Characterization of nanoembedded alloyed thermoelectrics

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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 $ZT = \frac{S^2 \sigma T}{k}$, where $k$, $T$, $\sigma$, 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.

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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 \( \text{Co}_3\text{O}_4 \) 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](image_url)

**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 \( \text{Co}_3\text{O}_4 \) (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$_3$O$_4$) 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.

After thermal treatment in catalytic environment the material (Sample B) was investigated to look for traces of the transformation of the precursors Co$_3$O$_4$ 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$_3$O$_4$[9], CoGe (high pressure crystal, a= 0.4637nm, space group P 21 3)[10], Co$_2$Ge (space group P n m a) [11], Co$_{0.5}$Ge$_{0.5}$ (a=0.35515 nm, space group F m -3 m) [12], Co(SiO$_3$) (space group P b c a) [13], polymorph crystals of cobalt orthosilicate Co$_2$(SiO$_4$) (I m m a, P b n m [14]; F d -3 m S[15]), and CoSi (a= 0.4438 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 |
|--------|----------------|------------------------|----------------------|--------------------------|--------------------------|
| Results from image 1A respect to Si0.8Ge0.2 |
| 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                    |
| Results from image 3a respect to CoSi2 |
| 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                    |
| Results from image 3a respect to Si0.8Ge0.2 |
| 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 CoSi₂, EDX spectra were acquired from the particle+matrix (point pt1) and from the area adjacent the particle (matrix only) (dashed box in figure3a, point pt2). Spectra are shown overlapped in Figure 3F with normalisation done on the area of the Ge-Lα1 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 CoSi₂ and not Si₀.₈Ge₀.₂.

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 CoSi₂ along [100]; e) simulated DP for Si₀.₈Ge₀.₂ 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 Co₃O₄ NPs, large grain and NPs from the SiGe matrix. Cobalt from the dispersed Co₃O₄ nanoparticles interacts with the SiGe host and forms CoSi₂ 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.

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