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Solvothermal synthesis of nanosized $CoSb_3$ skutterudite*

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Abstract: Nanostructures enhance phonon scattering and improve the figure of merit of thermoelectric materials. Nanosized $CoSb_3$ skutterudite was synthesized by solvothermal methods using $CoCl_2$ and $SbCl_3$ as the precursors. A "two-step" model was suggested for the formation of $CoSb_3$ based on the X-ray diffraction analysis. The first step is the formation of cobalt diantimonide in the earlier stage during the synthesis process. Diantimonide was then combined with antimony atoms to form the skutterudite structured triantimonide, $CoSb_3$, in the later stage of the synthesis process as the second step. The synthesized $CoSb_3$ powders consist of irregular particles with sizes of about 20 nm and sheets of about 80 nm.

Key words: Skutterudite, Solvothermal synthesis, Nanosized materials
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INTRODUCTION

Novel high temperature thermoelectric (TE) materials are of increasing interest due to their potential applications in power generators using waste heat or use for remote area and deep space shoot shuttles (DiSalvo, 1999; Tritt, 1999). Among a number of new materials, the family of skutterudites is of special interest for the development of advanced TE materials with high figures of merit, $Z=\alpha^2\sigma/\kappa$, where α is the Seebeck coefficient, σ and κ are the electrical and thermal conductivity, respectively. Since Slack and Tsoukala (1994) found that $IrSb_3$, a compound with skutterudite structure, has the special property of "electron-crystal and phonon-glass" (ECPG) (Sales *et al*., 1997), i.e., a high σ like that of a crystalline material and a low κ like that of a glass at the same time, and Sales *et al*.(1996) reported their work on filled skutterudite in 1996, various skutterudites have been intensively investigated (Keppens *et al*., 1998; Nolas *et al*., 1997). Barium filled iron/cobalt antimonide skutterudite with the dimensionless figure of merit, *ZT*, higher than 1 had been reported (Tang *et al*., 2001; Dyck *et al*., 2002).

Skutterudites are prepared mainly by high temperature routines, such as solid state reaction sintering (Sharp *et al*., 1995; Caillat *et al*., 1996; Leithe-Jasper *et al*., 1999), hot-pressing (Puyet *et al*., 2004), high-pressure synthesis (Kihou *et al*., 2004), spark plasma sintering (Yang *et al*., 2004), and high-temperature electrochemical synthesis (DeMattei *et al*., 2001). Wang *et al*.(1999) reported the preparation of $CoSb_3$ skutterudite via a quasi-solution chemical route, during which, only a precursor containing cobalt oxalate and antimony

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oxide was obtained. The precursor was then calcined and reduced with hydrogen at high temperature to form $CoSb_3$ skutterudite. However, the $CoSb_3$ skutterudite powders grew up to sub-micrometer sizes due to the relatively high temperature treatment. Simple chemical route without high temperature calcination could produce nanosized $CoSb_3$ skutterudites, which would help for reducing further the thermal conductivity of the materials. Solvothermal synthesis (Yu *et al*., 1998; Deng *et al*., 2002) is a low-temperature routine enabling mass synthesis of materials with designed chemical compositions, nanosized crystals and also little contamination on the materials. Liu *et al.*(2002) reported the hydrothermal synthesis of nanostructured $NaFe_4P_{12}$ skutterudite. In our present work, we made an attempt to synthesize nanosized $CoSb_3$ skutterudite by solvothermal route. However, it was found that single-phased $CoSb_3$ was difficult to obtain even at high temperature (280 °C). On the other hand, single-phased nano-crystalline $CoSb_2$ was successfully synthesized by a solvothermal routine. During the synthesis of $CoSb_2$, we found that $CoSb_3$ is a by-product with the increasing temperature. Here we report the solvothermal synthesis of nanosized $CoSb_3$ skutterudite on the basis of the synthesis of nanosized $CoSb_2$ and investigate the formation mechanism of $CoSb_3$.

EXPERIMENTAL DETAILS

Synthesis of nanosized $CoSb_3$

Analytically pure $CoCl_2{\cdot}6H_2O$ and $SbCl_3$ were used as the precursors in the solvothermal synthesis. The precursors with the designed molar ratio of Co:Sb were put into a teflon-lined autoclave which was then filled with ethanol up to 85% of its volume. After adding sufficient $NaBH_4$ (A.R.) as the reductant, the autoclave was sealed immediately and heated to a temperature for the synthesis reaction. Then the autoclave was cooled down to room temperature naturally. The obtained precipitate was filtered, washed several times with ethanol and distilled water, and then dried under a vacuum of about 1 Pa at 110 °C for 12 h. In the present work, 6 samples were prepared, as listed in Table 1. In the sample names, B means Co:Sb molar ratio is 1:2 in the starting material, T means Co:Sb molar ratio is 1:3 in the starting material, d means the autoclave was heated to 240 °C directly after heated at 190 °C for 24 h without opening the autoclave and further adding the starting material, and s means the autoclave was opened after headed for 24 h and cooled to room temperature, and the autoclave was heated for the second time at 240 °C after further adding the starting material.

Characterization

The powders were analyzed by X-ray diffraction (XRD) using a Rigaku-D/MAX-2550PC diffractometer equipped for Cu-K_a radiation (λ=1.5406 Å) in the range of 2θ=10°~80°. The powder morphology was observed on a JEM-2110 transmission electron microscope (TEM) and a FEI SIRION field emission scanning electron microscope (FESEM).

RESULTS AND DISCUSSION

Fig.1 shows the XRD patterns of powders prepared by solvothermal routes. With the Co:Sb molar ratio of 1:2, single phase of the designed $CoSb_2$ (space group $P2_1/c$ according to JCPDS 29-0126) was obtained for sample B190 synthesized at 190 °C for 24 h. However, $CoSb_3$ skutterudite could not be synthesized simply by increasing the Co:Sb molar ratio of the precursors to 1:3 with the same route used for $CoSb_2$. As indicated in Fig.1, no visible diffraction peaks of designed $CoSb_3$ can be found in the XRD pattern of

Table 1 Synthesis condition of the samples

Sample	Precursors	Co:Sb	Synthesis Route
B190	$CoCl_2$, $SbCl_3$	1:2	190 °C 24 h
T190	$CoCl_2$, $SbCl_3$	1:3	190 °C 24 h
T280	$CoCl_2$, $SbCl_3$	1:3	280 °C 24 h
T24d	$CoCl_2$, $SbCl_3$	1:3	190 °C 24 h+240 °C 24 h
T48d	$CoCl_2$, $SbCl_3$	1:3	190 °C 24 h+240 °C 48 h
T24s	B190, $SbCl_3$	1:3	240 °C 24 h

sample T190 synthesized at 190 °C for 24 h. The dominant diffraction peaks for T190 are from antimony (space group $R\bar{3}m$, JCPDS 85-1322) and $CoSb_2$ phase. Skutterudite structured $CoSb_3$ can be formed during solvothermal synthesis when the temperature increases to 280 °C, sample T280. However, $CoSb_2$ and Sb exist even at such a high temperature. Single $CoSb_3$ skutterudite phase might be synthesized if the temperature were further increased. However, this will exceed the temperature limit of the teflon lined in the autoclave. An alternative way is to prolong the reaction time. Three samples with prolonging reaction time were prepared using two-step routes in the present work. Sample T24d and sample T48d were synthesized with the first reaction step at 190 °C for 24 h and the directly following second reaction step at 240 °C for 24 h and 48 h, respectively. Sample T24s was synthesized using $CoSb_2$ (sample B190) and antimony as the precursors and with the second reaction step at 240 °C for 24 h. The XRD patterns showed that the dominating phase of T24d, T48d and T24s is the skutterudite $CoSb_3$ phase, whose standard diffraction peaks are indexed in Fig.1 according to JCPDS 76-0470 (space group Im3).

The possible chemical reactions during the solvothermal synthesis involve the reduction of Co^{2+} and Sb^{3+} ions:

$$CoCl_2+2NaBH_4\rightarrow Co+2BH_3+2NaCl+H_2 \quad (1)$$

$$3SbCl_3+9NaBH_4\rightarrow 3Sb+9BH_3+9NaCl+9/2H_2 \quad (2)$$

and the combination of Co and Sb atoms to cobalt antimonides:

$$Co+2Sb\rightarrow CoSb_2 \quad (3)$$

$$CoSb_2+Sb\rightarrow CoSb_3 \quad (4)$$

During the process the reduction of both Co^{2+} and Sb^{3+} ions, reaction (1) and (2), should be very fast due to the strong reducing effect of excessive $NaBH_4$. Here two individual combination reactions, (3) and (4), are suggested according to the present work. From the XRD patterns in Fig.1, we conclude firstly that the reaction (3) is the dominating process during the early stage of the synthesis and its product, $CoSb_2$, acts then as an intermediate product for the formation of $CoSb_3$, reaction (4), in the later stage. Hence a "two-step" model applies, i.e., the diantimonide formed in the first step at 190 °C and the triantimonide in the second step at 240 °C. After the second step of the synthesis at 240 °C for 24 h (sample T24d) the diffraction peaks of both Sb and $CoSb_2$ are remarkably reduced in comparison with those after the first reaction step at 190 °C (sample T190). The "two-step" reaction can be either a continuous process as that for sample T24d, or a discontinuous routine as that for sample T24s using pre-synthesized $CoSb_2$ as the precursor for the formation of $CoSb_3$ in the second step. We noted that the $CoSb_2$-peaks in the diffraction pattern of T24s are also remarkably reduced compared with those of B190. It should not be surprising that there are no visible Sb-peaks in the pattern of T24s, since the amount of fresh charged $SbCl_3$ in the second step for T24s is small, the reduced Sb would be diluted in the solution and therefore the excess antimony could hardly form crystals large enough to produce visible XRD diffractions. The second conclusion we drew from Fig.1 is that the reaction time plays an important role in the formation of $CoSb_3$ compound although a high temperature

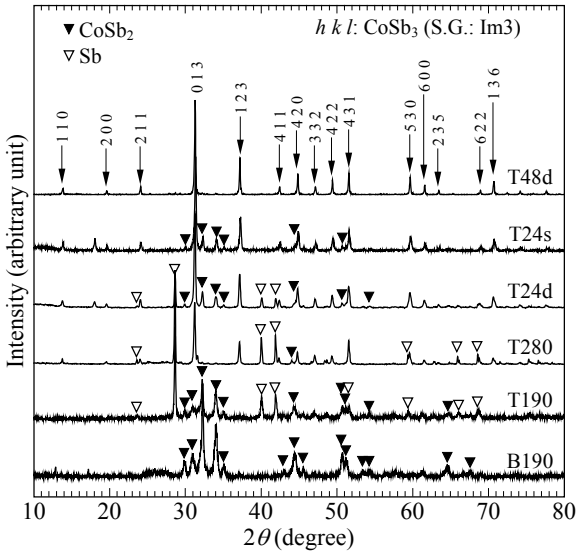
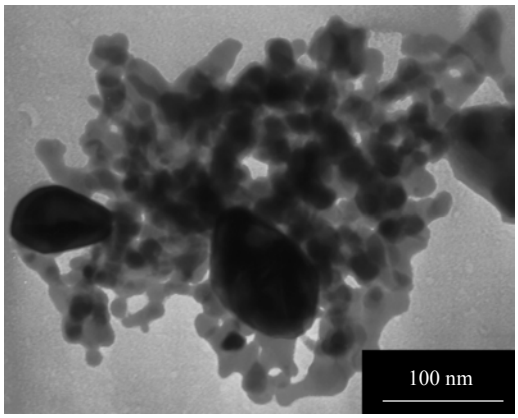


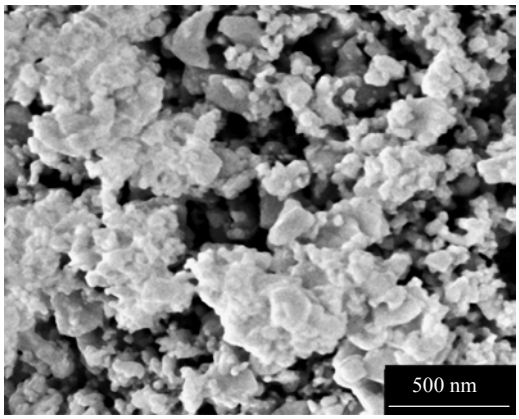
Fig.1 XRD patterns of solvothermally synthesized cobalt antimonide powders with different Co:Sb ratio of the precursors and synthesis conditions

could also speed up the reaction. As we see from Fig.1 that the single skutterudite $CoSb_3$ phase was successfully synthesized after a two-step reaction for sample T48d (firstly, the autoclave was heated at 190 °C for 24 h; secondly, the autoclave was heated at 240 °C for 48 h without opening the autoclave and further adding the starting material). The unit cell parameter of the synthesized $CoSb_3$ is a=9.033 Å, which is consistent with the standard value, a=9.034 Å according to JCPDS 76-0470.

Fig.2 shows both the TEM image (a) and the SEM photo (b) of the $CoSb_3$ powder from sample T48d. As shown in the figure, the powder is composed of small granules with about 20 nm particles and also some large 50~100 nm sheets. Considering the phonon scattering effect of nanostructures, the synthesis of nanosized $CoSb_3$ provides a profitable way to develop novel nanostructured skutterudite based thermoelectric materials.



(a)



(b)

Fig.2 TEM (a) and SEM (b) images of $CoSb_3$ powders prepared by solvothermal synthesis

CONCLUSION

Nanosized skutterudite compound $CoSb_3$ was successfully synthesized by solvothermal method using $CoCl_2$ and $SbCl_3$ as the precursors. A "two-step" model is suggested for the formation of $CoSb_3$. For the first step, an intermediate, cobalt diantimonide, was formed in the earlier stage, which was then combined with antimony atoms to form the skutterudite structured triantimonide, $CoSb_3$, in the later stage of the synthesis process as the second step. Both TEM and SEM observations show that the synthesized $CoSb_3$ powders consist of irregular particles with sizes of about 20 nm and sheets of about 80 nm. The synthesis of nanosized $CoSb_3$ provides a profitable way to develop novel nanostructured skutterudite based thermoelectric materials.

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