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Synthesis and crystal structure of $Ca_xCo_4Sb_{12}$ skutterudites

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Abstract

New skutterudite compounds $Ca_xCo_4Sb_{12}$ ($0<x\leqslant 0.2$) have been prepared by traditional metallurgical synthesis. The compounds have been characterized by X-ray powder diffraction (XRD), electron probe microanalysis (EPMA) and neutron powder diffraction. Rietveld refinement of the structures against neutron powder diffraction data (on $Ca_{0.1}Co_4Sb_{12}$, $Im\bar{3}$, $a = 9.0429$ Å, $\chi^2 = 1.55$; $wR_p = 1.52$) enabled the location of Ca in the voids of the skutterudite structure to be verified. The large displacement ellipsoid for Ca is consistent with "rattling" in the cage of the crystalline structure. XRD combined with EPMA analyses showed that the maximum occupancy of Ca atoms is about 0.2.

Keywords: Skutterudite; Neutron diffraction

1. Introduction

Materials with the skutterudite crystal structure possess attractive transport properties and exhibit thermoelectric performance substantially higher at elevated temperature than state-of-the-art thermoelectric materials [1,2].

Binary skutterudites are chemical compounds with a generic formula MX_3 where M represents a transition metal atom of Co group (Co, Rh, Ir) and X stands for some of the group-V elements notably P, As, and Sb, often referred to as pnictogens. These compounds crystallize with a body-centered cubic structure in space group $Im\bar{3}$. This structure can be described as consisting of square planar rings of four pnictogen atoms with the rings oriented along either the (100), (010), or (001) crystallographic directions, whereas the transition metal atoms form a simple cubic sublattice. Alternatively, the structure can be viewed a network of all-corner-sharing MX_6 octahedron. In each octahedron, the metal atom M lies in the center and is octahedrally coordinated by the pnictogen atoms X. This crystal structure offers interesting possibilities to alter both the electronic and lattice properties. The open structure of skutterudites, typified by the presence of two large voids in the unit cell, 12-coordinate by X, is able to accept foreign ions that "fill" the structure. The rattling motion of the filler ions in the voids of the structure results in a dramatic decrease of the lattice thermal conductivity that enhances the thermoelectric performance [1,2]. So far, intensive research has focused on the thermoelectric properties of $CoSb_3$ [3–8] and its partially filled forms, referred to as $R_xCo_4Sb_{12}$ where R is the filler element [9–23]. Several kinds of atoms were used to fill the voids: rare-earth ions (Ce, La, Eu, Yb) [9–19], Tl [20], Sn [21–23] and Ba [24] ions. For electronic stability reasons, the filling fraction x is usually a small fraction of the full occupancy ($x = 1$). All $R_xCo_4Sb_{12}$ compounds are n-type semiconductors and among them $Ba_{0.3}Co_4Sb_{12}$ is one of the most promising for thermoelectric applications at high temperature [24].

In the search of the identification of new n-type skutterudite compounds, we present an investigation on $CoSb_3$ partially filled with the alkaline earth Ca. In this paper, we report on the synthesis process and on the crystal structure of $Ca_xCo_4Sb_{12}$ compounds determined from analysis of time of flight neutron diffraction data. We also investigated the Ca filling fraction limit.

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2. Synthesis

The synthesis of $Ba_xCo_4Sb_{12}$ compounds requires a two step solid-state reaction, due to the highly exothermic reaction between Ba and Co or Sb [24,25]. In the case of $Ca_xCo_4Sb_{12}$ compounds, the synthesis was achieved by a traditional metallurgical technique we developed. High-purity Ca pellets (99.5%), Co powder (99.998%) and Sb shot (99.999%) were used as the starting materials. Stoichiometric amounts of these elements were loaded into a silica ampoule in an argon-atmosphere glovebox. The nominal fraction x of Ca was varied between 0 and 0.6. The tube was sealed under He/H_2 atmosphere and transferred into a programmable furnace. The ampoule was heated up to 750°C at a rate of 1°C/min and left at 750°C for 84 h. At the end of the process, the furnace was shut off and allowed to cool down to room temperature. The heating rate must be kept very slow because of the high exothermic reaction between Ca and Co or Sb. The solid product obtained was then ground in an agate mortar into a fine powder ($<100\,\mu m$), and compacted into pellets without any lubricant in a steel die. To achieve complete reaction and to obtain the expected crystallographic phase, the pellets were annealed in a quartz ampoule under He/H_2 atmosphere at 620°C for 84 h. These materials were powdered again and densified. The densification was accomplished by hot pressing using graphite dies in an argon atmosphere at 600°C for 2 h under $660\,kg/cm^2$.

3. Analyses

X-ray powder diffraction (XRD) was performed on all the ground materials obtained before the sintering phase. Experiments were conducted with a Siemens d500 diffractometer using Co$K\alpha$ radiation and equipped with a curved primary beam monochromator and a linear detector (PSD). X-ray diffraction patterns were recorded in the $\theta - 2\theta$ mode between $20° \leqslant 2\theta \leqslant 100°$ with a 2θ step of 0.032° and a total counting time of 8 h. To obtain accurate lattice parameters, high-purity silicon ($a_0 = 5.4309$ Å) was added as an internal standard. As shown in the next section, the Rietveld refinement against the XRD pattern did not enable us to unequivocally determine the location of calcium.

For a deeper insight in the location of calcium, neutron powder diffraction analyses were performed. The neutron scattering lengths (Ca: 4.90 fm; Co: 2.50 fm; Sb: 5.61 fm) mean that Ca makes a relatively larger contribution to the total Bragg scattering than in X-ray diffraction.

Time of flight data were collected on 2 g of material using the diffractometer POLARIS at the ISIS facility, Rutherford Appleton Laboratory, UK. We used ^{3}He tube detector banks at 35° and 145° and the ZnS scintillation detector bank at 90° to access an overall d-spacing range between 0.3 and 8 Å. The measurement was made for an integrated proton current at the production target of 200 μA h at room temperature. The sample was contained in an 11 mm diameter vanadium cylindrical can. Rietveld refinement was carried out on the data using the Fullprof program [26].

Chemical composition information on the hot-pressed samples was obtained through electron-beam microprobe analysis (EPMA) with a CAMEBAX SX50 instrument. All the compositions were normalized to full occupancy of the cobalt site, "nominal composition" will refer to the reaction mixture and "solubility limit" to the EPMA results.

4. Results and discussion

All the peaks of the X-ray diffraction patterns were indexed on a body-centered cubic lattice isotypic with $CoSb_3$ from which lattice constants, a, can be derived (Table 1). Some weak peaks due to elemental Sb were detected for all samples. The ratio between the highest Sb peak and the highest skutterudite peak is less than 1%. The presence of this Sb secondary phase has been generally encountered in the synthesis of many skutterudites [3,27,28]. For nominal Ca contents greater than $x = 0.4$, small additional peaks appeared attributed to impurity phases that were not identified. The influence of the presence of Ca is clearly evidenced on the lattice parameter (Table 1). It becomes constant for nominal Ca contents greater than $x = 0.4$, suggesting that the solubility limit is reached at this composition.

The hot pressed samples exhibiting only the Sb secondary phase were carefully analyzed by EPMA. Backscattered electron imaging revealed that the overwhelming majority of each sample was constituted of a single phase. Small and occasional precipitates of a Ca-rich phase of >90 at% Ca were also identified. No other secondary phases could be detected by EPMA. The antimony phase observed by XRD was not detected. It is likely that it is distributed at the grain boundaries. The composition of the major phase of each sample was determined at 50 random locations. Atomic compositions and the mean standard deviations are listed in Table 1. From these results, one can see that all samples are calcium deficient relative to the nominal concentration and that the Co/Sb ratio is not affected by the Ca content.

From these observations, it can be said that the solubility limit of Ca in the $Ca_xCo_4Sb_{12}$ samples prepared by the synthesis method described previously extends to at least $x = 0.2$. This value is in good agreement with the solubility limit observed with La

Table 1
Summary of chemical composition determined by electron probe microanalysis and lattice parameters determined by X-ray powder diffraction of the Ca-filled skutterudites at room temperature

Nominal composition	$CoSb_3$	$Ca_{0.15}Co_4Sb_{12}$	$Ca_{0.2}Co_4Sb_{12}$	$Ca_{0.25}Co_4Sb_{12}$	$Ca_{0.4}Co_4Sb_{12}$	$Ca_{0.5}Co_4Sb_{12}$	$Ca_{0.6}Co_4Sb_{12}$
Real composition	$Co_4Sb_{12.24(3)}$	$Ca_{0.05(1)}Co_4Sb_{12.43(3)}$	$Ca_{0.08(1)}Co_4Sb_{12.45(3)}$	$Ca_{0.10(1)}Co_4Sb_{12.44(3)}$	$Ca_{0.20(1)}Co_4Sb_{12.46(3)}$	—	—
a (Å)	9.0360(1)	9.0390(1)	9.0423(1)	9.0429(1)	9.0498(1)	9.0497(1)	9.0498(1)
Secondary phases	Sb, Ca rich phases	Sb, Ca rich phases	Sb, Ca rich phases	Sb, Ca rich phases	Sb, Ca rich phases	Many secondary phases	Many secondary phases

[12], Tl [20], or Yb [16,19] ions but is lower than in the case of Eu ($x = 0.44$) [14] and Ba where $x = 0.45$ [24].

Fig. 1 shows the relationship between the lattice parameters and the composition determined by EPMA for $Ca_xCo_4Sb_{12}$ compounds. The lattice parameter increases linearly with increasing Ca content in the range of $x = 0-0.2$, following Vegard's law. This variation in lattice parameter is analogous to that observed for rare-earth and other filler atoms [10,17,24] and suggests that Ca is located in the 12-coordinate voids of the skutterudite structure.

We tried to refine the positions of the elements by using the Rietveld method with the Fullprof program [26]. The refinement of the structures of all the compounds against XRD data using the published structure of $CoSb_3$ as a starting model led to good agreement factors. If a fixed amount of Ca with a fixed thermal parameter (B_{iso}) was placed in the expected (0,0,0) position, no significant improvement of the agreement factors was observed. When Ca was placed at the alternative $(0, 1/2, 1/2)$ site or on the Co or Sb sites, the Rietveld refinement lead to poorer agreement factors. Analysis of X-ray powder data is not inconsistent with the location of Ca at the (0,0,0) position, but the sensitivity of the X-ray diffraction analysis is not appropriate for the determination of all the atomic positions, bond lengths and atomic displacement parameters (ADPs).

The structure of the partially filled skutterudite formed by the solid-state reaction was confirmed by Rietveld refinement of the model against neutron powder diffraction data. Analysis was performed on the compound with $x = 0.1$ (as determined by EPMA analysis). First, the structure was refined against the data of the three detector banks using the structure of $CoSb_3$ as a starting model, with the presence of the secondary Sb phase. The refinements of the neutron data easily converged to a fully ordered atom arrangement with regard to the respective site distribution of Co and Sb atoms ($\chi^2 = 1.74$; $wR_p = 1.66$). Ca was then

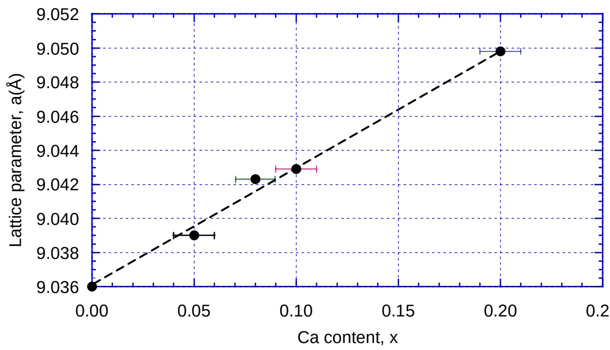

Fig. 1. Lattice parameters from powder X-ray diffraction measurements versus x content in $Ca_xCo_4Sb_{12}$ determined by EPMA analysis. The line is a guide to the eye.

Table 2
Results from the Rietveld refinement; atomic positions, atomic displacement parameters and agreement factors from neutron refinement for $Ca_{0.1}Co_4Sb_{12}$ (EPMA composition) and $CoSb_3$ (without Ca) at 293 K

		$CoSb_3$		$Ca_{0.1}Co_4Sb_{12}$	
Atom	Position	Occ.	x	y	z
Co	8c	1	1/4	1/4	1/4
Ca	2a	0.10(1)	0.0	0.0	0.0
Sb	24g	1	0.0		
Sb(y)		0.3352(1)		0.3353(1)	
Sb(z)		0.1578(1)		0.1581(1)	
Lattice parameter (Å)		9.0360(1)		9.0429(1)	
Space group			$Im\bar{3}$		
ADP or $B_{\text{equivalent}}$ (Å^2)					
Co	0.33(1)	0.31(1)			
Sb	0.45(1)	0.43(1)			
Ca		0.68(2)			
Anisotropic Thermal parameter (Å^2)					
Co					
$U_{11} = U_{22} = U_{33}$		0.0042(1)		0.0040(1)	
U_{12}, U_{13}, U_{23}		0,0,0		0,0,0	
Sb					
U_{11}, U_{22}, U_{33}		0.0042(1), 0.0073(2), 0.00536(1)		0.0038(1), 0.0078(2), 0.0048(1)	
U_{12}, U_{13}, U_{23}		0,0,0		0,0,0	
Ca					
$U_{11} = U_{22} = U_{33}$				0.00866(2)	
U_{12}, U_{13}, U_{23}				0,0,0	
Agreement factors					
R_p		2.17		2.13	
wR_p		1.51		1.52	
R_{exp}		1.24		1.22	
χ^2		1.49		1.55	

placed either on the Co or Sb sites, or on the (0,0,0) vacant site. No improvement was observed when Ca was placed in the substituted positions and it was not possible to produce a convergent refinement with a positive Ca content value. Contrarily, the refinements with Ca in the (0,0,0) crystallographic position resulted in an improvement of the agreement factors ($\chi^2 = 1.66$; $wR_p = 1.62$). To make the comparison, neutron powder diffraction data were collected for $CoSb_3$. The results of Rietveld refinement are shown in Table 2. In the refinement of the structure of $CoSb_3$, the fractional occupancy of Ca placed on the (0,0,0) site, with a thermal displacement parameter equal to that obtained from the refinement of $Ca_{0.1}Co_4Sb_{12}$, refined to zero. Because of expected strong correlation between the ADP and the level of occupancy, the occupancy of Ca on the (0,0,0) site in $Ca_{0.1}Co_4Sb_{12}$ was fixed at the EPMA value and refinement of an isotropic ADP was carried out. Fig. 2 shows the fit to the POLARIS data from the 145° data bank. The atomic positions, the isotropic and anisotropic (for Sb) ADPs, and the agreement factors are reported in Table 2.

The ADP values for Co and Sb are typical for these elements in compounds with similar coordination numbers. The isotropic ADP value of the Ca is higher than for the Co and Sb atoms. As shown in other skutterudite compounds, the relatively high ADP may result from the "rattling" of the inserted atom around its equilibrium position in the large 12-coordinate site [20]. The obtained ADP of Ca is smaller than that of Tl in $Tl_xCo_4Sb_{12}$ ($B_{iso} = 3.9$) [20] or La ($B_{iso} = 1.6$) in the compensated charge $R_xFe_yCo_{4-y}Sb_{12}$ [29–31], but its value is close to the value found for Ba in $Ba_xFe_yCo_{4-y}Sb_{12}$ ($B_{iso} = 0.61$) [25].

The interatomic distances and bond angles are also given in Table 3. The values for the compounds $CoSb_3$ without calcium are also included for comparison. All interatomic distance in $Ca_{0.1}Co_4Sb_{12}$ are slightly longer than in $CoSb_3$. We can explain the expansion of the lattice parameter with the increase of the calcium content by the main expansion of the nearest Sb–Sb bond (0.27%) and by small changes in the other bond length and in the bond angle [21].

In summary, $CoSb_3$ skutterudite compounds partially filled with Ca have been successfully synthesized through solid-state reactions. The structure of these compounds has been refined with time of flight neutron powder diffraction data. Good agreement factors support the insertion of calcium in the 12-coordinate void sites in the skutterudite framework. Moreover, the

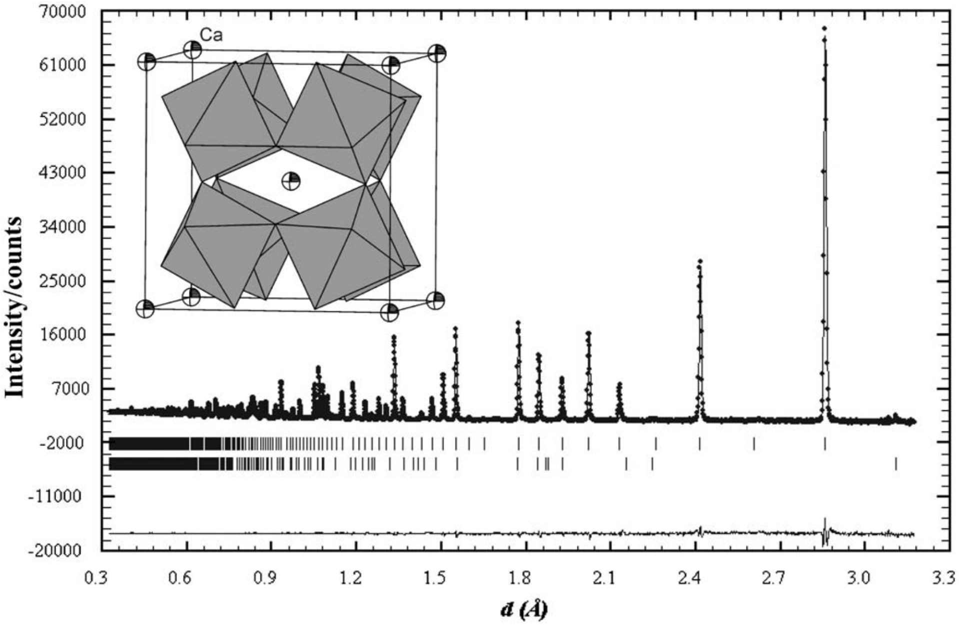

Fig. 2. Rietveld refinement of neutron time-of-flight (backscattering detectors $2\theta = 145°$) diffraction pattern of $Ca_{0.1}Co_4Sb_{12}$. The observed data are shown as points, the calculated model is the solid line, and the difference curve is shown below. Markers indicate the position of the Bragg reflections from $Ca_{0.1}Co_4Sb_{12}$ (top) and Sb (phase fraction = 0.50(6)%) (bottom). In inset is represented the crystal structure of $R_xCo_4Sb_{12}$ in the two dimension view. The $CoSb_6$ octahedrals are outlined and the R atoms are represented in the 0 0 0 position.

Table 3
Interatomic distances (Å) and bond angles (deg) in $Ca_{0.1}Co_4Sb_{12}$ and $CoSb_3$ determined from refinement against powder neutron diffraction data

	$Ca_{0.1}Co_4Sb_{12}$	$CoSb_3$	
Distances			
Co–Sb	2.5291(3)	2.5278(3)	× 48
Sb–Sb	2.8594(4)	2.8518(3)	× 6
	2.9787(3)	2.9783(3)	× 12
Ca–Sb	3.3523(4)		× 36
Angles			
Sb–Co–Sb	85.46(1)	85.52(1)	× 48
Sb–Co–Sb	94.53(1)	94.47(1)	× 48
Co–Sb–Sb	107.75(1)	107.73(1)	× 24
Co–Sb–Sb	109.18(1)	109.24(1)	× 24
Co–Sb–Co	126.72(1)	126.67(1)	× 12
Sb–Sb–Sb	90	90	

larger ADP values of Ca relative to Co or Sb suggest the possibility for Ca atoms to rattle in the voids of the crystalline structure. This usually decreases the lattice thermal conductivity in these compounds and $Ca_xCo_4Sb_{12}$ is now under investigation for its thermoelectric properties. The filling fraction limit was found to be 0.2. This value is smaller than in the case of the other alkaline earth element Ba where the maximum occupancy has been determined to be 0.44. The reason why is not yet clear. Several factors may contribute simultaneously as for instance the valence, the ionic radius and the electronegativity of the filler [32].

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