Andrea Amaldi · Francois Tang *Editors*

Proceedings of the 11th European Conference on Thermoelectrics

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Editors
Andrea Amaldi
Science and Applications Division
European Space Agency
Noordwijk, The Netherlands

Francois Tang
Science and Applications Division
European Space Agency
Noordwijk, The Netherlands

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Preface

The growing energy demands and the urgent necessity to curb greenhouse gas emissions have promoted the advancements of a broad range of possible solutions meant to mitigate the impact of our society on our environment. Among the different approaches to limit our footprint, thermoelectric materials have been positioned as a prime candidate to recover energy from heat that would otherwise deemed wasted. The physics of thermoelectricity alone, namely the Seebeck effect, is unambiguously appealing. However, the engineering and commercial realities have been a major obstacle to the wider acceptance of thermoelectrics in practical applications. *Economically* viable generators have so far evaded the thermoelectric community.

The 11th European Conference on Thermoelectrics provided an international forum for discussion and a dissemination venue for thermoelectrics. Under the mandate of the European Thermoelectric Society, the event was organized by the European Space Agency at the European Science and Technology Centre (ESTEC) in Noordwijk, The Netherlands on November 18–20th, 2013. The Proceedings from the 11th European Conference on Thermoelectrics are a collection of 26 manuscripts that cover topics from material syntheses, the measurement of thermoelectric properties, and the design of modules and generators. The proceedings are being complemented by fully peer-reviewed manuscripts that will appear in a special issue of the *Journal of Electronic Materials*.

The large emphasis of these proceedings on the design of thermoelectric modules and generators reflects the need to grow thermoelectricity beyond investigations limited to the fundamental physical understanding and the material characterization. The future of thermoelectricity may lie in the discovery of new high-ZT material, but we believe that it resides as much, and perhaps even more, in the design of modules and generators where these materials can be best exploited.

We are thankful to all the participants and the authors who submitted manuscripts to the 2013 European Conference on Thermoelectrics. We hope that these proceedings correctly reflect the time and effort that each invested to achieve these results.

Noordwijk, The Netherlands

Andrea Amaldi
Francois Tang

Contents

Contributors

Z. Ancik Unis, a.s., Mechatronic & Embedded Systems, Brno, Czech Republic

D. Andersson Swerea IVF, Mölndal, Sweden

M.A. Ashari Department of Micro-Energy & Green Technology, Kuala Lumpur, Malaysia

F. Assion Sensor Technology Department, University of Paderborn, Paderborn, Germany

M. Baricco Dipartimento di Chimica and NIS, Università degli Studi di Torino, Torino, Italy

S. Barison Institute for Energetics and Interphases, National Research Council of Italy, Padova, Italy

G. Bastian Faculty of Technology and Bionics, Rhein-Waal University of Applied Sciences, Kleve, Germany

S. Battiston Institute for Energetics and Interphases, National Research Council of Italy, Padova, Italy

J.P. Bedecarrats Laboratoire de Thermique, Energétique et Procédés, Université Pau & Pays Adour, LaTEP – EA 1932, ENSGTI, PAU, France

S. Bernadet School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, UK

S. Boldrini Institute for Energetics and Interphases, National Research Council of Italy, Padova, Italy

M. Brignone Centro Ricerche FIAT, Orbassano, TO, Italy

K. Brinkfeldt Swerea IVF, Mölndal, Sweden

R. Carlini Dipartimento di Chimica e Chimica Industriale, Università di Genova, Genova, Italy

Unità di Ricerca di Genova, INSTM, Genova, Italy

S. Caron Dipartimento di Elettronica e Telecomunicazioni, Politecnico di Torino, Torino, Italy

A. Castellero Dipartimento di Chimica and NIS, Università degli Studi di Torino, Torino, Italy

D. Champier Laboratoire des Sciences de l'Ingénieur Appliquées à la Mécanique et au Génie Electrique (SIAME), Université Pau & Pays Adour, Pau Cedex, France

I.A. Dimitriadou European Thermodynamics Limited, Kibworth, Leicester, UK

R.A. Dorey University of Surrey, Guildford, Surrey, UK

M. Edwards Swerea IVF, Mölndal, Sweden

L. Exel Chair of Automation, Saarland University, Saarbrucken, Germany

M. Fabrizio Institute for Energetics and Interphases, National Research Council of Italy, Padova, Italy

A. Famengo Institute for Energetics and Interphases, National Research Council of Italy, Padova, Italy

C. Fanciulli Unità di Lecco, CNR, Istituto per l'Energetica e le Interfasi, Lecco, Italy

C. Favarel Laboratoire de Thermique, Energétique et Procédés, Université Pau & Pays Adour, LaTEP – EA 1932, ENSGTI, PAU, France

M.I. Fedorov Ioffe Physical-Technical Institute, St. Petersburg, Russia

Saint-Petersburg National Research University of Information Technologies, Mechanics and Optics, St. Petersburg, Russia

S. Fiameni Institute for Energetics and Interphases, National Research Council of Italy, Padova, Italy

F. Finsterwalder Daimler AG, Ulm, Germany

G. Fischerauer University of Bayreuth, ZET, Chair of Metrology and Control Engineering, Bayreuth, Germany

M. Follmer Magna Powertrain – Engineering Center Steyr GmbH & Co KG, St. Valentin, Austria

G. Frey Chair of Automation, Saarland University, Saarbrücken, Germany

A. Fujibayashi Steel Research Laboratory, JFE Steel Corporation, Kawasaki, Kanagawa, Japan

Steel Research Laboratory, Environmental Process Research Department, JFE Steel Corporation, Kawasaki, Kanagawa, Japan

A. Fulham European Thermodynamics Limited, Kibworth, Leicester, UK

V. Geneiß Fraunhofer ENAS – Advanced System Engineering, Paderborn, Germany

V. Giaretto Dipartimento Energia, Politecnico di Torino, Torino, Italy

Unità di Ricerca, Consorzio Nazionale Interuniversitario di Scienze fisiche della Materia (CNISM), Politecnico di Torino, Torino, Italy

S. Piles Guillem School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, UK

H. Hachiuma Thermo Generation Business Development Division, KELK Ltd., Hiratsuka, Kanagawa, Japan

Z. Hadas Faculty of Mechanical Engineering, Brno University of Technology, Brno, Czech Republic

C. Hedayat Fraunhofer ENAS – Advanced System Engineering, Paderborn, Germany

M. den Heijer RGS Development B.V., Oudkarspel, The Netherlands

B. Hesse University of Duisburg-Essen, Duisburg, Germany

U. Hilleringmann Sensor Technology Department, University of Paderborn, Paderborn, Germany

Fraunhofer ENAS – Advanced System Engineering, Paderborn, Germany

Institute of Electrical Engineering and Information Technology, University of Paderborn, Paderborn, Germany

M. Ioannou Department of Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus

M. Jägle Fraunhofer IPM, Institute for Physical Measurement Techniques, Freiburg, Germany

E.M. Jakubczyk School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, UK

L. Janak Faculty of Mechanical Engineering, Brno University of Technology, Brno, Czech Republic

P. Jones School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, UK

K. Kabeya Corporate Planning Department, JFE Steel Corporation, Chiyoda-ku, Tokyo, Japan

H. Kaibe Thermo Generation Business Development Division, KELK Ltd., Hiratsuka, Kanagawa, Japan

Y.P. Kim Department of Environmental Science and Engineering, Ewha Womans University, Seoul, Republic of Korea

D. Knospe Magna Powertrain – Engineering Center Steyr GmbH & Co KG, St. Valentin, Austria

J. König Fraunhofer IPM, Institute for Physical Measurement Techniques, Freiburg, Germany

P. Kopecek Unis, a.s., Mechatronic & Embedded Systems, Brno, Czech Republic

T. Kousksou Laboratoire des Sciences de l'Ingénieur Appliquées à la Mécanique et au Génie Electrique (SIAME), Université Pau & Pays Adour, Pau Cedex, France

B. Kraaijveld RGS Development B.V., Oudkarspel, The Netherlands

T. Kuroki Steel Research Laboratory, Environmental Process Research Department, JFE Steel Corporation, Kawasaki, Kanagawa, Japan

T. Kyratsi Department of Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus

J. Laroche School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, UK

K. Makino Thermo Generation Business Development Division, KELK Ltd., Hiratsuka, Kanagawa, Japan

E.A. Man Department of Energy Technology, Aalborg University, Aalborg, Denmark

A. De Marchi Dipartimento di Elettronica e Telecomunicazioni, Politecnico di Torino, Torino, Italy

Unità di Ricerca, Consorzio Nazionale Interuniversitario di Scienze fisiche della Materia (CNISM), Politecnico di Torino, Torino, Italy

G. Min School of Engineering, Cardiff University, Cardiff, UK

A. Miozzo Institute for Energetics and Interphases, National Research Council of Italy, Padova, Italy

M. Morschel Faculty of Technology and Bionics, Rhein-Waal University of Applied Sciences, Kleve, Germany

A. Muscio Dipartimento di Ingegneria "Enzo Ferrari", Università di Modena e Reggio Emilia, Modena, Italy

M. Nesarajah Chair of Automation, Saarland University, Saarbrucken, Germany

S. Noel CEA, Grenoble Cedex 9, France

S.V. Novikov Ioffe Physical-Technical Institute, St. Petersburg, Russia

M. Ostorero Dipartimento di Chimica and NIS, Università degli Studi di Torino, Torino, Italy

E.Z. Parparov Ioffe Physical-Technical Institute, St. Petersburg, Russia

F. Passaretti Unità di Lecco, CNR, Istituto per l'Energetica e le Interfasi, Lecco, Italy

P.-Y. Pichon RGS Development B.V., Oudkarspel, The Netherlands

B. Plochmann University of Bayreuth, ZET, Chair of Functional Materials, Bayreuth, Germany

C. Potyrala School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, UK

A.A. Abd. Rahman Department of Micro-Energy & Green Technology, MIMOS Bhd., Kuala Lumpur, Malaysia

J. Räthel Fraunhofer IKTS, Dresden, Germany

M. Rauscher Daimler AG, Ulm, Germany

T. Richter Daimler AG, Ulm, Germany

M.C. Robbins European Thermodynamics Limited, Kibworth, Leicester, UK

K. Romanjek CEA, Grenoble Cedex 9, France

L. Rosendahl Department of Energy Technology, Aalborg University, Aalborg, Denmark

T. Sakamoto Department of Materials Science and Technology, Tokyo University of Science, Japan

C.L. Sansom School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, UK

E. Schaltz Department of Energy Technology, Aalborg University, Aalborg, Denmark

A. Schönecker RGS Development B.V., Oudkarspel, The Netherlands

M. Schönhoff Institute of Electrical Engineering and Information Technology, University of Paderborn, Paderborn, Germany

D. Schramm Universität Duisburg-Essen, Duisburg, Germany

M. Da Silva Swerea IVF, Mölndal, Sweden

J. Simon CEA, Grenoble Cedex 9, France

K. Simpson European Thermodynamics Limited, Kibworth, Leicester, UK

B. Steiner Magna Powertrain – Engineering Center Steyr GmbH & Co KG, St. Valentin, Austria

S. Sulaiman Department of Micro-Energy & Green Technology, MIMOS Bhd., Kuala Lumpur, Malaysia

H. Tjoa University of Bayreuth, ZET, Chair of Metrology and Control Engineering, Bayreuth, Germany

A. Tona Dipartimento di Elettronica e Telecomunicazioni, Politecnico di Torino, Torino, Italy

D. Wee Department of Environmental Science and Engineering, Ewha Womans University, Seoul, Republic of Korea

J. Wood School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, UK

N. Youn Department of Environmental Science and Engineering, Ewha Womans University, Seoul, Republic of Korea

G. Zanicchi Dipartimento di Chimica e Chimica Industriale, Università di Genova, Genova, Italy

Unità di Ricerca di Genova, INSTM, Genova, Italy

A. Ziggiotti Centro Ricerche FIAT, Orbassano, TO, Italy

About the Editors

Andrea Amaldi is an aeronautical engineer working at the Space Research and Technology Centre of the European Space Agency (ESA/ESTEC) in Noordwijk, The Netherlands. He works on materials and energy related projects and coordinates the EC-funded project ThermoMag on thermoelectricity R&D. He received his M.Sc. in Aeronautical Engineering from La Sapienza University of Rome in 1992 and in Materials Science from KU Leuven in 1995.

Francois Tang is currently a Research Fellow at the European Space Agency. His interests include the discovery of structural and functional light alloys, including thermoelectric materials, and additive manufacturing processes. He received his B.A.Sc. (2004) from the University of Ottawa and obtained his Ph.D. (2011) from McGill University in Mechanical Engineering where he studied the combustion of reactive dust mixtures.

Chapter 1
Effect of Structure and Microstructure on the Thermoelectric Properties of $Yb_{0.19}Co_4Sb_{12}$ Alloy

A. Castellero, M. Ostorero, A. Ziggiotti, M. Brignone, and M. Baricco

Abstract In this work, we report the results of the synthesis and characterisation of the n-type $Yb_{0.19}Co_4Sb_{12}$ thermoelectric alloy that is among the most promising materials for automotive applications with a value of ZT ranging around 1 at 600 K.

Sample preparation consisted of a sequence of three steps: (1) a solid/liquid reaction between the individual elements at 660 °C in a resistance furnace, (2) complete melting in an induction furnace, and (3) annealing at 730 °C in a resistance furnace for 0.75, 1.5, 3 and 6 h.

The unannealed samples consist of a mixture of Sb, $YbSb_2$, CoSb, $CoSb_2$ and $CoSb_3$. Only a fraction (about 50 %) of the thermodynamically stable $CoSb_3$-type phase could be obtained by free cooling of the melt. This is due to the complex solidification path, involving two peritectic transformations, that does not allow the system to reach the equilibrium.

Annealing at 730 °C promotes the formation of the desired $CoSb_3$-type phase up to fractions ~98 % after 3–6 h.

Thermoelectric properties were measured between 300 and 500 K. Longer annealing time caused an increase of the absolute values of the Seebeck coefficient as a consequence of the higher fraction of the $Yb_xCo_4Sb_{12}$ thermoelectric phase. In the case of electrical conductivity, no clear trend as a function of annealing time was observed.

Keywords Skutterudite • Processing • Thermoelectric material

A. Castellero (✉) • M. Ostorero • M. Baricco
Dipartimento di Chimica and NIS, Università degli Studi di Torino,
Via P. Giuria 7, 10125 Torino, Italy
e-mail: alberto.castellero@unito.it

A. Ziggiotti • M. Brignone
Centro Ricerche FIAT, Orbassano (TO), Italy

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Introduction

Filled skutterudites emerged as potential candidates for thermoelectric (TE) power generation in the 700–800 K temperature range [1]. In the case of n-type $CoSb_3$, a figure of merit (ZT) exceeding unity could be achieved with suitable Yb doping [2, 3]. Processing routes for obtaining the $CoSb_3$ single phase consist of several steps and are often time and energy consuming. Alloying of the elements can be typically obtained by ball milling (BM) [3], by continuous reaction between solid Co and liquid Sb [4] or by direct melting of the pure elements [5, 6]. BM processing allows complete alloying in one step and the as-milled powders are ready for subsequent compaction. However, BM processing typically favours contamination and surface oxidation of the powder. On the other hand, samples prepared from the liquid are often not homogeneous from the microstructural point of view. In fact, a complex solidification path, involving two peritectic reactions, slows down the kinetics of phase transformations. Therefore, extremely long annealing time (up to 10 days) is currently used for promoting the formation of the $CoSb_3$ single phase [6].

Attempts to shorten the synthesis were made by non-equilibrium techniques such as rapid solidification [7, 8], that also promotes nanostructuring and supersaturation of the phase with the dopant [7].

Despite the technological importance of controlling and optimising the synthesis of $CoSb_3$ single phase, only few systematic studies have been carried out. For example, Kim et al. [9] performed isochronal annealing in vacuum of undoped $CoSb_3$ at temperatures between 300 and 800 °C. Complete formation of the single phase was achieved after annealing at 400 °C for 24 h [9].

In this work, $Yb_{0.19}Co_4Sb_{12}$ was synthesised with a sequence of three steps: (1) a solid/liquid reaction between the pure elements, (2) complete melting in an induction furnace, and (3) annealing at 730 °C. The effect of the annealing time on the evolution of phase structure and microstructure is studied and correlated to the thermoelectric properties. It is shown that annealing for 6 h at 730 °C promotes the formation of $Yb_{0.1}Co_4Sb_{12}$ single phase. However, the samples are characterised by porosity (10–20 vol.%) that is detrimental for thermoelectric applications.

Experimental

Samples with nominal composition $Yb_{0.19}Co_4Sb_{12}$ (at.%) were prepared using elemental Co (Alfa Aesar, 99.8 % powder), Sb (Alfa Aesar, 99.999 % shot), and Yb (Aldrich, 99.9 % chip). A small excess of Sb (about 3 at.%) was added in order to compensate the loss of this element as a consequence of its evaporation during the thermal treatments. The elements were sealed in a BN-coated quartz crucible under an Ar atmosphere (6.1 kPa) and were heated at 660 °C for 2.5 h in a resistance furnace. The melting reaction was then completed in an induction furnace, under an Ar atmosphere. Finally, samples in bulk form (rods with diameter 9 mm and height 30 mm) were annealed at 730 °C for 0.75, 1.5, 3 and 6 h.

Structural analysis on ground powders obtained from the bulk samples was performed by X-ray diffraction (XRD) in transmission geometry (PANalytical X' Pert PRO, Cu Kα), using a rotating capillary. The experimental patterns were refined by Rietveld analysis using the MAUD software [10].

Microstructure and phase compositions were investigated by scanning electron microscopy (SEM) (Leica Stereoscan 420) equipped with an energy dispersive spectroscopy (EDS) microprobe (Oxford Instruments).

The density of the samples was measured with a pycnometer.

The electrical conductivity (σ) was measured with the four-probe method. The Seebeck coefficient (α) was measured with a homemade apparatus where the sample is held between two plates. The whole sample holder can be inserted inside a vertical electrical furnace under an inert atmosphere. The temperature difference between the two plates during a heating ramp is maintained by heating the lower plate by Joule effect. Thermocouple wires were used to measure both the temperature of the plates and the potential difference generated by the sample. The Seebeck coefficient was obtained by the following equation:

$$\alpha = \alpha_{\text{wires}} - \frac{\Delta V}{\Delta T} \tag{1.1}$$

where α_{wires} represents the Seebeck coefficient of the thermocouple wires, ΔV is the measured potential difference and ΔT is the measured temperature difference. All the measurements were performed in an Ar atmosphere in a temperature range between 25 and 300 °C.

Results and Discussion

Figure 1.1 shows XRD patterns related to the phase evolution in the bulk samples after annealing at 730 °C for different times. The XRD pattern of the non-annealed sample clearly shows the crystallographic reflections of additional phases to $CoSb_3$ (i.e. Sb, CoSb and $CoSb_2$). As expected, increasing the annealing time promotes the formation of the desired $CoSb_3$-type phase. The evolution of the volume fraction of the various phases is shown in Fig. 1.2 as a function of annealing time. It can be seen that, after only 3–6 h of annealing, the formation of the $CoSb_3$-type single phase is almost completed. Table 1.1 shows the values of the lattice parameter for the $CoSb_3$-type phase after different annealing times, together with the values of R_w indicating the quality of the fit for the Rietveld refinement. The increase of the lattice parameter with annealing time indicates that the $CoSb_3$-type phase progressively solubilises a larger amount of Yb. From the comparison of the lattice parameter for the sample annealed for 6 h ($a = 9.0462$ Å) with those reported in literature for undoped Co_4Sb_{12} ($a = 9.0347$ Å [11]) and $Yb_{0.18}Co_4Sb_{12}$ ($a = 9.0531$ Å [6]), we estimated that the maximum amount of Yb solubilised in $Yb_xCo_4Sb_{12}$ is $x \sim 0.1$ indicating that the annealing is not enough for obtaining a complete dissolution (i.e. $Yb_{0.19}Co_4Sb_{12}$).

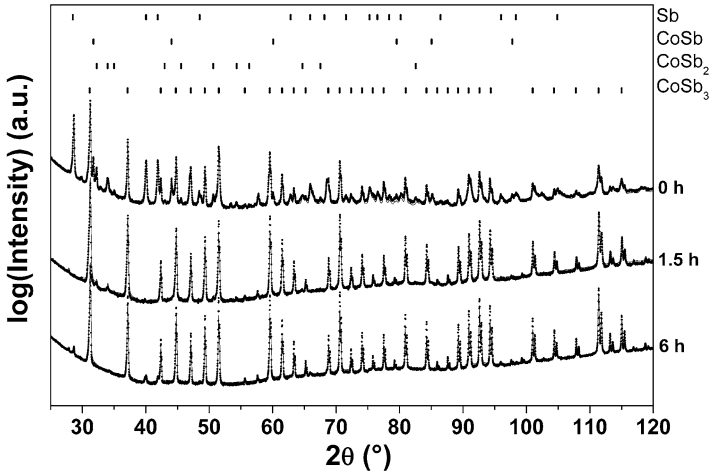

Fig. 1.1 X-ray diffraction patterns for $Yb_xCo_4Sb_{12}$ for selected annealing times. *Scattered curves*: experimental patterns; *continuous curves*: fitted patterns

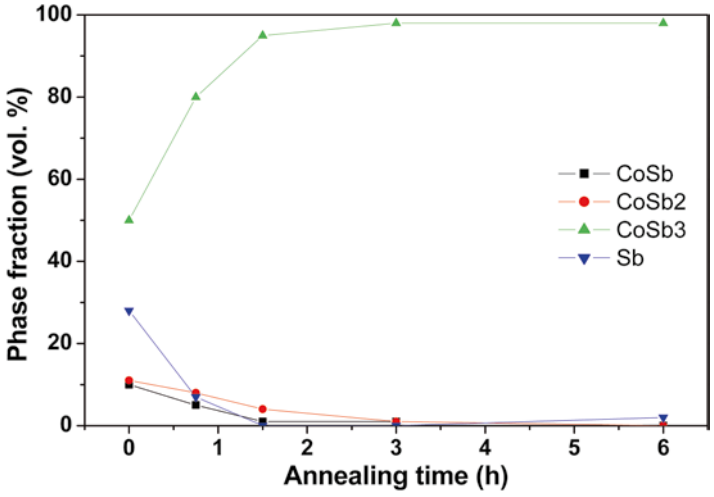

Fig. 1.2 Evolution of the phase volume fraction as a function of annealing time

The microstructural evolution as a function of the annealing time is shown by the backscattered electron SEM images in Fig. 1.3. In the unannealed sample, Fig. 1.3a, large dendrites of the primary CoSb phase are surrounded by $CoSb_2$ and $CoSb_3$ phases, where CoSb, $CoSb_2$ and $CoSb_3$ are immersed in an Sb matrix. The inset of Fig. 1.3a shows a eutectic microstructure consisting of $YbSb_2$ and Sb, showing that the Yb atoms were not fully dissolved in the skutterudite structure. After 0.75 h of annealing, Fig. 1.3b, CoSb, $CoSb_2$ and Sb tend to disappear in favour of $CoSb_3$, while a small fraction of the $YbSb_2$/Sb eutectic is still present (see inset).

Table 1.1 Values of the lattice parameter, a, of $Yb_xCo_4Sb_{12}$ and R_w for the Rietveld refinement of the X-ray diffraction patterns at different annealing times

Annealing time (h)	Lattice parameter of $Yb_xCo_4Sb_{12}$, a (Å)	R_w (%)
0	9.0403	2.5
0.45	9.0422	5.8
1.5	9.0428	5.4
3	9.0455	3.9
6	9.0462	6.1

After 3 h of annealing, Fig. 1.3c, only residual traces of CoSb and $CoSb_2$ are present, whereas the $YbSb_2$/Sb eutectic fully disappears. Finally, after 6 h of annealing, the microstructure shown in Fig. 1.3d becomes more homogeneous, with only a small fraction of Sb segregated at the grain boundaries of $CoSb_3$.

According to the Co-Sb equilibrium phase diagram [12], the sequence of reactions upon cooling is the following:

$$\sim 1065\,^{\circ}\mathrm{C}:\mathrm{L} \rightarrow \mathrm{CoSb} + \mathrm{L}' \tag{1.2}$$

$$936\,^{\circ}\mathrm{C}:\mathrm{L}' + \mathrm{CoSb} \rightarrow \mathrm{CoSb_2} \tag{1.3}$$

$$874\,^{\circ}\mathrm{C}:\mathrm{L}'' + \mathrm{CoSb_2} \rightarrow \mathrm{CoSb_3} \tag{1.4}$$

where L, L′ and L″ represent the liquid phase with different compositions. The presence of significant amounts of Sb, CoSb and $CoSb_2$ in the unannealed sample indicates that the two peritectic reactions (1.3) and (1.4) were not completed during the uncontrolled cooling after induction melting, due to the need of long-range diffusion. The effect of annealing is to homogenise the microstructure progressively, favouring the formation of the expected $CoSb_3$-type phase. The presence of residual Sb in the sample annealed for 6 h indicates that the excess of Sb added at the beginning did not evaporate completely. All the samples show a significant amount of porosity (ranging between 10 and 20 vol.%) irrespective of the annealing time. The measured density ranges between 6.2 and 7.0 $g.cm^{-3}$, corresponding to 81–92 % of the theoretical density (7.60 $g.cm^{-3}$). According to Geng et al. [5], the mechanism of the formation of porosity is the one explained below. During the peritectic reaction (1.3), $CoSb_2$ dendrites form inside the network of primary dendrites of CoSb formed from reaction (1.2). As a consequence of the solidification contraction, empty volumes remain between the solid phases because the pores cannot be easily filled by the remaining liquid. Since the pore fraction does not show a trend with annealing time, it can be supposed that porosity is caused by the mechanism described by Geng et al. [5] rather than from the evaporation of Sb. This is also supported by the fact that the excess of Sb was not fully evaporated, as evidenced in Fig. 1.3d. Finally, pores tend to become more rounded when the annealing time increases as a consequence of the reduction of the surface area.

The results of the thermoelectric properties are reported in Fig. 1.4. The evolution of the Seebeck coefficient, α, and of the electrical conductivity, σ, measured at different temperatures in function of the annealing time is reported in Fig. 1.4a, b, respectively.

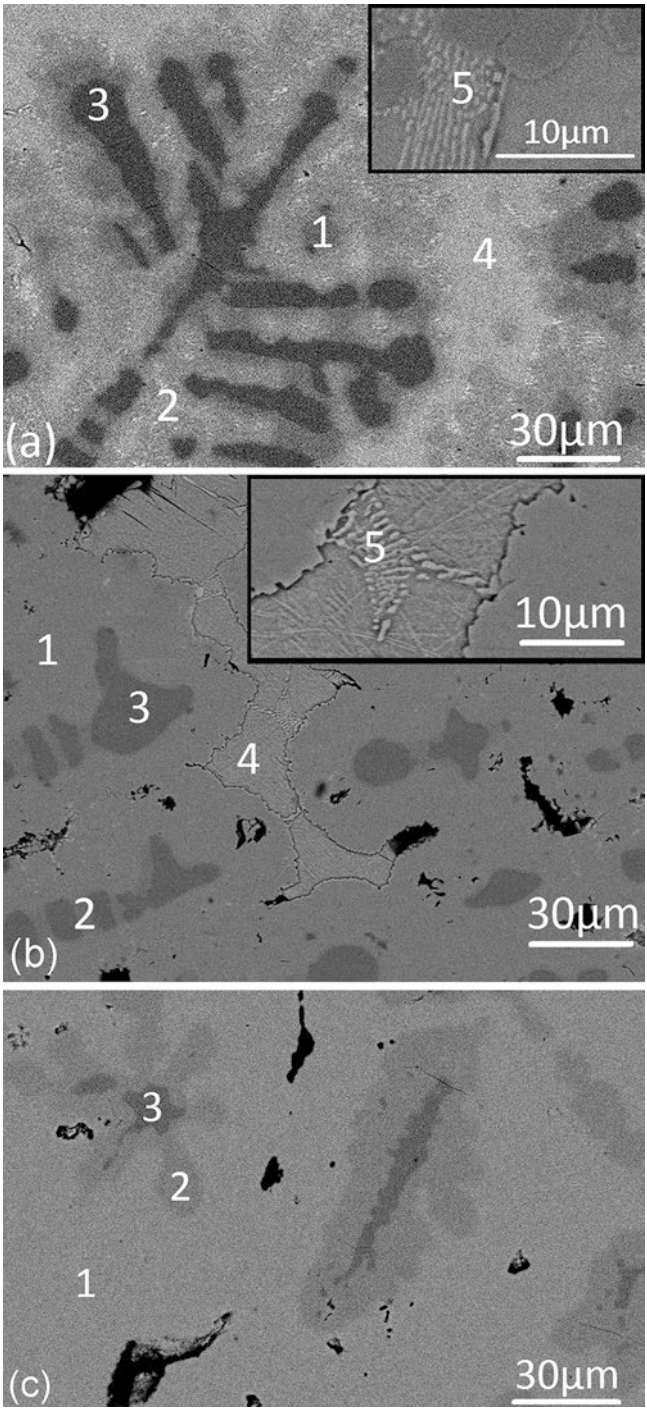

Fig. 1.3 SEM backscattered electron images of the microstructure evolution in $Yb_xCo_4Sb_{12}$ at different annealing times: (**a**) 0 h, (**b**) 0.75 h, (**c**) 3 h, and (**d**) 6 h. The *numbers* in the micrographs indicate the corresponding phases: (*1*) $CoSb_3$, (*2*) $CoSb_2$, (*3*) CoSb, (*4*) Sb, (*5*) $YbSb_2$