

Synthesis of Filled Skutterudite Compounds: BayFexCo_{4-x}Sb₁₂

著者	Chen L. D., Tang X. F., Goto T., Hirai T.
journal or publication title	Journal of Materials Research
volume	15
number	11
page range	2276-2279
year	2000
URL	http://hdl.handle.net/10097/52192

doi: 10.1557/JMR.2000.0325

Synthesis of filled skutterudite compounds: $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$

L. Chen, X. Tang, T. Goto, and T. Hirai
Institute for Materials Research, Tohoku University,
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

(Received 3 March 2000; accepted 3 August 2000)

Ba-filled skutterudite compounds, $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$, were synthesized by a two-step solid reaction method. A binary compound of Sb_3Ba and a ternary compound of $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$ were first synthesized at 900 and 973 K, respectively. The presynthesized Sb_3Ba and $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$ were then mixed with Sb and heated at 973 K in an Ar atmosphere. The resulting powder was of single phase with a composition of $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$, having skutterudite structure with the Sb-dodecahedron voids fractionally filled by Ba. The lattice constant of $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ increased with Ba and Fe content. The maximum filling fraction of Ba (y_{max}) in $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ was found to be greater than that of Ce or La in $\text{Ln}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$, especially in the lower Fe content region. The y_{max} varied from 0.35 to near 1.0 when Fe content (x) changed from 0 to 4.

Recently, $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ and $\text{La}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ have received great attention as candidates for thermoelectric materials.¹⁻⁴ These compounds are members of the so-called “filled skutterudite” class of materials with the general formula RM_4X_{12} . The binary, or “unfilled,” skutterudite crystal structure MX_3 consists of a simple cubic sublattice of metal (M) atoms (M = Co, Rh, or Ir) and nearly square planar rings of four pnictogen (X) atoms (X = P, As, or Sb) with the rings oriented along either the (100), (010), or (001) crystallographic direction.^{5,6} The “filled” structure is obtained by introducing rare-earth (R) atoms into the two remaining “holes” (called Sb-dodecahedron voids) in the unit cell.^{1,2,6,7}

It has been reported that the filling of the Sb-dodecahedron voids by rare-earth atoms significantly depresses the lattice thermal conductivity due to the “rattling” of these atoms positioned in the oversized voids.^{1-3,8-11} In this case, both the thermal conductivity and electrical properties, such as carrier type, carrier concentration, and carrier effective mass, of the filled skutterudites were influenced by the amount of filling. Singh¹² and Sales² reported that a high La filling and a low hole concentration may lead to better thermoelectric properties of $\text{La}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. On the other hand, the intersubstitution of Fe and Co also have great effects on both the electrical and thermal properties by changing carrier concentration and providing some additional phonon scattering.^{1,3,10,13} Therefore, the thermoelectric performance is sensitively affected by the subtle interplay between the Fe/Co ratio and the filling fraction, and optimization of the composition is required for improving the thermoelectric figure of merit of filled skutterudites.

However, the Fe/Co ratio and the filling fraction of rare-earth atoms, which can be adopted, are interdependent and difficult to change as desirable. In fact, it has been found that the amount of rare-earth atoms that can be incorporated into the structure decreases significantly when Co content increases.^{4,10,13} The low solubility of filling atoms has become an obstacle to changing the Fe/Co ratio and the filling fraction independently for improving thermoelectric properties. It has thus become important to search for new filled skutterudite compounds with a wide range of filling fractions.

In general, Ce and La have been suggested to be trivalent in $\text{Ln}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$; i.e., one Ce or La provides three electrons to the skutterudite structure.^{4,6,9,10,12-14} Replacing Co with Fe in CoSb_3 leads to the creation of one hole in the valence band.^{1,4,7,13} The structural stability requires a match between the filling and the Fe/Co intersubstitution for charge compensation. From the viewpoint of crystal chemistry, it is expected that the filling fraction might be variable in a wider range if a bivalent alkaline-earth atom were to fill the Sb void in the skutterudite structure. Stetson *et al.*⁷ synthesized $\text{BaFe}_4\text{Sb}_{12}$ and $\text{BaRu}_4\text{Sb}_{12}$, but no report has been found on the synthesis of $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$, and the filling limits of Ba in $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ are unknown. In the present work, we attempted to synthesize $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. This communication reports the synthesis process and the crystal structure of the obtained $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ compounds. The relationship between the Ba filling limit and Fe content was also investigated.

Highly pure metals of Ba (99.9%, plate), Sb (99.9999%, powder), Fe (99.99%, powder), and Co (99.99%, powder) were used as the starting materials.

Because the reaction between Ba and Co(Fe) or Sb is highly exothermic, it is difficult to directly melt or react the mixture of the constituent elements. In the present study, a two-step solid reaction was used. A binary compound of Sb_3Ba and a ternary compound of $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$ were first synthesized by reacting the constituent elements in a BN crucible under a flowing Ar atmosphere. Reaction temperatures of 900 and 973 K were used for the syntheses of Sb_3Ba and $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$, respectively. In both cases, the heating time at the reaction temperatures was 96 h. For the synthesis of a Sb_3Ba compound without unreacted Ba, it is important that the samples be heated slowly (<1 K/min) from room temperature to 800 K and be kept at that point for 12 h before being heated to the reaction temperature (900 K). The obtained Sb_3Ba was stable in air and easily handled. The resulting compounds, Sb_3Ba and $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2$, were then crushed and mixed with Sb in various Ba:(Fe + Co):Sb = y :4:12 molar ratios and pressed into pellets. The pellets were heated at 973 K under an Ar atmosphere for 96 h. The chemical compositions were determined by an inductively coupled plasma emission spectroscopy (ICPES), and the lattice constants were determined by x-ray diffractometric analysis.

The typical x-ray diffraction (XRD) patterns of the presynthesized Sb_3Ba , and the final compound $\text{Ba}_{0.6}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ are shown in Fig. 1. By prereacting Ba and Sb at 900 K, Sb_3Ba was obtained with a slight amount of remaining Sb. After the second stage reaction at 973 K, the single phase of $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ was obtained when $x \leq 2$, but the reacted powder consisted

of $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ as the main phase with trace impurity phases of Sb and $(\text{Fe},\text{Co})\text{Sb}_2$ when $x > 2$. The impurity phases [Sb and $(\text{Fe},\text{Co})\text{Sb}_2$] were removed by washing in a HCl + HNO_3 mixed acid.

Rietveld analysis was used to determine and refine the crystal structure of the obtained $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ using the x-ray powder diffraction data in a wide 2θ range (10° to 130°). The resulting unit cell was consistent with filled skutterudite having space group of $Im\bar{3}$, and the lattice constant varied with Fe and Ba contents. As an example, Table I shows the data collection and the refinement parameters for the Rietveld analysis of $\text{Ba}_{0.6}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. Figure 2 shows the observed and calculated XRD patterns and the difference profile for $\text{Ba}_{0.6}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. The final refinement yielded good reliability with reliability factors $R_1 = 4.81\%$, $R_F = 3.73\%$ and $S = 1.17$. The refined atomic coordinates are given in Table II. The refined Ba filling fraction (y) was in good agreement with the Ba contents obtained by ICPES analysis. Atomic coordinates for the Sb site differed slightly from those of CoSb_3 ,⁵ but were close to those of $\text{BaFe}_4\text{Sb}_{12}$.⁷ The thermal parameters (B) of Ba, Sb, and Co(Fe) were 0.61, 0.12, and 0.16, respectively. Several other samples with different compositions ($\text{Ba}_{0.41}\text{Fe}_{1.0}\text{Co}_{3.0}\text{Sb}_{12}$, $\text{Ba}_{0.35}\text{Co}_4\text{Sb}_{12}$, etc.) were also examined by Rietveld analysis, and similar results were obtained. Sale *et al.*^{2,15} and Chakoumakos *et al.*⁸ reported that the thermal parameter values (the atomic displacement parameters) can be used to determine the degree of the vibration of the atom about its equilibrium position. They also indicated that the anomalously large value of thermal parameter of the La atom in $\text{La}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ means that the La is poorly bound in the structure and rattles about its equilibrium position. In the present study, the finding of $B_{\text{Ba}} \gg B_{\text{Sb}}$ and $B_{\text{Ba}} \gg B_{\text{Co,Fe}}$ supported the possibility that Ba atoms rattled in $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$. However, the thermal param-

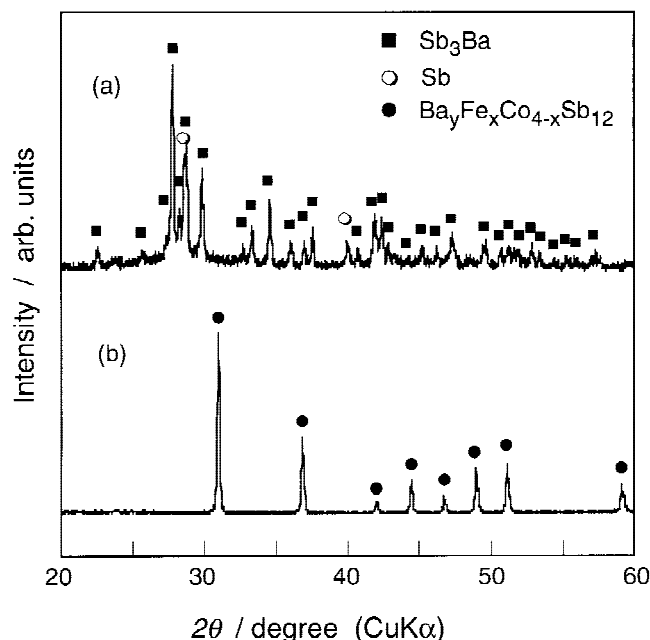


FIG. 1. XRD patterns of (a) Sb_3Ba and (b) $\text{Ba}_{0.6}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ synthesized at 900 and 973 K, respectively.

TABLE I. Powder x-ray Rietveld refinement for $\text{Ba}_{0.6}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

Chemical formula	$\text{Ba}_{0.6}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$
Formula weight	1778.31
Space group	$Im\bar{3}$
a (Å)	9.1180(7)
V (Å ³)	758.3
Density (g/cm ³)	7.80(7)
Powder color	gray
X-ray radiation	Cu K_α
Monochromator	Graphite
2θ range (degree)	10.00–130.00
Step width (degree)	0.01
Counting time (s/step)	4
Temperature (K)	293
Reliability factors	
R_1	0.0481
R_F	0.0373
S	1.17

eter of Ba obtained in the present study was smaller than that of Ce or La in $\text{Ln}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$.^{2,8} This may be due to the larger ionic radius of Ba,⁷ implying that the ionic size of the filling atoms gives influence on the thermal parameters. It should be interesting to investigate the influence of ionic radius of filler atoms on the thermal conductivity.

Figure 3 shows the Ba content (y) dependence of lattice parameter (a) for $\text{Ba}_y\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$. When Fe content (x) was fixed at 1.6, the cubic lattice parameters linearly increased with y in the region of $y < 0.60$ and became almost constant in the region of $y > 0.60$. From these results it was suggested that the maximum filling

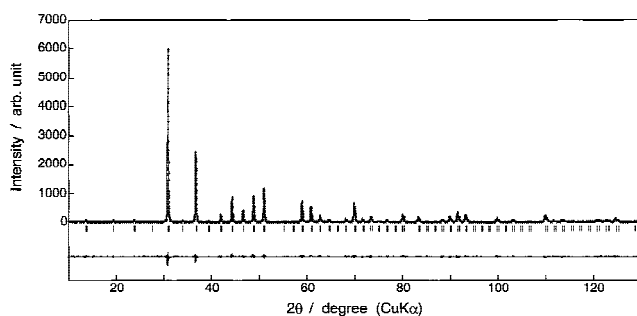


FIG. 2. X-ray Rietveld refinement profile for $\text{Ba}_{0.6}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

TABLE II. Atomic coordinates for $\text{Ba}_{0.6}\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

Atom	Position	Occ.	x	y	z	$B(\text{Å}^2)$
Ba	$2a$	0.60	0.0	0.0	0.0	0.61
Fe/Co	$8c$	1.00	0.25	0.25	0.25	0.12
Sb	$24g$	1.00	0.0	0.1600(0)	0.3380(2)	0.16

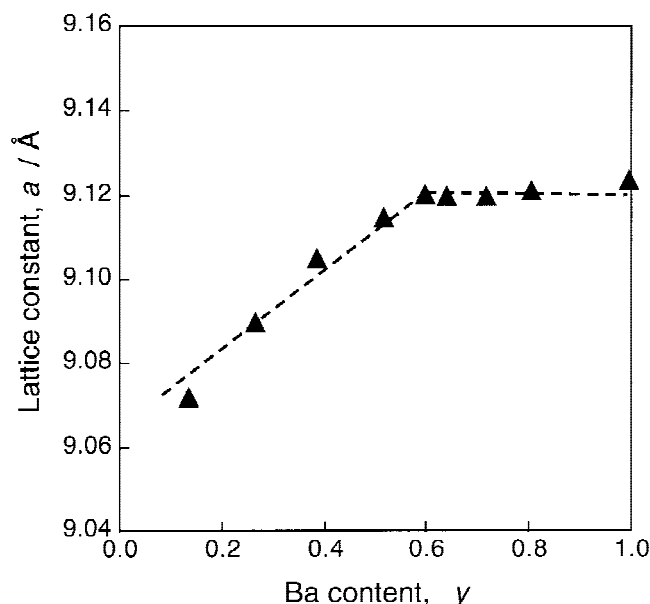


FIG. 3. Relationship between Ba content and lattice constant for $\text{Ba}_y\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$.

fraction (y_{max} ; solid solubility) of Ba in $\text{Ba}_y\text{Fe}_{1.6}\text{Co}_{2.4}\text{Sb}_{12}$ is about 0.60. Similarly, y_{max} values at various Fe contents (x) were also obtained from the measured lattice parameters. The relationship between Ba solubility (y_{max}) and Fe content (x) is shown in Fig. 4. Similar to that observed in the $\text{Ce}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ system, the maximum filling fraction of Ba increased with Fe content, while it was somewhat larger than that of Ce. For example, at $x = 0$ and 1.0, the solubility of Ba in $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ was about 0.35 and 0.5 (Fig. 4) in the present experiment, while that of Ce in $\text{M}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ has been reported to be about 0.067 and 0.31.⁴ The difference between $y_{\text{max}}(\text{Ce})$ and $y_{\text{max}}(\text{Ba})$ may be caused by the difference of the valences between Ba (2+) and Ce (3+). However, it is notable that the filling fraction did not change simply in proportion to the difference of valence. In other words, at lower Fe contents, the difference of filling amounts between Ba and Ce was much larger than that at higher Fe contents. As Fe content increased, the difference between $y_{\text{max}}(\text{Ba})$ and $y_{\text{max}}(\text{Ce})$ decreased. At $x = 4$, the filling limits of both Ba and Ce reached nearly 1.0 (Fig. 4). The reason for the nonlinear relation between the valence and filling fraction is unknown, and further investigation of the crystal structure and valence band is required.

In conclusion, $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ system compounds with a filled skutterudite structure were synthesized by a two-step solid reaction. The result of Rietveld analysis showed high reliability with filling fraction values consistent with the ICPES analysis. The thermal parameter (B) of Ba was larger than those of Sb and Co(Fe). This supports the possibility of rattling of Ba atoms in

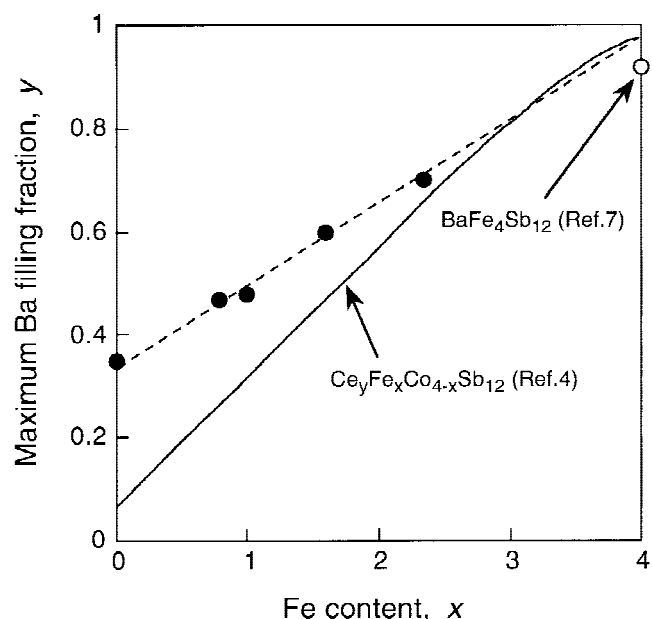


FIG. 4. Relationship between Fe content and Ba filling fraction for $\text{Ba}_y\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$.

$Ba_yFe_xCo_{4-x}Sb_{12}$. The lower valence of Ba (2+) seemed to allow more Ba to fill the Sb-dodecahedron voids than Ce, especially in the lower Fe content region. The wide range of the filling fraction of Ba is expected to lead to various possibilities of changing the composition of $Ba_yFe_xCo_{4-x}Sb_{12}$ and to facilitate the search for advanced materials with high thermoelectric performance. The electrical and thermal transport properties of the $Ba_yFe_xCo_{4-x}Sb_{12}$ system compounds are now under investigation.

ACKNOWLEDGMENTS

This work was partly supported by the Reserach Foundation for materials Science, Japan, and a research grant from the Mazda Foundation, Japan.

REFERENCES

1. B.C. Sales, D. Mandrus, and R.K. Willams, *Science* **272**, 1325 (1996).
2. B.C. Sales, D. Mandrus, B.C. Chakoumakos, V. Keppens, and J.R. Thompson, *Phys. Rev. B* **56**, 15081 (1997).
3. X. Tang, L. Chen, T. Goto, and T. Hirai, *Jpn. Inst. Met.* **63**, 1412 (1999).
4. B.X. Chen, J.H. Xu, C. Uher, D.T. Morelli, G.P. Meisner, J-P. Fleurial, T. Caillat, and A. Borshchevsky, *Phys. Rev. B* **55**, 1476 (1997).
5. T. Schmidt, G. Kliche, and H.D. Lutz, *Acta Cryst. C* **43**, 1678 (1987).
6. D. Jung, M-H. Whangbo, and S. Alvarez, *Inorg. Chem.* **29**, 2252 (1990).
7. N.T. Stetson, S.M. Kauzlarich, and H. Hope, *J. Solid State Chem.* **91**, 140 (1991).
8. B.C. Chakoumakos, B.C. Sales, D. Mandrus, and V. Keppens, *Acta Cryst. B* **55**, 341 (1999).
9. G.S. Nolas, J.L. Cohn, and G.A. Slack, *Phys. Rev. B* **58**, 164 (1998).
10. G.P. Meisner, D.T. Morelli, S. Hu, J. Yang, and C. Uher, *Phys. Rev. Lett.* **80**, 3551 (1998).
11. G.S. Nolas, G.A. Slack, D.T. Morelli, T.M. Tritt, and A.C. Enrich, *J. Appl. Phys.* **79**, 4002 (1996).
12. D.J. Singh and I.I. Mazin, *Phys. Rev. B* **56**, R1650 (1997).
13. D.T. Morelli, G.P. Meisner, B.X. Chen, S.Q. Hu, and C. Uher, *Phys. Rev. B* **56**, 7376 (1997).
14. D.J. Braum and W. Jeitschko, *J. Less-Common Met.* **72**, 147 (1980).
15. B.C. Sales, B.C. Chakoumakos, and D. Mandrus, *J. Solid State Chem.* **146**, 528 (1999).