Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Fabrication of thermoelectric materials - Thermal stability and reproducibility of achieved efficiencies

Sima Aminorroaya Yamini[1]*, Mathew Brewis[1], Jacob Byrnes[1], Rafael Santos[1], Andrew Manettas[1], YanZhong Pei[2]

1. *Australian Institute for Innovative Materials, University of Wollongong, North Wollongong, NSW 2500, Australia*
2. *School of Materials Science and Engineering, Tongji University, 4800 Caoan Road, Shanghai 201804, China.*

Thermoelectric properties

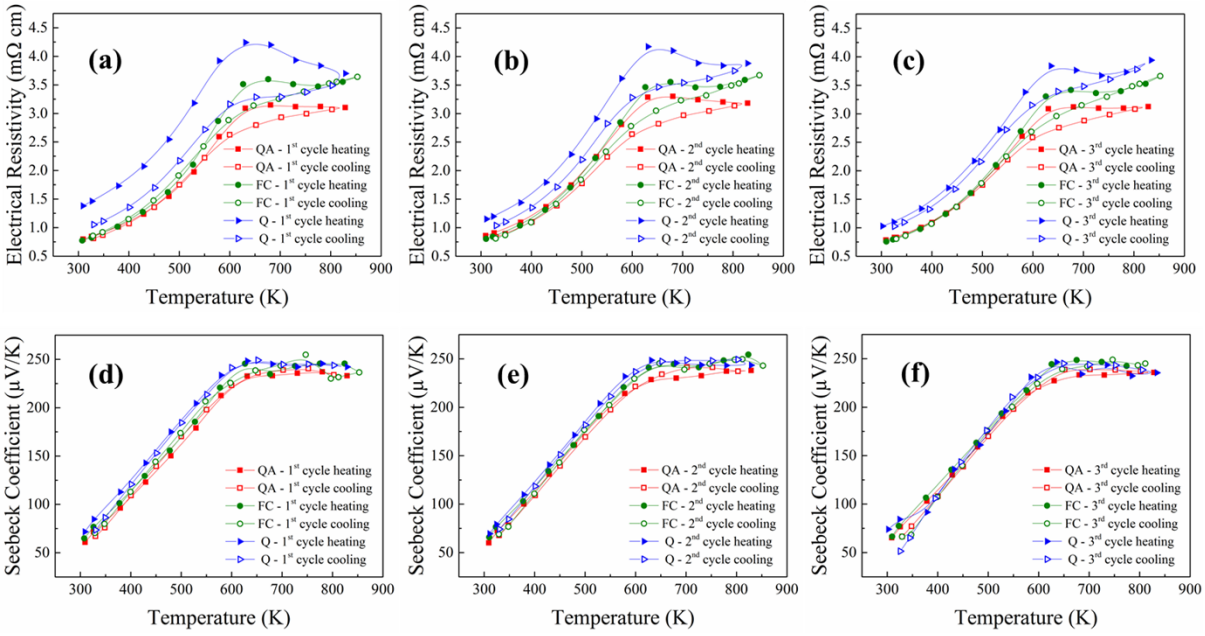

Figure S1. Temperature dependent electrical resistivity (mΩ·cm) of Q, FC and QA sintered bulk sodium-doped $(PbTe)_{0.55}$ $(PbS)_{0.35}(PbSe)_{0.1}$ samples for (a) first run, (b) second run, (c) third run of measurement; Temperature dependent Seebeck coefficient (μV/K) of Q, FC and QA sintered bulk sodium-doped $(PbTe)_{0.55}$ $(PbS)_{0.35}(PbSe)_{0.1}$ samples for (a) first run, (b) second run, (c) third run of measurements.

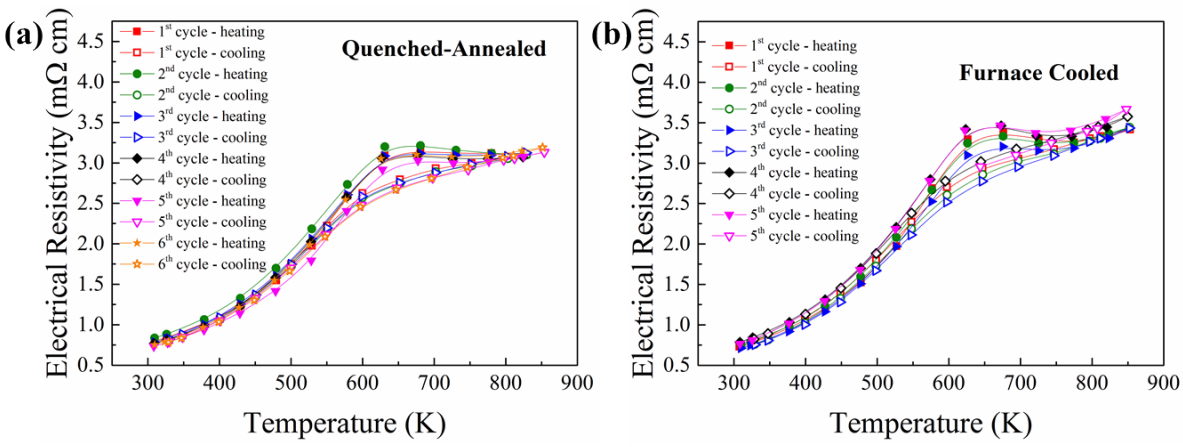

Figure S2. Temperature dependent electrical resistivity (mΩ·cm) of (a) QA and (b) FC sintered bulk sodium-doped $(PbTe)_{0.55}$ $(PbS)_{0.35}(PbSe)_{0.1}$ samples for frequent cycles of measurement

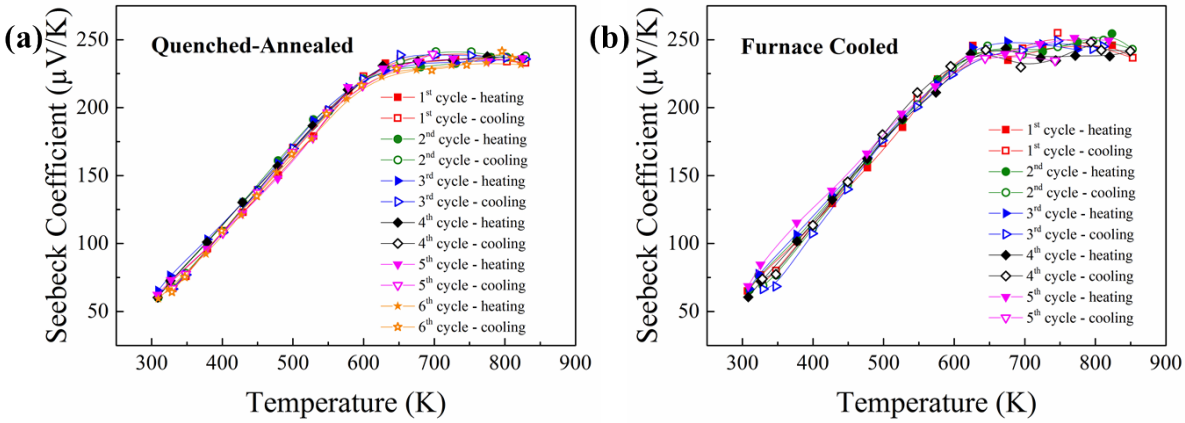

Figure S3. Temperature dependent Seebeck coefficient (μV/K) of (a) QA and (b) FC sintered bulk sodium-doped $(PbTe)_{0.55}$ $(PbS)_{0.35}(PbSe)_{0.1}$ samples for frequent cycles of measurements.

Crystal structure analysis

The XRD patterns obtained from sintered samples in Figure 1(b), show that all samples contain both PbS-rich and PbTe-rich phases. Detailed microstructural study of these samples by SEM and particle size analysis in Figure 5 revealed that FC sample contain precipitates much larger in size than QA one and Q sample presents the smallest precipitate size distribution. The average crystallite size was also calculated from the full width at half maximum (FWHM) of the reflected peaks, using Williamson-Hall plot for all sintered samples. The calculated crystallite size values are summarized in Table S1. The extracted data indicate that the crystallite size increases from Q to QA and FC samples. This confirms

the grain growth with annealing time. The longer the sample is exposed to high temperature, the larger is the crystallite size. This is in agreement with particle size distribution discussed in Figure 5. It should be noted that the individual precipitates observed in Figure 5 contain more than one crystallite. The low ratio of precipitates (< 30 wt%) in the matrix also results in peaks with low intensities in the XRD patterns, which contributes to an error in calculating the crystallite size.

Table S1. Average crystallite size for sintered sample, using Williamson-Hall plots

Sample	Quenched		Quenched Annealed		Furnace Cooled	
Phase	PbTe	PbS	PbTe	PbS	PbTe	PbS
Crystallite size (nm)	38	30	38	46	111	65

Electron microscopy analysis

The SEM image of the sintered FC sample, presented in Figure S4(a), illustrates the morphology and distributions of precipitates within the matrix. Compositional analysis of precipitates and matrix was performed using energy dispersive X-ray spectroscopy (EDS), using SEM. Figure S4(b) to (d) shows the X-ray map of the area shown in Figure S2(a) for Te, S and Se elements respectively. The composition of precipitates was found to be distinct from the matrix, with a larger concentration of sulfur and a deficiency of tellurium within precipitates. Figure S4 shows EDS spectra obtained from the precipitate and the matrix. The The Pb M line (2.342 keV) and sulfur K line (2.307 keV) overlap, and this composite peak is much more intense for the PbS precipitate (Pb + S) compared with the matrix (Pb only). Selenium was detected in both phases. This confirms that the matrix is a PbTe-rich phase and precipitates are PbS-rich.

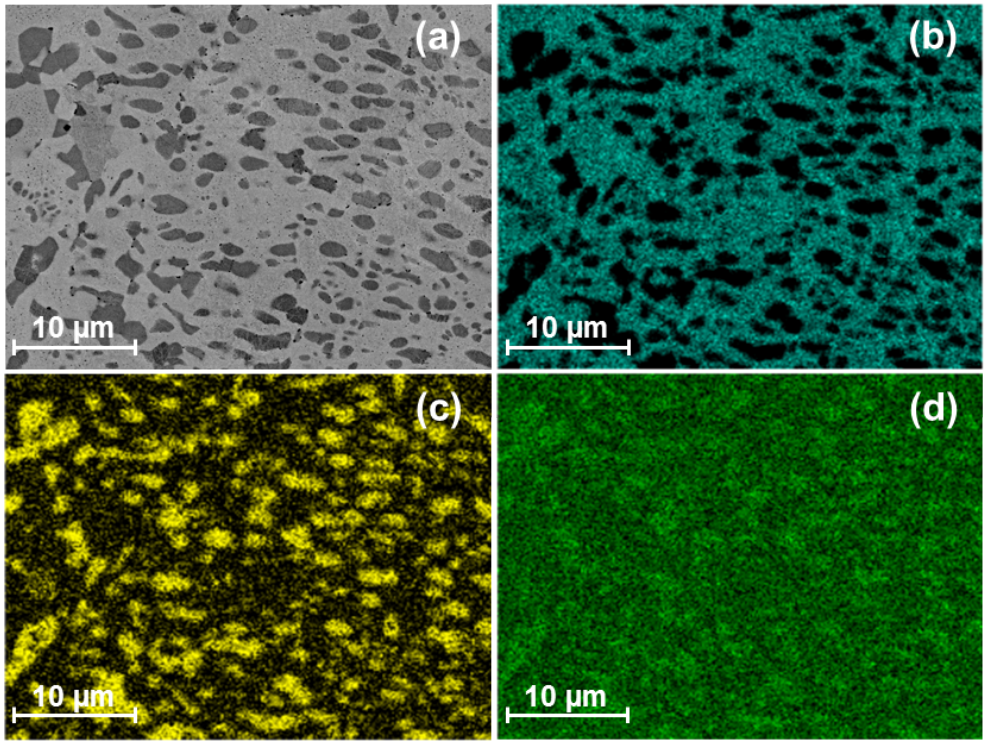

Figure S4. (a) SEM micrograph of sintered FC sample; X-ray spectroscopy map of (b) Te, (C) S, (d) Se on the region shown in (a).

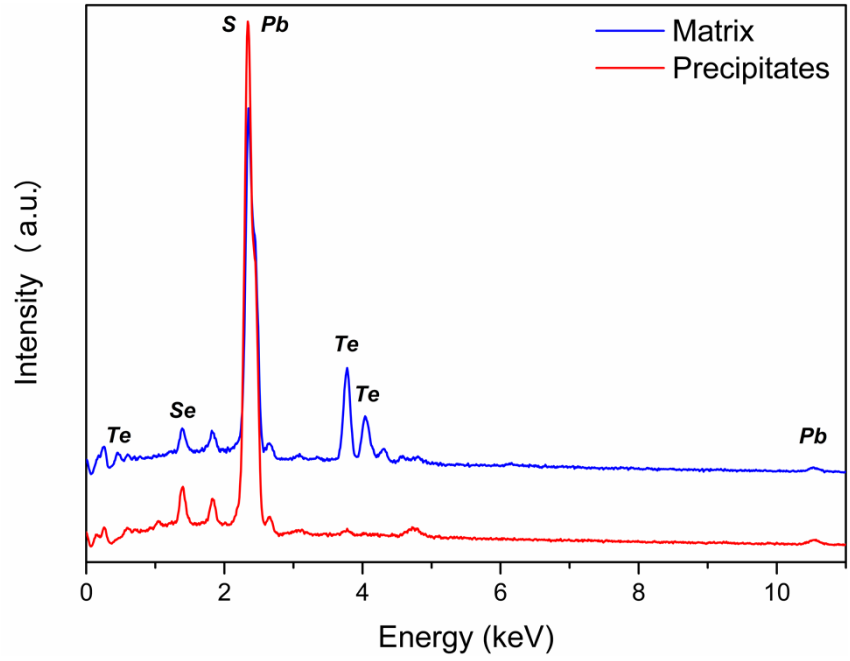

Figure S5. EDS spectra obtained from the matrix and the precipitates. The precipitate contains almost no Te.