J Therm Anal Calorim (2011) 103:23–27
DOI 10.1007/s10973-010-1034-z

Synthesis and characterisation of the compound CoSbS

R. Carlini · C. Artini · G. Borzone · R. Masini · G. Zanicchi · G. A. Costa

AICAT2010 Special Chapter

Abstract In the search for new intermetallic materials with high thermoelectric performances, the Co–Sb–S ternary system has been explored and polycrystalline CoSbS samples have been prepared by a vapour phase technique starting from the pure elements. The crystal cell of CoSbS belongs to the *Pbca* space group and shows an orthorhombic structural arrangement with the following lattice parameters: $a = 5.8341(2)$ Å; $b = 5.9477(2)$ Å, and $c = 11.6540(4)$ Å. The structure belongs to the pyrite–marcasite family, as Co forms tilted corner- and edge-sharing octahedra with three Sb and three S atoms. Scanning electronic microscopy (SEM), electron-probe microanalysis (EPMA) and X-ray powder diffraction were used to investigate the microstructure and to carry out the structural analysis; the crystal structure was refined by the Rietveld method using the DBWS-9807 program. The thermal stability of CoSbS was investigated referring to the ternary Co–S–Sb phase diagram and by differential thermal analysis (DTA) measurements. Thermoelectric power measurements at room temperature were also performed by a home-made instrument.

R. Carlini · C. Artini · G. Borzone · G. Zanicchi · G. A. Costa
DCCI, University of Genoa, Via Dodecaneso 31, 16146 Genoa, Italy

R. Carlini · G. Borzone · G. Zanicchi
INSTM – Genoa Research Unit of National Consortium of Materials Science and Technology, Via Dodecaneso 31, 16146 Genoa, Italy

C. Artini (✉) · G. A. Costa
CNR-SPIN Genova, Corso Perrone 24, 16152 Genoa, Italy
e-mail: artini@chimica.unige.it

R. Masini
CNR-IMEM, Via Dodecaneso 33, 16146 Genoa, Italy

Keywords Thermoelectrics · Intermetallics · Seebeck effect · Phase stability

Introduction

Skutterudites have been identified as promising materials for thermoelectric applications, being characterised by a high Seebeck coefficient and high electrical conductivity [1]. To this class belong compounds with formula MX_3, where M = Co, Rh or I and X = P, As, or Sb; they crystallize in a cubic cell with space group *Im-3*. Among them, $CoSb_3$ has been extensively studied [2–4]; due to its high thermal conductivity, the figure of merit $ZT = S^2\sigma T/k$ (where S is the Seebeck coefficient, σ is the electrical conductivity and k is the thermal conductivity) is too low to allow an extensive use of this material. In order to improve this parameter, two paths are currently followed: (i) a heavy atom, generally a rare earth such as Y [5], Sm [6], La [7], is introduced in the two vacancies at 0, 0, 0 and 1/2, 1/2, 1/2, so that the guest atom acts as a filler and lowers the lattice thermal conductivity; (ii) partial substitutions of Sb by Te [8], Te and Pd [9], Sn [10], Se [11], or of Co by Fe [12] or Ni [13] are performed to increase the carrier concentration and as a consequence the electrical conductivity. GaTe, for example, recently resulted to be a promising thermoelectric material [14].

Ternary skutterudites with mixed anion occupancy, characterised by the formula $MY_{1.5}Q_{1.5}$ (where M = Co, Rh or I, Y belongs to the 14th group and Q to the 16th group), exist too and crystallize in a modified structure where the symmetry is lowered from cubic (space group *Im-3*) to rhombohedral (space group *R-3*). To this class belong compounds like $CoGe_{1.5}S_{1.5}$ [15] and $IrSn_{1.5}Te_{1.5}$ [16]. A higher amount of Co leads on the contrary to the

obtainment of compounds with general formula MYQ, that in many cases show a higher stability than the corresponding skutterudite $MY_{1.5}Q_{1.5}$ [17, 18].

We studied the Co–Sb system and the possibility of doping at the Sb site by chalcogenide elements, in particular by S, in order to increase the carrier concentration. As in the latter case described, the introduction of S at the Sb site resulted in the formation of the compound CoSbS, that shows to be the most stable in the Co–Sb–S ternary system [19, 20]. With respect to the skutteruditic structure, the crystal cell of CoSbS exhibits a lowering of the symmetry from cubic to orthorhombic (space group: *Pbca*). Co forms corner- and edge-sharing tilted octahedral with three Sb and three S atoms, analogously to the aforementioned CoGeTe compound. In this work a structural and microstructural analysis is reported, together with some preliminary results on the thermoelectric properties of the compound.

Experimental

Cobalt rod (purity: 99.999%), antimony rod (purity: 99.99%) and sulphur powder (purity: 99.99%) were used as starting materials. Cobalt and antimony were ground in an agate mortar and mixed in the stoichiometric amounts; the powders were then twice pressed ($P = 15$ MPa) to obtain a pellet. The binary CoSb alloy was prepared melting in induction furnace the pellet in an Al_2O_3 crucible, sealed in a silica tube under partial pressure of Ar. The sample was then ground again and the obtained powder was mixed with a slight excess of S. After pressing twice ($P = 15$ MPa), the powder was again put in an Al_2O_3 crucible; the latter was then sealed in a silica tube under partial pressure of Ar and subsequently put in an iron tube; the sample was then treated in a horizontal furnace at 550 °C for 24 h, then at 780 °C for 48 h and finally at 500 °C for 48 h; afterwards it was slowly cooled. The microstructure of the alloy was first investigated by light optical microscopy (LOM). Compositional and microstructural analyses were performed by scanning electron microscopy (SEM) and electron-probe microanalysis (EPMA) based on energy dispersive X-ray spectroscopy (EPMA-EDS). The surface of the specimens was polished and the microstructure investigated; the compositional contrast between the different phases was observed by means of a back-scattered electrons (BSE) or secondary electrons (SE) detector. For quantitative EPMA, the samples were analysed at 20 kV acceleration voltage using cobalt as a calibration standard of the beam current, gain and resolution of the spectrometer. The structural properties were investigated by X-ray powder diffraction (XRD) collecting diffractograms by means of a Philips PW1830 diffractometer (Cu K_α radiation)

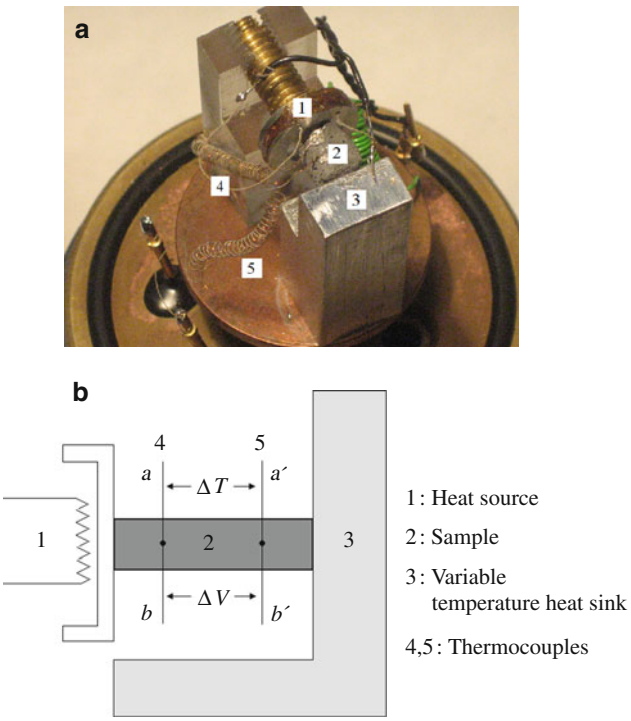

Fig. 1 Simplified apparatus for thermoelectric power measurements: **a** photo and **b** schematic diagram

in the range $10° \leq 2\theta \leq 90°$ and refining data by Rietveld method using the DBWS-9807 program [21]. The thermoelectric power was measured by means of a home-made instrument shown in Fig. 1. A heater applied on a face of a cylindrical sample produces a thermal flow through the sample. Heat is then discharged on a thermal mass held at constant temperature by a thermostat at a temperature ranging between 15 and 115 °C. Two thermocouples are welded onto the surface of the rod, measuring the temperature difference, as well as the Seebeck voltage of the material. The thermoelectric power is then calculated.

The thermal stability of CoSbS was measured by means of differential thermal analysis (DTA) by a 404S Netzsch Pegasus (Selb, Germany) instrument on a powdered sample enclosed in sealed tantalum crucible. The thermal schedule consisted of a heating step from room temperature up to 900 °C at 10 °C/min in flowing argon.

Results and discussion

The structural analysis performed on the powders shows that the compound is almost monophasic, with orthorhombic CoSbS as the majority phase; traces of Sb_2S_3, detected also by EPMA, appear too. For the Rietveld analysis 12 structural parameters and four profile parameters were refined; the Rietveld plot is reported in Fig. 2.

The peaks have been indexed and refined in the *Pbca* space group; the lattice parameters are $a = 5.8341(2)$ Å, $b = 5.9477(2)$ Å and $c = 11.6540(4)$ Å. The structure, shown in Fig. 3, is similar to the one described for CoGeTe [17, 18] and is part of the pyrite–marcasite family. Co is in fact octahedrally coordinated to three Sb and three S atoms; each octahedron shares one S–S edge with a neighbouring octahedron (similarly to pyrite, where each octahedron shares two edges) and the remaining corners with 10 neighbouring octahedra (similarly to marcasite, where each octahedron shares its corners with 12 neighbours). $[CoSb_3S_3]$ octahedra show a significant deviation from the ideal arrangement, as Co–Sb distances range between 2.497 and 2.563 Å and Co–S between 2.252 and 2.324 Å, meaning that the deviation is stronger than in CoGeTe and CoAsSe [17]. The atomic positions obtained from refinement are reported in Table 1.

The compositions of the binary phase CoSb and the compound CoSbS, together with the structural and compositional data obtained by EPMA, are reported in Table 2. The SEM analysis performed on the ternary alloy (Fig. 4a, b) shows the presence of CoSbS, which appears in large grey crystals; traces of Sb_2S_3 can be noticed too. The phase $CoSb_3$ was not detected; the binary phase Sb_2S_3 does not show any Co solubility.

Room temperature (298 K) thermoelectric power (S) resulted to be around 200 μV K^{-1}. Resistivity was also measured and a value of 5×10^{-4} Ω cm was found; the power factor, defined as $S^2\sigma$ (where σ is the electric conductivity), was then calculated and resulted to be 0.8×10^{-2} W $K^{-2}m^{-1}$. Thermal conductivity was not measured, but assuming that the Wiedemann–Franz law is valid for the studied compound, the calculated value of the thermal conductivity k would be 1.5 W K^{-1} m^{-1}. Using these data, the figure of merit $ZT = S^2\sigma T/k$ would result to be 1.6, i.e. close to the values typical of skutterudites [22].

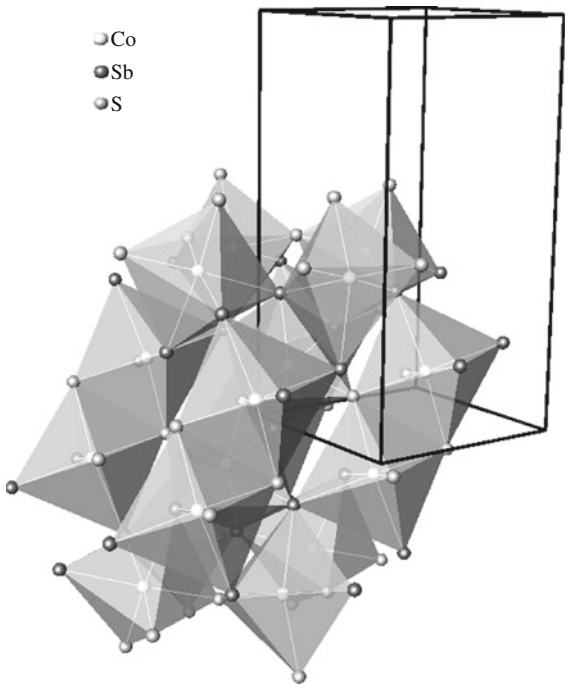

Fig. 3 Crystal structure of CoSbS; the octahedral dimers are visible

Table 1 Refined atomic positions for CoSbS

	x	*y*	*z*
Co	0.0192 (1)	0.169 (1)	0.1169 (6)
Sb	0.1172 (5)	0.0468 (4)	0.3199 (2)
S	0.359 (2)	0.316 (1)	0.0657 (9)

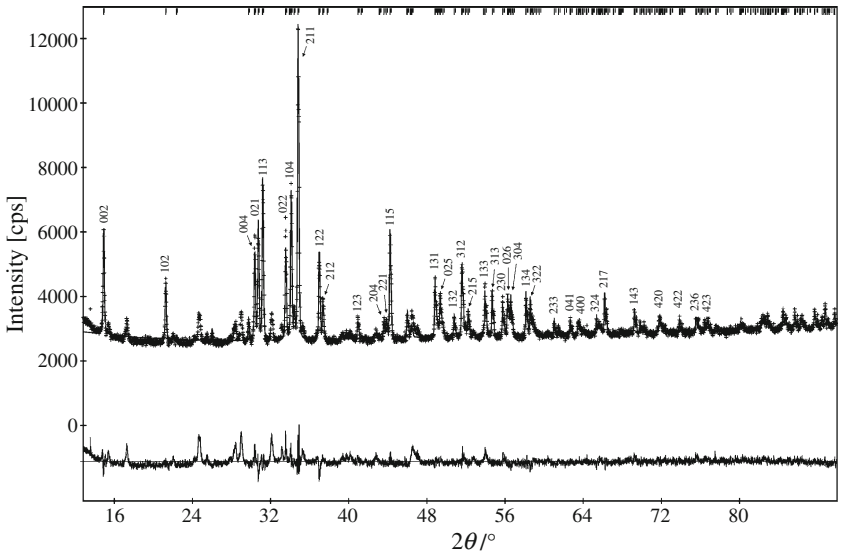

Fig. 2 Rietveld refinement plot for CoSbS from X-ray diffraction data

Table 2 Phase structure and composition observed by SEM and EPMA

Alloy nominal composition/ at.%	Observed phases	Phase composition from EPMA/at.%	Crystal structure
Co 45.5	β—Co–Sb	Co 46.5 Sb 53.5	hP4—NiAs
Sb 54.5	γ—Co–Sb	Co 32.0 Sb 68.0	oP6—$FeAs_2$
Co 26.0	CoSbS	Co 31.3 S 33.5 Sb 35.2	oP24—CoSbS
S 38.4	Sb_2S_3	S 59.0 Sb 41.0	oP20—Sb_2S_3
Sb 35.6			

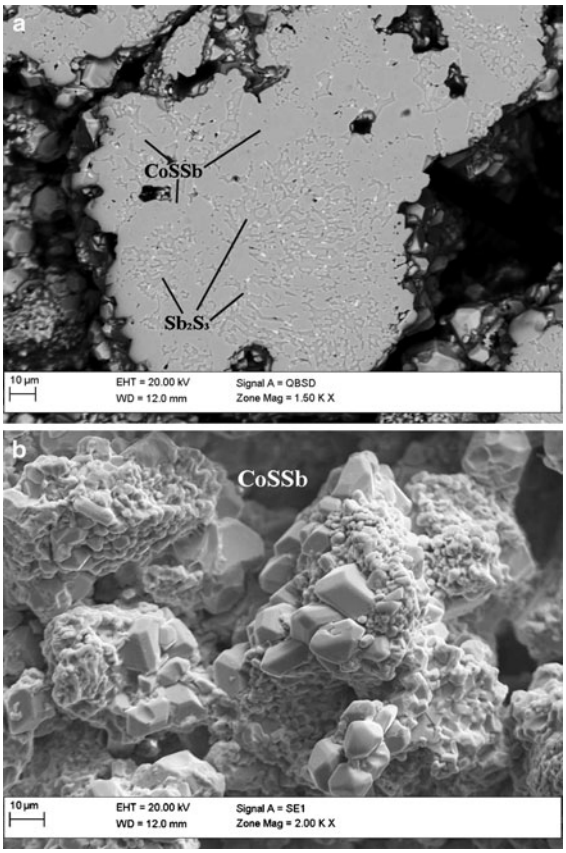

Fig. 4 SEM-BSE (**a**) and SEM-SE (**b**) micrographs of the ternary alloy

Thermal analysis revealed a decomposition temperature slightly lower than the one reported by Allazov et al. [20]; for this reason a thorough investigation of the Co–Sb–S ternary system is currently scheduled.

Summary

In the search for new thermoelectrics materials the Co–Sb–S system was investigated and the compound CoSbS was synthesised by a vapour phase technique. The crystal structure was investigated and found to belong to the *Pbca* space group and to the pyrite–marcasite family. The Seebeck number and the electrical resistivity were measured and found around 200 $\mu V\ K^{-1}$ and $0.5 \times 10^{-4}\ \Omega$ cm, respectively. The figure of merit *ZT*, calculated using the Wiedemann–Franz law to obtain the thermal conductivity, showed a promising value, compared to the ones reported for thermoelectric skutterudites.

Acknowledgements The authors gratefully acknowledge Dr. D. Macciò for his helpful contribution with DTA measurements.

References

1. Snyder GJ, Toberer ES. Complex thermoelectric materials. Nat Mater. 2008;7:105–14.
2. Kawaharada Y, Kurosaki K, Uno M, Yamanaka S. Thermoelectric properties of $CoSb_3$. J Alloys Compd. 2001;315:193–7.
3. Zhang JX, Lu QM, Liu KG, Zhang L, Zhou ML. Synthesis and thermoelectric properties of $CoSb_3$ compounds by spark plasma sintering. Mater Lett. 2004;58:1981–4.
4. Furuyama S, Iida T, Matsui S, Akasaka M, Nishio K, Takanashi Y. Thermoelectric properties of undoped p-type $CoSb_3$ prepared by vertical Bridgman crystal growth and spark plasma sintering. J Alloys Compd. 2006;415:251–6.
5. Nakamoto G, Yoshida Y, Vu LV, Huong NT, Anh DTK, Kurisu M. Effect of segregated impurity phases on lattice thermal conductivity in Y-added $CoSb_3$. Scr Mater. 2007;56:269–72.
6. Jiang YP, Jia XP, Su TC, Dong N, Yu FR, Tian YJ, Guo W, Xu HW, Deng L, Ma HA. Thermoelectric properties of $Sm_xCo_4Sb_{12}$ prepared by high pressure and high temperature. J Alloys Compd. 2010;493:535–8.
7. Mi JL, Zhao XB, Zhu TJ, Tu JP. Nanosized La filled $CoSb_3$ prepared by a solvothermal-annealing method. Mater Lett. 2008;62:2363–5.
8. Wojciechowski KT. Effect of tellurium doping on the thermoelectric properties of $CoSb_3$. Mater Res Bull. 2002;37:2023–33.
9. Chitroub M, Besse F, Scherrer H. Thermoelectric properties of semi-conducting compound $CoSb_3$ doped with Pd and Te. J Alloys Compd. 2009;467:31–4.
10. Kim I-H, Park K-H, Ur S-C. Thermoelectric properties of Sn-doped $CoSb_3$ prepared by encapsulated induction melting. J Alloys Compd. 2007;442:351–4.
11. Wojciechowski KT, Tobola J, Leszczyński J. Thermoelectric properties and electronic structure of CoSb doped with Se and Te. J Alloys Compd. 2003;361:19–27.
12. Kim IH, Ur SC. Electronic transport properties of Fe-doped $CoSb_3$ prepared by encapsulated induction melting. Mater Lett. 2007;61:2446–50.
13. Kitagawa H, Wakatsuki M, Nagaoka H, Noguchi H, Isoda Y, Hasezaki K, Noda Y. Temperature dependence of thermoelectric properties of Ni-doped $CoSb_3$. J Phys Chem Solids. 2005;66:1635–9.
14. Al-Ghamdi AA. Thermoelectric power (TEP) of layered chalcogenides GaTe crystals. J Therm Anal Calorim. 2008;94:597–600.
15. Vaqueiro P, Sobany GG, Stindl M. Structure and electrical transport properties of the ordered skutterudites $MGe_{1.5}S_{1.5}$ (M = Co, Rh, Ir). J Solid State Chem. 2008;181:768–76.
16. Bos JWG, Cava RJ. Synthesis, crystal structure and thermoelectric properties of $IrSn_{1.5}Te_{1.5}$-based skutterudites. Solid State Commun. 2007;141:38–41.

17. Laufek F, Navrátil, Plášil J, Plecháček T. Crystal structure determination of CoGeTe from powder diffraction data. J Alloys Compd. 2008;460:155–9.
18. Vaqueiro P, Sobany GG, Guinet F, Leyva-Bailen P. Synthesis and characterization of the anion-ordered tellurides MGeTe. Solid State Sci. 2009;11:1077–82.
19. Schenck R, Von der Forst P. Gleichgewichtsstudien and erzbildenden Sulfiden III. Z Anorg Allg Chem. 1942;249:76–87.
20. Allazov MR, Gulieva ZT. Physicochemical interaction in the CoS–Sb and NiS–Sb systems. Russ J Inorg Chem. 1988;33:1075–8.
21. Young RA, Sakthiel A, Moss TS, Paiva-Santos CO. DBWS-9411, an upgrade of the DBWS*.* programs for Rietveld refinement with PC and mainframe computers. J Appl Cryst. 1995;28:366–7.
22. Uher C. Skutterudite-based thermoelectrics. In: Rowe DM, editor. Thermoelectrics handbook. Boca Raton: Taylor & Francis; 2006. p. 34-1–17.