

OPEN ACCESS

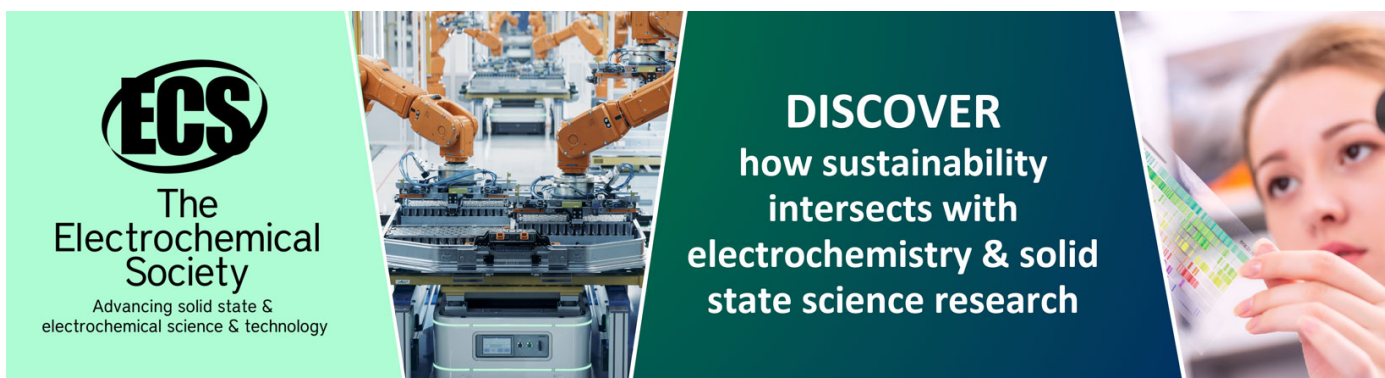
Characterization of nanoembedded alloyed thermoelectrics

To cite this article: L Lari *et al* 2014 *J. Phys.: Conf. Ser.* **522** 012040

View the [article online](#) for updates and enhancements.

You may also like

- [A novel ANN adaptive Riemannian-based kernel classification for motor imagery](#)
Fodil Yacine, Haddab Salah, Kachenoura Amar et al.
- [On the nature of superconductivity in the anisotropic dichalcogenide \$\text{NbSe}_2\(\text{CoCp}_2\)_x\$](#)
E-W Scheidt, M Herzinger, A Fischer et al.
- [Self-consistent modeling of microwave activated \$\text{N}_2/\text{CH}_4/\text{H}_2\$ \(and \$\text{N}_2/\text{H}_2\$ \) plasmas relevant to diamond chemical vapor deposition](#)
Michael N R Ashfold and Yuri A Mankelevich



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Characterization of nanoembedded alloyed thermoelectrics

L. Lari^{1,2,3}, C.J. Nuttall⁴, M.P. Copley⁴, R.J. Potter⁴, J. Simon⁵, N. Mingo⁵, and D.Ozkaya⁴

²Department of Physics, University of York, Heslington, YO10 5DD, York, UK.

³The York JEOL Nanocentre, York Science Park, Heslington, YO10 5BR, York, UK

⁴Johnson Matthey Technology Centre, Sonning Common, Reading, RG4 9NH, UK

⁵CEA-LITEN, 17 rue des Martyrs, BP166, 38042 Grenoble, France

E-mail: leonardo.lari@york.ac.uk

Abstract. Nano-structured alloyed materials have been demonstrated with a large improvement of their thermoelectric properties. These improvements have been obtained by tailoring a reduction in the material thermal conductivity. However, such improvements have not yet been demonstrated for bulk materials. Recently, a new approach based on phonon scattering theory has been successfully applied to bulk materials. In this approach, nanoparticles are embedded in a hosting matrix and act as multi-scale phonon scattering centres providing a reduction in the material thermal conductivity. In this work, {CoSi₂ (nanoparticle): SiGe (host)} nanocomposite thermoelectric materials and their precursors for the synthesis were investigated. The purpose of the investigation is to understand the inherent interactions of the nanoparticles with the support material.

1. Introduction

The performance of a thermoelectric device, in terms of energy conversion, depends on its thermoelectric *figure of merit* (ZT) which is defined as $ZT = S^2 \sigma T / k$, where k , T , σ , and S are respectively the thermal conductivity, the absolute temperature, the electrical conductivity, and the Seebeck coefficient [1]. While it has been a challenge for decades to increase ZT beyond unity, the so-called “alloy limit”, in the last decade $ZT > 1$ has been demonstrated by nanostructuring thermoelectric materials [2,3]. These improvements have been obtained by tailoring a reduction in the material thermal conductivity. However, such improvements have not yet been demonstrated for bulk materials. Recently, a new approach based on phonon scattering theory has been successfully applied to bulk materials demonstrating a $ZT \sim 1.7$ [4]. In this approach, nanoparticles (NPs) are embedded in a hosting matrix and act as multi-scale phonon scattering centres providing a reduction in the material thermal conductivity [5]. In this work, {CoSi₂ (NPs): SiGe (host)} nanocomposite thermoelectric materials and their precursors for the synthesis were investigated. CoSi₂ was chosen here because of a close cell parameters match (within 2%) with the hosting SiGe matrix. Due to similar contrast for precursors and product NPs in the images, as well as a close lattice match between matrix grains and product NPs, analytical and high resolution electron microscopy is needed to verify the transformation

¹ To whom any correspondence should be addressed.



occurrence during the material synthesis. Here we apply these techniques to understand the inherent interactions of the nanoparticles with the support material.

2. Methods

Two samples, labelled here *A* and *B* were provided for electron microscopy investigations. Sample *A* consisted of Co_3O_4 nanoparticles (NPs) in a hosting $\text{Si}_{0.8}\text{Ge}_{0.2}$ matrix. A homogenised powder was obtained from the sample using standard industrial mixing-milling equipment. Sample *B* was obtained from Sample *A* after proprietary thermal treatment of the homogenised powder under controlled catalytic environment.

TEM samples were prepared by using the following method: firstly holey carbon films supported by standard Cu TEM grids were heat treated by contact with a hot surface (lamp bulb) for 30 second on each side with temperature ramping from about 80 °C to 130°C; powders were then finely crushed between two glass slides and the grids were finally dusted with the crushed powders.

Electron microscopy analyses were performed using a CEOS double aberration corrected JEOL 2200FS (scanning) transmission electron microscope operating at 200keV equipped with an in-column Omega filter and a Thermo Scientific Noran 7 EDX detector system. Samples were “beam showered” [6] for 20min at the beginning of the investigations to limit hydrocarbon contamination.

3. Result and discussion

Figure 1a) shows a characteristic overview bright field (BF) STEM image of the homogenised powder from Sample *A* dispersed on holey carbon film (scale bar 1 micron). Nanoparticles are combined with the hosting matrix in clusters up to few microns in size. Figure 1b) shows a high resolution (HR) BF-STEM image of a NP with lattice resolution. Fast Fourier Transform (FFT) analysis was applied to the area in the red box inset in Figure 1b). Figure 1c) is a Bragg filtered image obtained by selecting the major Bragg spots (see inset) in the FFT image. Lattice spacing as shown in the FFT (figure 2d) were measured and compared with simulated diffractograms obtained using JEMS software [7].

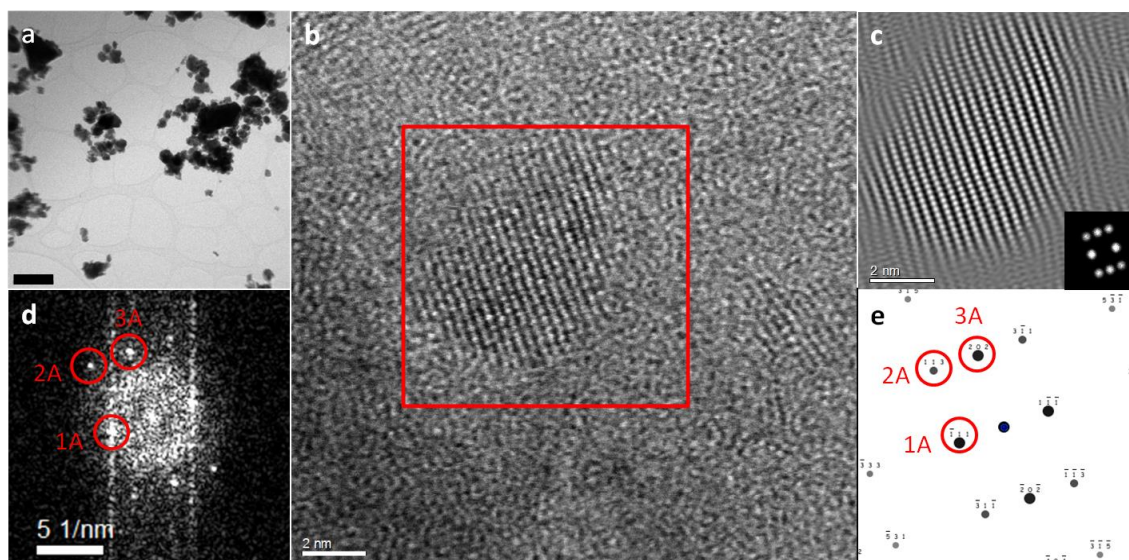


Figure 1. a) Overview of the sample (scale bar 1micron); b) BF-STEM image of a NP on the matrix; c) FFT filtered image using Bragg spots as in the inset; d) FFT from the area in the red box in b), spot labels refer to Table 1; e) simulated diffraction pattern for $\text{Si}_{0.8}\text{Ge}_{0.2}$ along the $[-1-21]$ zone axis

Lattice parameters were found to be consistent within 1-2% with $\text{Si}_{0.8}\text{Ge}_{0.2}$ ($a=0.54722$ nm, space group Fd-3m) [8] imaged along the $[-1-21]$ zone axis as in Figure 1e) (see Table 1 for the details). The closest diffractogram configuration for Co_3O_4 ($a=0.8084$ nm, space group Fd-3m) [9] was found to be along $[11-6]$ zone axis direction with a discrepancy of about 10% on the expected value. Other

crystallographic directions for the two crystals were excluded being inconsistent with the measured angle and distances. This result shows that the mix-milling process is able to finely grind the matrix down to nanoparticles with 5-10 nm in diameter.

The presence of the precursor oxidised Co nanoparticles (namely Co_3O_4) onto the matrix of sample *A* was confirmed by EDX analysis. The HAADF image in Figure 2a) shows a large grain decorated by NPs with sizes up to 20nm. EDX point analyses were applied to the NPs as well as the matrix. Co:Si and O:Si ratios are larger when the spectrum is acquired on the particle (point 2 Figure2) respect to when on the matrix (point 1 figure2) indicating a Co-O compound for the particle.

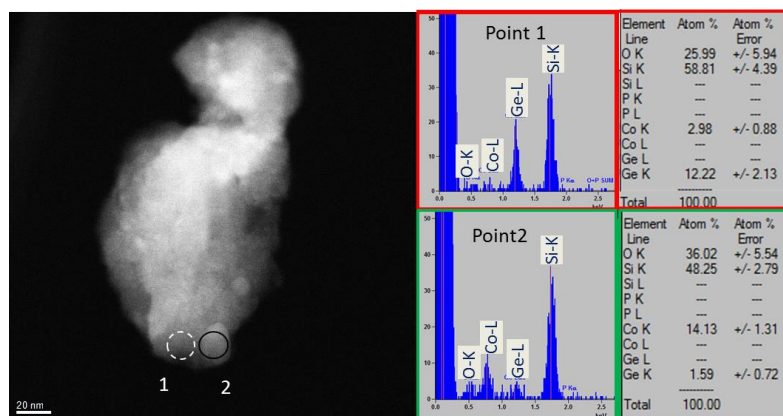


Figure 2. Sample *A*; EDX point analysis from the hosting matrix (point 1) and a Co_3O_4 particle on top of the matrix (point 2).

After thermal treatment in catalytic environment the material (Sample *B*) was investigated to look for traces of the transformation of the precursors Co_3O_4 nanoparticles into CoSi_2 . FFT analysis of HR-STEM images was applied to NPs found on the surface of the matrix (see Figure 3a). The lattice spacing visible along the zone axis imaged were measured in the Fourier transform and compared against the possible combination of crystals available within the set of elements

present in the sample. These include: Co_3O_4 [9], CoGe (high pressure crystal, $a=0.4637\text{nm}$, space group P 21 3)[10], Co_2Ge (space group P n m a) [11], $\text{Co}_{0.9}\text{Ge}_{0.1}$ ($a=0.35515\text{nm}$, space group F m -3 m) [12], $\text{Co}(\text{SiO}_3)$ (space group P b c a) [13], polymorph crystals of cobalt orthosilicate $\text{Co}_2(\text{SiO}_4)$ (I m m a, P b n m [14]; F d -3 m S[15]), and CoSi ($a=0.4438\text{nm}$, space group P 21 3)[16]. Analysis of the lattice spacings and their relative angles show values are consistent within 1% experimental error with CoSi_2 imaged along [001] zone axis as shown in Figure 3d) and Table 1. However, also SiGe grains along the same zone axis show close distances within 2-3%. This is expected since this combination of materials is chosen to minimise the lattice mismatch between hosting matrix and nanoparticles. Figure 3e) shows the simulated diffractogram for SiGe with additional crossed spots corresponding to Bragg spots with half lattice distance visible in the FFT which would be a forbidden reflection on a real electron diffraction pattern.

Table 1. FFT analysis of particles as from Figure 1 and 3.

Spot #	lattice planes	Measured lattice (nm)	Expected values (nm)	Measured angle to Spot 1	Expected angle to Spot 1
<i>Results from image 1A respect to $\text{Si}_{0.8}\text{Ge}_{0.2}$</i>					
1A	(-111)	0.320	0.3159(1.3%)	0.00	0.00
2A	(113)	0.168	0.1650(1.8%)	60.2	58.52
3A	(202)	0.194	0.1935(0.2%)	91.5	90.00
<i>Results from image 3a respect to CoSi_2</i>					
1Ba	(-220)	0.188	0.1897 (+0.7%)	0.00	0.00
2Ba	(-200)	0.268	0.2682(-0.1%)	44.40	45.0
3Ba	(0-20)	0.267	0.2682(+0.4%)	135.46	135.0
<i>Results from image 3a respect to $\text{Si}_{0.8}\text{Ge}_{0.2}$</i>					
1Bb	(2-20)	0.188	0.1935 (-3%)	0.00	0.00
2Bb	(200)	0.268	0.2737 (-2%)	44.40	45.0
3Bb	(020)	0.267	0.2737 (-2%)	135.46	135.0

To ascertain the presence of Co so the composition of the particle shown in Figure 3 can be attributed to CoSi_2 , EDX spectra were acquired from the particle+matrix (point *pt1*) and from the area adjacent the particle (matrix only) (dashed box in figure 3a, point *pt2*). Spectra are shown overlapped in Figure 3f with normalisation done on the area of the Ge-L α 1 peak. The spectrum from the particle+matrix shows larger Co and Si peaks. Quantification with calculated K factors, under thin film approximation, confirms that with the same amount of Ge on the particle+matrix and on the matrix, the changes in Co are due to the particle being CoSi_2 and not $\text{Si}_{0.8}\text{Ge}_{0.2}$.

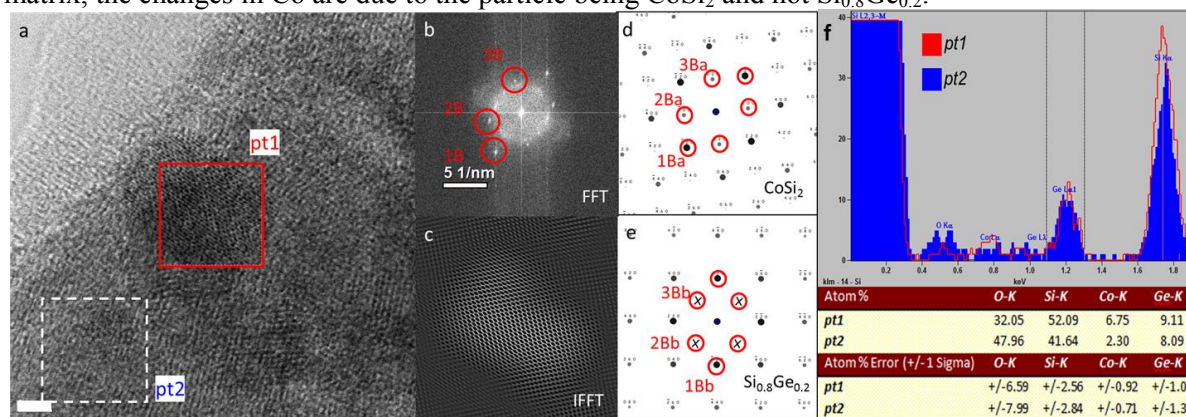


Figure 3. Sample B; a) BF-STEM image (scale bar 2nm); b) FFT from red box in a); c) Inverse FFT selecting 1B,2B,3B spot pairs; d) simulated DP for CoSi_2 along [100]; e) simulated DP for $\text{Si}_{0.8}\text{Ge}_{0.2}$ along [100]; f) EDX analyses from red and dashed boxes in Figure 3a).

4. Conclusions

In this paper a thermoelectric nano-composite material and its precursors were investigated by high resolution and analytical STEM. Structural analysis shows that the mix-milling preparation of the precursor materials produced a mixture of Co_3O_4 NPs, large grain and NPs from the SiGe matrix. Cobalt from the dispersed Co_3O_4 nanoparticles interacts with the SiGe host and forms CoSi_2 as a result of the proprietary thermal treatment. This is a desired transformation and should result in improved performance.

Acknowledgements

Financial support from EU Seventh Framework Programme FP7 NEAT “Nanoparticle Embedded in Alloys Thermoelectrics” is gratefully acknowledged.

References

- [1] Majumdar A., 2004 Science **303**
- [2] Hsu K. F. *et al.*, 2004 Science **303** 818.
- [3] Harman T. C. *et al.*, 2002 Science **297** 2229
- [4] Kim W *et al.*, 2006 Physical Review Letters 045901
- [5] Mingo N. *et al.*, 2009 Nanoletters **9** 711
- [6] Egerton RF, *et al.* 2004 Micron **35** 399
- [7] P. Stadelmann software <http://cimewww.epfl.ch/people/stadelmann/jemswebsite/jems.html>
- [8] Dismukes J.P. *et al.* 1964 J. Phys. Chem. **68** 3021-7
- [9] Smith, W.L. *et al.* 1982 Acta Crystallographica B **24** 1968
- [10] Larchev, V.I. *et al.* 1982 Journal of the Less-Common Metals **87** 53-57
- [11] Panday, P.K. *et al.* 1969 Journal of the Less-Common Metals **18** 175-202
- [12] Lecocq, P. *et al.* 1963 Annales de Chimie (Paris) **1963** 85-116
- [13] Sasaki, S. *et al.* 1982 Zeitschrift fuer Kristallographie **158** 279-297
- [14] Morimoto, N. *et al.* 1974 American Mineralogist **59** 475-485
- [15] Marumo, F. *et al.* 1977 Acta Crystallographica B **33** 713-716
- [16] P.A.Doyle and P.S.Turner 1968 Acta Cryst. **A24** 390.