal conductivity, respectively; therefore, the total thermal conductivity decreases with increasing of La filling fraction. The thermal conductivity of $La_{0.6}Co_{3.6}Ni_{0.4}Sb_{12}$ decreases to about a half that of the $Co_{3.6}Ni_{0.4}Sb_{12}$ skutterudite and is about one fourth that of the pure $CoSb_3$ skutterudite at room temperature.

Figure of merit ZT, expressed as $ZT = \alpha^2 T/\rho\kappa$, where α, ρ and κ are Seebeck coefficient, electrical resistivity and thermal conductivity, respectively, is usually taken as a parameter for evaluation of thermoelectric property. The figures of merit of the filled skutterudites were calculated and shown in Fig. 6, and ZT values of pure $CoSb_3$ and $Co_{3.6}Ni_{0.4}Sb_{12}$ skutterudite were also given in the figure. It can be seen that the figure of merit of pure $CoSb_3$ is very low and even close to zero. Owing to the thermal conductivity decrease resulting from La filling, the figure of merit of filled skutterudite increases with increasing of La filling fraction. The maximum figure of merit is obtained as 0.31 at 400 °C when La filling fraction is 0.6. The figure of merit of the filled skutterudite prepared by MA–HP method in this paper is not so high yet. The rather high electrical resistivity, which might result from the superfine microstructure shown below, should be the main reason.

Fig. 7 shows a fractograph microstructure of $La_{0.6}Co_{3.6}Ni_{0.4}Sb_{12}$-filled skutterudite compound. In the center of the

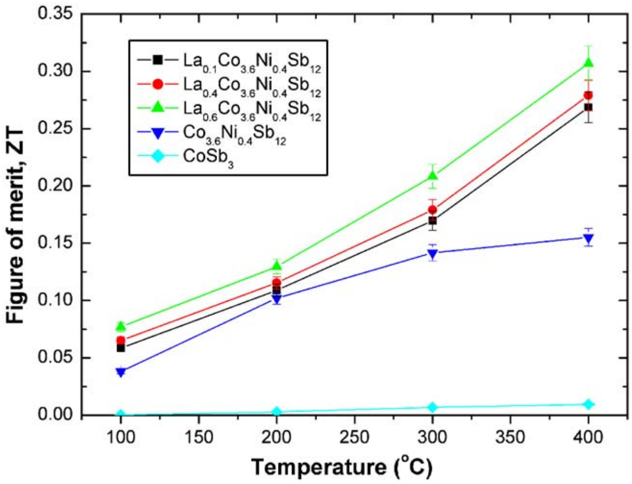

Fig. 6. Figure of merit of the filled skutterudites versus temperature and La filling content.

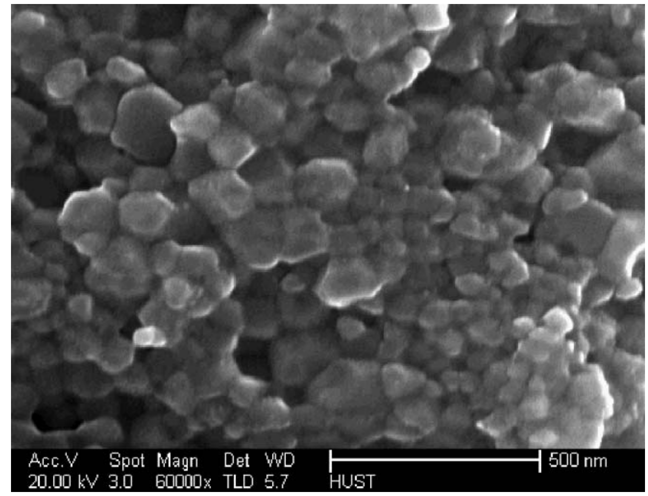

Fig. 8. An enlarged SEM micrograph of the as-HPed $La_{0.6}Co_{3.6}Ni_{0.4}Sb_{12}$-filled skutterudite.

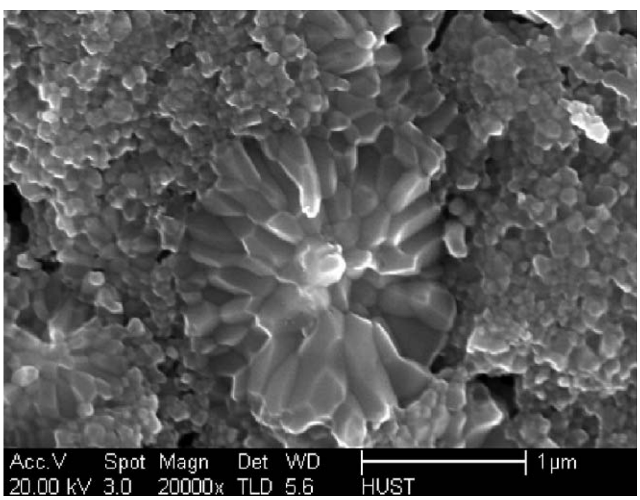

Fig. 7. Fractograph of the as-HPed $La_{0.6}Co_{3.6}Ni_{0.4}Sb_{12}$-filled skutterudite.

image, there is a coral-like cluster, which includes some radial branches or spokes with an average size about 150 nm in width and 300 nm in length, lies in a superfine nanocrystalline matrix. An amplified micrograph of the matrix is shown in Fig. 8. It can be seen that the matrix has a very fine nanocrystalline microstructure; the average grain size is about 50 nm. As shown in Fig. 1, the as hot pressed $La_{0.6}Co_{3.6}Ni_{0.4}Sb_{12}$ has a single-phase filled skutterudite structure; furthermore, EDAX composition analysis shows that both the coral-like cluster and the matrix have almost the same composition as the nominal $La_{0.6}Co_{3.6}Ni_{0.4}Sb_{12}$. That is to say, both the nanocrystalline matrix and the coral-like cluster have the same crystal structure and composition.

As we know, mechanical alloying is a powerful tool to produce powders with nanoscale microstructure [16]. In the present case, as shown in Fig. 1, the as-MAed powders are a mixture of the unreacted elements and small amount of filled skutterudite phase. During the hot press process, the prime filled skutterudite phase produced directly by MA develops into the coral-like species with large grain size; on the other hand, the remnant elements reacted into filled skutterudite phase during the process of hot pressing. This lately formed filled skutterudite phase, which has the same nucleation condition and experiences less grain growth than the prime filled skutterudite phase prepared by MA, has a very fine grain that develops equiaxially during hot pressing to form the nanocrystalline matrix. Therefore, a composite microstructure was observed in the fractograph.

As suggested by Hicks et al. [17–19], low-dimensional or nanocrystalline materials, such as quantum dot, and quantum well, could attain a very high figure of merit due to the quantum size effect. Recently a $ZT = 2.4$ has been reported by Venkatasubramanian et al. [20] in Bi_2Te_3/Sb_2Te_3 nanosuperlattice, and a $ZT = 1.6$ was also reported by Harman et al. [21] in PbSeTe quantum dot materials. However, it seems that there is no relevant improvement to thermoelectric properties of the bulk nanocrystalline skutterudites obtained in this work. One possible reason is that the nanostructure obtained in this work is not fine enough to cause a notable quantum confinement effect in this system; on the contrary, large amounts of grain boundary may exert some detrimental effect on thermoelectric properties. Further research work on microstructure control is under way in our lab.

4. Conclusions

Single-phase $La_xCo_{3.6}Ni_{0.4}Sb_{12}$-filled skutterudites with different filling fraction x ($x = 0$, 0.1, 0.4, 0.6) were synthesized by MA–HP method in this paper. With increasing of La fraction, the lattice spacing of filled skutterudite phase increases and its variation follows the Vegard's law. The magnitudes of the Seebeck coefficient and electrical resistivity slightly increase with increasing La filling fraction; thermal conductivity of the filled skutterudite decreases and the resultant figure of merit increases with increasing of La filling fraction. The as-HPed filled skutterudite has a composite nanocrystalline microstructure, which includes some coral-like clusters with relatively large spoke-like grain about 300 nm in length and a superfine equiaxial nanocrystalline matrix with an average grain size of about 50 nm. The coral-like clusters correspond to the prime filled skutterudite formed directly by MA, while the filled skutterudite formed during hot pressing, which has the same nucleation condition and experiences less grain growth, develops equiaxially into the superfine nanocrystalline matrix.

Acknowledgments

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