Direct measurement of the thermoelectric properties of electrochemically deposited Bi$_2$Te$_3$ thin films

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The best known thermoelectric material for near room temperature heat-to-electricity conversion is bismuth telluride. Amongst the possible fabrication techniques, electrodeposition has attracted attention due to its simplicity and low cost. However, the measurement of the thermoelectric properties of electrodeposited films is challenging because of the conducting seed layer underneath the film. Here, we develop a method to directly measure the thermoelectric properties of electrodeposited bismuth telluride thin films, grown on indium tin oxide. Using this technique, the temperature dependent thermoelectric properties (Seebeck coefficient and electrical conductivity) of electrodeposited thin films have been measured down to 100 K. A parallel resistor model is employed to discern the signal of the film from the signal of the seed layer and the data are carefully analysed and contextualised with literature. Our analysis demonstrates that the thermoelectric properties of electrodeposited films can be accurately evaluated without inflicting any damage to the films.

Thermoelectric (TE) materials can directly convert heat into electricity. The canonical TE material is described as a "phonon-glass electron-crystal": a material that has the electrical properties of a crystal but the thermal properties of a glass$^1$. This ideal situation can only be achieved through the optimisation of the conflicting properties embedded in the dimensionless figure-of-merit, $zT = S^2\sigma T/(\kappa_e + \kappa_{ph})$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa_e$ is the electronic thermal conductivity, $\kappa_{ph}$ is the phonon thermal conductivity and $T$ is the temperature$^2$. The best material for room temperature applications is bismuth telluride (Bi$_2$Te$_3$), which has been synthesized employing a plethora of methods, such as co-evaporation$^{3,4}$, molecular beam epitaxy (MBE)$^5$, Metal Organic Chemical Vapour Deposition (MOCVD)$^6$, pulsed layer deposition (PLD)$^7$ and hydrothermal synthesis$^8$. Among them, the electrodeposition technique offers high deposition rates and scalability, as well as the ability to tune multiple parameters for the desired output$^9$. In addition, multiple materials can be electrodeposited, such as antimonides$^{10}$, oxides$^{11}$, metal–organic frameworks$^{12}$ and nitrides, among others$^{13}$. Many electrolytes have been utilised for the electrodeposition of bismuth telluride but undoubtedly, the electrodeposition from aqueous-acidic electrolytes is the most widespread$^{14}$. However, TE measurement of electrodeposited thin films has been extremely challenging due to the metallic seed layer underneath the electrodeposited film$^{15,16}$. Two approaches have been traditionally employed and are summarised in Supplementary Table I. The first approach is to eliminate the contribution of the seed layer by mechanically separating it from the electrodeposited thin film. The main issue with this approach is that the properties of thin films are highly affected by stress and strain phenomena induced during the transfer, as they are directly involved in the creation of defects. These defects will in turn change the electrical conductivity and Seebeck coefficient. Hence, the measured properties will not correspond to the as-synthesized film$^9$. The second approach is to measure the TE properties directly on top of the seed layer. This approach has proven to be troublesome or inaccurate thus far, as the seed layer can short-circuit the voltage along the layer during the measurement of the Seebeck coefficient and/or overestimate the value of the electrical conductivity$^2$.

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Our work demonstrates that the TE properties of electrodeposited films can indeed be accurately measured, building upon the second approach. We leverage upon the measurement technique developed by Kumar et al. and extend it to apply to electrochemically fabricated thin films\(^1\). For this purpose, bismuth telluride thin films have been electrodeposited onto indium tin oxide (ITO). The bismuth telluride films have been characterised in order to obtain a complete understanding of the morphology, composition and crystal structure and their impact on the TE properties. Thereafter, the temperature dependent TE properties of both ITO seed layer and Bi\(_2\)Te\(_3\) have been evaluated and the data thoroughly analysed. A proper benchmarking of the experimental data herein collected with the literature led to the conclusion that the electrodeposited films can be measured in an accurate manner without damages.

**Results**

The morphology of the electrodeposited films was investigated by means of Scanning Electron Microscopy (SEM). A typical image for the electrodeposited film has been shown in Fig. 1a. Nodular morphology was observed in all films, which is expected since all were grown at the same deposition potential (see “Methods” and Supplementary Section 2). The features comprising the film have a cauliflower-like shape, characteristic of films electrodeposited onto indium tin oxide (ITO). The bismuth telluride films have been characterised in order to obtain a complete understanding of the morphology, composition and crystal structure and their impact on the TE properties. Thereafter, the temperature dependent TE properties of both ITO seed layer and Bi\(_2\)Te\(_3\) have been evaluated and the data thoroughly analysed. A proper benchmarking of the experimental data herein collected with the literature led to the conclusion that the electrodeposited films can be measured in an accurate manner without damages.

**Figure 1.** (a) Typical top view SEM image of an electrodeposited bismuth telluride thin film. Scale bar is 10 μm (inset: SEM image showing the microstructure. Scale bar is 100 nm), (b) core-level Te 3d spectrum, (c) core-level Bi 4f spectrum and (d) Typical diffraction patterns for bismuth telluride films (Y\(_{\text{obs}}\) black circles) with the corresponding Rietveld refinement (Y\(_{\text{calc}}\) red line), the difference between experimental and modelled data (Y\(_{\text{obs}}\) − Y\(_{\text{calc}}\) blue line) and the respective Bragg positions of the different phases: Bi\(_2\)Te\(_3\) (green), ITO (orange) and TeO\(_2\) (purple). Inset: Typical 2D XRD pattern collected for the films. The rings indicate the polycrystalline nature of the sample.

Energy-dispersive X-ray spectroscopy (EDX) was carried out to obtain the composition of the films. Spectra were recorded across three different areas of the films in order to make the measurement reliable. The
composition of the samples is constant, deviated from the theoretical 40% atomic Bi and 60% atomic Te, corresponding to stoichiometric Bi2Te3. A summary of the results can be found in Table 1.

X-ray Photoelectron Spectroscopy (XPS) was used to investigate the oxidation state of the bonded elements as well as to further determine the composition of the electrodeposited films. Three measurements in different parts of the thin film were recorded and the standard deviation calculated (see Supplementary Section 9 for details about error calculations). The crystallite size (D_XRD) was calculated using the Scherrer equation (see Supplementary Section 3 for further details).

| Sample | t (μm) | EDX at.%Bi | EDX at.%Te | XPS at.%Bi | XPS at.%Te | D_XRD (nm) |
|--------|--------|------------|------------|------------|------------|------------|
| 1      | 1.20 ± 0.08 | 41.09 ± 0.21 | 58.91 ± 0.21 | 43.97 | 56.03 | 33.10 ± 0.16 |
| 2      | 2.50 ± 0.04 | 38.90 ± 0.14 | 61.10 ± 0.14 | 40.52 | 59.48 | 24.33 ± 0.10 |
| 3      | 3.75 ± 0.03 | 41.33 ± 0.31 | 58.67 ± 0.31 | 43.80 | 56.20 | 21.21 ± 0.12 |

Table 1. Summary of elemental and structural parameters of the three electrodeposited bismuth telluride thin films (referred to as Sample 1, Sample 2 and Sample 3). The thickness of the film (t) was determined by profilometry. Three measurements in different parts of the thin film were recorded and the standard deviation calculated (see Supplementary Section 9 for details about error calculations). The crystallite size (D_XRD) was calculated using the Scherrer equation (see Supplementary Section 3 for further details).

Figure 2. (a) Schematic representation of the fabrication workflow of the devices for TE measurements. First, the ITO area in which the bismuth telluride thin film will be electrodeposited is defined by masking with Kapton tape (represented by the orange stripe). Subsequently the unmasked ITO is etched out by immersion in a 6 M HCl solution (1), and only the defined ITO area for deposition is left. The second step (2) in the fabrication process is the electrodeposition of a bismuth telluride thin film on top of the ITO seed layer, purposely left out after etching. Finally, the device elements are evaporated (3): two thermometers, another two probes for resistivity measurement (labelled "Gold probe") and two heaters (labelled "Heater"), all visible in the optical microscope image in (a). (b) Schematic representation of the two-band model deployed for the modelling of the ITO seed layer (with properties S1, σ1 and t1) and the electrodeposited film (with properties S2, σ2 and t2).

composition of the samples is constant, deviated from the theoretical 40% atomic Bi and 60% atomic Te, corresponding to stoichiometric Bi2Te3. A summary of the results can be found in Table 1.

X-ray Photoelectron Spectroscopy (XPS) was used to investigate the oxidation state of the bonded elements as well as to further determine the composition of the electrodeposited films. Figure 1b and c shows the core-level of Te 3d and Bi 4f spectrum, respectively. The presence of the peaks at 573.15 eV and 583.5 eV in Fig. 1b and the peaks at 158.7 eV and 164 eV in Fig. 1c confirm that non-stoichiometric bismuth telluride (Bi2Te3) has been formed, in agreement with the EDX data. The extra peaks in both Fig. 1b and c indicate that a mixed phase comprising bismuth oxide and tellurium oxide has been formed, well along the lines of previous reports. Interestingly, the Bi content is higher in the surface part (XPS, sampling depth ~ 10 nm) for two samples (see data for Sample 1 and Sample 3 in Table 1) than that of Te compared to the vice-versa in the bulk (EDX, sampling depth depends on accelerating voltage but it is in the ~ 2–3 μm range). These results were compared to previous studies and made us conclude that there is no strong, clear correlation between the electrochemical method and the higher content of atomic Bi in the surface of the film (measured by XPS) compared to higher content of atomic Te in the bulk of the film (measured by EDX). Hence, the only thing we can say conclusively is that both techniques indicate non-stoichiometry. Thus, we have attributed this discrepancy to the different sampling depth between both techniques, as several authors also concluded. The crystal structure of the electrodeposited films is investigated by means of x-ray diffraction (XRD). Figure 1d shows a typical diffraction pattern with the corresponding Rietveld refinement. The majority of peaks are fitted to the "Thellurobismutithe" file (JCPDS file n° 01-083-5976). Other peaks are assigned to the substrate, indium tin oxide (ITO, JCPDS file n° 01-089-4596) and tellurium oxide (TeO2, JCPDS file n° 01-070-4297). The low intensity of the peaks corresponding to TeO2 indicates that it is only present in the surface, which is in line with the results obtained during XPS analysis.
The crystallite size ($D_{\text{XRD}}$) of the films are summarised in Table 1. A detailed analysis of the XPS spectra and the XRD pattern and crystallite size can be found in Supplementary Section 3.

Finally, the device structure for TE measurements is fabricated containing two heaters, two resistance-based thermometers with four probe contacts, and two additional electrodes for four-probe electrical resistivity measurements (Fig. 2). Before proceeding to the measurement, the film is disconnected from the heaters to prevent electrical leakage. The temperature dependent in-plane Seebeck coefficient and electrical conductivity have been measured simultaneously\(^1\). The temperature dependent homemade thermoelectric measurement setup is designed inside a high-vacuum cryostat. The device is mounted on a 24-pin chip carrier using GE varnish. The electrical connections between the device and chip holder were made using a West Bond wire-bonder, threaded with aluminium wire.

A two-band model is applied to the seed layer, 30 nm of ITO (Material 1) and electrodeposited bismuth telluride (Material 2) thin film; samples with different thicknesses for Material 2 are fabricated. These two films are modelled as two resistors electrically connected in parallel (see Fig. 2b). Equations 1 and 2 describe the effective conductivity ($\sigma_{\text{eff}}$) and effective Seebeck coefficient ($S_{\text{eff}}$) measured for the parallel combination of seed layer and thin film\(^3\):

\begin{align}
\sigma_{\text{eff}} &= \frac{\sigma_1 t_1 + \sigma_2 t_2}{t_1 + t_2} \\
S_{\text{eff}} &= \frac{S_1 \sigma_1 t_1 + S_2 \sigma_2 t_2}{\sigma_1 t_1 + \sigma_2 t_2}
\end{align}

where $S_1$, $\sigma_1$, $S_2$, $\sigma_2$ are the Seebeck coefficient and electrical resistivity of ITO and Bi$_2$Te$_3$, respectively. The thickness of the materials is represented by $t_1$ and $t_2$ and they correspond to ITO and Bi$_2$Te$_3$.

In order to obtain the electrical conductivity of the electrodeposited films, the materials must be chosen carefully. According to Eq. (1), if one of the materials has a much larger conductivity than the other one for similar thickness range (for instance, when the product $\sigma_1 t_1$ is larger than $\sigma_2 t_2$), the signal that will be read ($\sigma_{\text{eff}}$) will be close to $\sigma_1$. Hence, each layer's electrical conductance should be of the same order of magnitude, although this is difficult in practice due to the metallic nature of seed layer and the semiconducting nature of the film. Regarding the ratio, ideally both materials should have similar range of thickness\(^3\). Thus, the chosen materials are ITO (Material 1) and Bi$_2$Te$_3$ (Material 2). ITO is a heavily doped semiconductor with high electrical conductivity, but lesser than that of common seed layers for electrodeposition (e.g., gold has a larger electrical conductivity, $\sigma \sim 4.1 \times 10^5$ S cm$^{-1}$). In addition, the ITO seed layer sits on top of quartz. This material has been chosen as substrate because it has a low thermal conductivity thus ensuring the ability to generate a sufficient temperature gradient\(^1,3,8,9\). Material 2 can be any electrodeposited material. In principle, the seed layer is chosen by choosing the target material. This means that oxides such as antimony doped tin oxide (SnO$_2$:Sb), which have slightly lower values of electrical conductivity ($\sim 10^3$ S cm$^{-1}$, depending on the fabrication technique) are more suitable for target materials that are less conductive, such as bismuth selenide. If Material 2 is a film even more insulating, for instance bismuth sulphide, an even more insulating oxide is to be utilized, such as amorphous indium and gallium doped zinc oxide (a-In-Ga-Zn–O, conductivities in the order of $10^4$–$10^5$ S cm$^{-1}$) in the case of a transparent conductive oxide or a semiconductor, such as phosphorus doped silicon (SiP, with conductivities in the order of $10^2$ S cm$^{-1}$)\(^4\). Of course, this will also be linked to the ability to electrodeposit Material 2 on Material 1, since electrodeposition requires good electrical contact between the two of them for the deposition current or voltage to be applied without impediment. We recommend the reader to take extra precaution because selecting the pair Materials 1–2 is very critical and of upmost importance in order to ensure a successful experiment and clear data interpretation.

Figure 3. (a) Temperature dependent 4-probe I-V measurements (I-source, V-measured) for ITO (30 nm) and (b) Temperature dependent electrical conductivity of the ITO seed layer, compared with the literature.
First, the temperature dependent TE properties of the ITO seed layer were characterised. Figure 3a shows the I-V curves performed at different temperatures in a 4-probe arrangement. The voltage rises linearly with the current, demonstrating the ohmic nature of the contact17. Figure 3b compares the temperature dependent electrical conductivity of the ITO seed layer ($\sigma_1$ in Eq. 1 and Eq. 2) with different literature values. As it can be seen, the values considerably differ from one author to others. This different values are attributed to the different carrier concentrations and different mobility of the ITO41. The crystallite size of the ITO films employed in this work was calculated using the Scherrer Equation, based on the XRD peak broadening of the (222) peak and is equal to 31.43 nm.

The carrier concentration of the ITO seed layer is determined by Hall measurements (see Supplementary Section 5) and equal to $4.42 \times 10^{21}$ cm$^{-3}$ at room temperature. The mobility was determined to be 2.11 cm$^2$ V$^{-1}$ s$^{-1}$ at the lowest temperature recorded in this work (30 K). Larger crystallite sizes have been associated with higher mobility and therefore higher conductivity, which explains why the ITO measured in this work has larger electrical conductivity than the values reported by Lin et al.42 and some samples synthesised by Kytin et al.43 and Liu et al.44 (see Supplementary Section 5 for more details). The difference in conductivity with respect to the conductivity reported by Li et al. probably is due to the fact that they did not conduct a direct measurement of the carrier concentration by means of Hall measurement, but they calculated their carrier concentration, using a value of effective mass of $m^* = 0.4m_e$ from a Seebeck measurement. Hence, it could be possible that the carrier concentration differs from the reported theoretical values45,46.

**Figure 4.** (a) Change in resistance of both thermometers ($R_{top}$ is the resistance of hot thermometer and $R_{bottom}$ is the resistance of cold thermometer) as a function of temperature for the ITO seed layer. The black lines correspond to linear fits $R(T) = R_0 + AT$. For the cold thermometer, this equation is $R(T) = 11.86 (\pm 0.042) + 0.068 (\pm 1.96 \times 10^{-4}) T$ and for the hot thermometer $R(T) = 12.90 (\pm 0.054) + 0.0681 (\pm 2.45 \times 10^{-4}) T$. (b) Open circuit voltage dependence with the temperature difference. The red line corresponds to a linear fit in order to obtain the Seebeck coefficient.

**Figure 5.** Temperature dependent Seebeck coefficient for the ITO seed layer ($S_1$ in Eq. 2) benchmarked against previous reports.
The general expression for the full Boltzmann Transport Equation (BTE) for the Seebeck coefficient can be given as:

\[ S = -\frac{k_B}{q} \left[ \eta - \frac{(r + \frac{3}{2}) F_{r+\frac{1}{2}}(\eta)}{(r + \frac{3}{2}) F_{r+\frac{1}{2}}(\eta)} \right] \]  

where \( k_B \) is the Boltzmann constant, \( q \) is the elemental charge, \( \eta \) is the reduced Fermi energy, \( F(\eta) \) is the Fermi integral and \( r \) is the scattering parameter. From Eq. (3), in the degenerate limit, the Mott formula can be used to understand the trend where the Seebeck coefficient depends on the ratio \( m^*/n^2/3 \). Thus, the change in the ratio is expected to be given by the change in carrier concentration for the different samples. This change is the direct cause of the change in the slopes of the curves, but it is difficult to estimate since the other experiments did not report a carrier concentration.

Next, calibration of the fabricated thermometers is performed: the correlation between the resistance of the thermometers and the temperature is evaluated (further discussion is presented in Supplementary Section 4), as depicted in Fig. 4a. A complete derivation of this procedure can be found elsewhere. Fig. 4b shows the measured open-circuit voltage (\( V_{oc} \)) as a function of temperature gradient (\( \Delta T \)). A linear relation is observed as expected with slope of \(-6.42 \mu V K^{-1}\). Considering the aluminium Seebeck coefficient of \(-1.7 \mu V K^{-1}\), the actual room temperature Seebeck coefficient of ITO was calculated using Supplementary Eq. S4 (see Supplementary Section 4) and found to be \(-7.8 \mu V K^{-1}\). This is in line with the reported values of Seebeck coefficient for ITO.

The temperature dependent Seebeck coefficient for different ITO samples is compared in Fig. 5. As observed, the change of Seebeck with respect to the temperature follows a linear decreasing trend but the slope is not the same. The general expression for the full Boltzmann Transport Equation (BTE) for the Seebeck coefficient can be written as:

\[ S = -\frac{k_B}{q} \left[ \eta - \frac{(r + \frac{3}{2}) F_{r+\frac{1}{2}}(\eta)}{(r + \frac{3}{2}) F_{r+\frac{1}{2}}(\eta)} \right] \]  

Figure 6. Temperature dependent electrical conductivities (a) and Seebeck coefficient (b) for different parallel combination samples (Sample 1 to Sample 3) and the exfoliated sample (Exfoliated Sample 2). The difference in electrical conductivity is a consequence of the different crystallite sizes for the samples (see Table 1).
temperature electrical conductivity of the films ranges from 40 to 100 S cm⁻¹, attributed to the different crystallite and 1 M HNO₃ (Fisher, 69%) were dissolved in deionised water. The volume employed for electrodeposition is 56, likely due to the fact that they measured bulk still far from the overdoped samples obtained by Zalar et al.55. However, Na and co-workers report larger Seebeck coefficient. They attributed it to a lower carrier concentration although no Hall measurements were reported. This is explained by two factors: (a) different plating bath and different precursors (8 mM Bi powder and 10 mM Te powder), leading to a different carrier concentration and (b) different electrochemical deposition (pulsed deposition), leading to different film quality (thus having a direct impact on the crystallite size and the compactness)55.

The power factor (PF = S²/σ) of these films is low, most likely due to the low Seebeck coefficient, being the maximum value 0.050 μW K⁻² cm⁻¹ at 350 K (Sample 1), as shown in Supplementary Fig. S13. These values are still far from the overdoped samples obtained by Zalar et al.56, likely due to the fact that they measured bulk samples (therefore better compactness and crystallite sizes) and we measured thin films. With respect to other electrodeposited films, reports by Trung et al. (PF = 0.5 μW K⁻² cm⁻¹) and Scidone et al. (PF = 0.60 μW K⁻² cm⁻¹), are what we should expect, since both deployed a similar electrochemical method for Bi₂Te₃ growth57,58. Na et al. used a different electrochemical technique, pulsed deposition for Bi₂Te₃ growth and obtained larger power factor (4.19 μW K⁻² cm⁻¹ and 4.22 μW K⁻² cm⁻¹), thanks to the improvement in the quality if the films55. It is noteworthy to mention that all the aforementioned authors mechanically separated the film from the seed, thus introducing more defects in the process. This will introduce uncertainties in the measurement, as well as changing the properties of the as-deposited films.

In general, however, the power factor of electrodeposited films is lower than the power factor of other thin film deposition techniques59. This is due to the better quality films (compactness and morphology) that result from physically growth techniques, such as flash evaporation (PF = 18.7 μW K⁻² cm⁻¹). Bulk Bi₂Te₃ also show larger power factor compared to electrodeposited films. Saleemi et al. reported PF of 28.25 μW K⁻² cm⁻¹ from sintered powders59. This large PF is achieved because their spark plasma sintering procedure rendered highly densified ingots whilst preserving the nanostructure. For electrodeposited films, addition of polyvinyl alcohol to the plating bath allowed Lei et al. to improve both thickness and compactness of the films60. A variety of such advanced thin films can be deposited and our parallel TE measurement technique allows for direct, in-plane characterization of the Seebeck coefficient and electrical conductivity, therefore providing researchers with a way to perform such experiments in the future.

Conclusions
Bismuth telluride thin films have been deposited onto commercially available ITO at low overpotentials. The morphology of the deposits is nodular, as expected from an electrodeposition at low over potential under mass transport regime. The films are non-stoichiometric, with the composition deviating from the ideal 40% atomic Bi – 60% atomic Te, being slightly Bi rich. The XPS analysis confirmed that most Bi is bound to Te although some appear to form an oxide Bi-O–Te. The crystallite size of the films has been calculated and the results range from ~21 to ~33 nm. A two-band model has been employed to fully understand the TE transport. The room temperature electrical conductivity of the films ranges from 40 to 100 S cm⁻¹, attributed to the different crystallite sizes of the films. The Seebeck coefficient shows almost no variation for the three samples for the same temperature range, with values from ~5 μV K⁻¹ to ca. ~20 μV K⁻¹. It is concluded that the main difference in the herein fabricated bismuth telluride and the literature values are the carrier concentrations. Particularly, the Seebeck coefficient is lower than optimal due to a very large number of antisite defects introduced during electroplating, that act as self-dopants and increase the carrier concentration past the optimal value. This is confirmed by Hall measurements conducted on an exfoliated film (Seebeck coefficient equal to ~11.8 μV K⁻¹ for a carrier concentration equal to 8.7 x 10²⁰ cm⁻³). Thus, we can affirm that our method accurately measures the TE properties of electrodeposited thin films without the involuntary introduction of defects due to external forces.

Methods
Reagents. Bismuth telluride was electrodeposited from an aqueous electrolyte previously reported by Martin-Gonzalez et al.34. Briefly, 7.5 mM of Bi (elemental, Alfa Aesar, 99.999%), 10.0 mM TeO₂ (Alfa Aesar, 99.999%) and 1 M HNO₃ (Fisher, 69%) were dissolved in deionised water. The volume employed for electrodeposition is 15 mL. Before electrodeposition, the electrolyte was degassed for at least 20 min by gently bubbling nitrogen.

Electrochemical techniques. Cyclic voltammetry (CV) and chronoamperometry were performed using an AutoLab Lab PGSTAT128N potentiostat/galvanostat. For CV experiments, a standard 3 electrode configuration with a Saturated Calomel Electrode (SCE, saturated KCl) reference electrode and platinum (Pt) grid counter electrode and a 1 mm diameter Pt disc working electrode (WE) were employed. For electrodeposition experiments, the reference and counter electrodes were kept the same while the WE was changed to a segment of 30 nm of indium tin oxide (ITO 80Ω/sq, composition SnO₂:In₂O₃ = 1:9, Latech) on top of 1.5 mm quartz substrate of area 7 x 7 mm². This 30 nm ITO on top of quartz WE will be referred to as substrate. Electrodeposition was conducted at constant potential equal to ~0.1 V vs. SCE. We kindly refer the reader to Supplementary Section 2 for further details.
Conducted using Full Prof61. The error of the fitting was 
all scans was 0.02°. Phase identification was conducted using Bruker’s EVA software. Rietveld refinement was 
the INCA software, available in the Jeol JSM 7600F FEG-SEM.

X-ray spectroscopy (EDX). Spectra were collected by means of an Oxford INCA EDS detector incorporated with 
the INCA software.

Theta Probe XPS equipped with a monochromatic Al Kα X-ray (hν = 1486.7 eV) X-ray source was used for spectra 
acquisition. The X-ray spot was adjusted to 400 μm in diameter with an x-ray incident angle fixed to 30° with 
respect to normal surface. Charge compensation was achieved using low energy electron flooding. Survey scan 
were acquired at step = 1 eV and pass energy of 200 eV whilst the narrow scans were acquired at step = 0.1 eV 
and pass energy = 40 eV. Peak deconvolution and elemental quantification were conducted using the Avantage 
software.

Data availability
Data available upon reasonable request from Jose Recatala-Gomez (j.recatala@soton.ac.uk).

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Characterization techniques. A Jeol JSM 7600F FEG-Scanning electron microscopy (SEM) was utilised to investigate the morphology of the samples. The composition of the samples was studied by Energy Dispersive X-ray spectroscopy (EDX). Spectra were collected by means of an Oxford INCA EDS detector incorporated with the INCA software, available in the Jeol JSM 7600F FEG-SEM. XRD was conducted by means of a Bruker D8 Advance equipped with a 2D detector. The step size used for all scans was 0.02°. Phase identification was conducted using Bruker’s EVA software. Rietveld refinement was conducted using Full Prof61. The error of the fitting was χ² = 13.5.

Data availability
Data available upon reasonable request from Jose Recatala-Gomez (j.recatala@soton.ac.uk).
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Author contributions

The project was conceived by K.H. and I.N. J.R.-G. and P.K. synthesized the samples, conducted the materials characterization and the thermoelectric measurements. A.S. and A.B. conducted X-ray diffraction experiments and analysed the data. J.R.-G., K.H. and I.N. wrote the manuscript. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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