

Supplementary Data

The Rietveld refinements of the starting target of composition Cu_6Sn_5 (Figure S1) and of the starting thin films (Figure S2) are given. The electrochemical potential profiles obtained at C/100 for Na- Cu_6Sn_5 are presented in Figure S3. Raw Mössbauer spectroscopy data and fits corresponding to a single peak response are shown in Figure S4. Alternative fits to the Mössbauer spectroscopy data are presented in Figure S5. The XRD patterns for the target and thin films of nominal composition ' $\text{Cu}_6\text{Sn}_{10}$ ' are shown in Figure S6, and the Rietveld refinement of the XRD pattern of the thin films is presented in Figure S7.

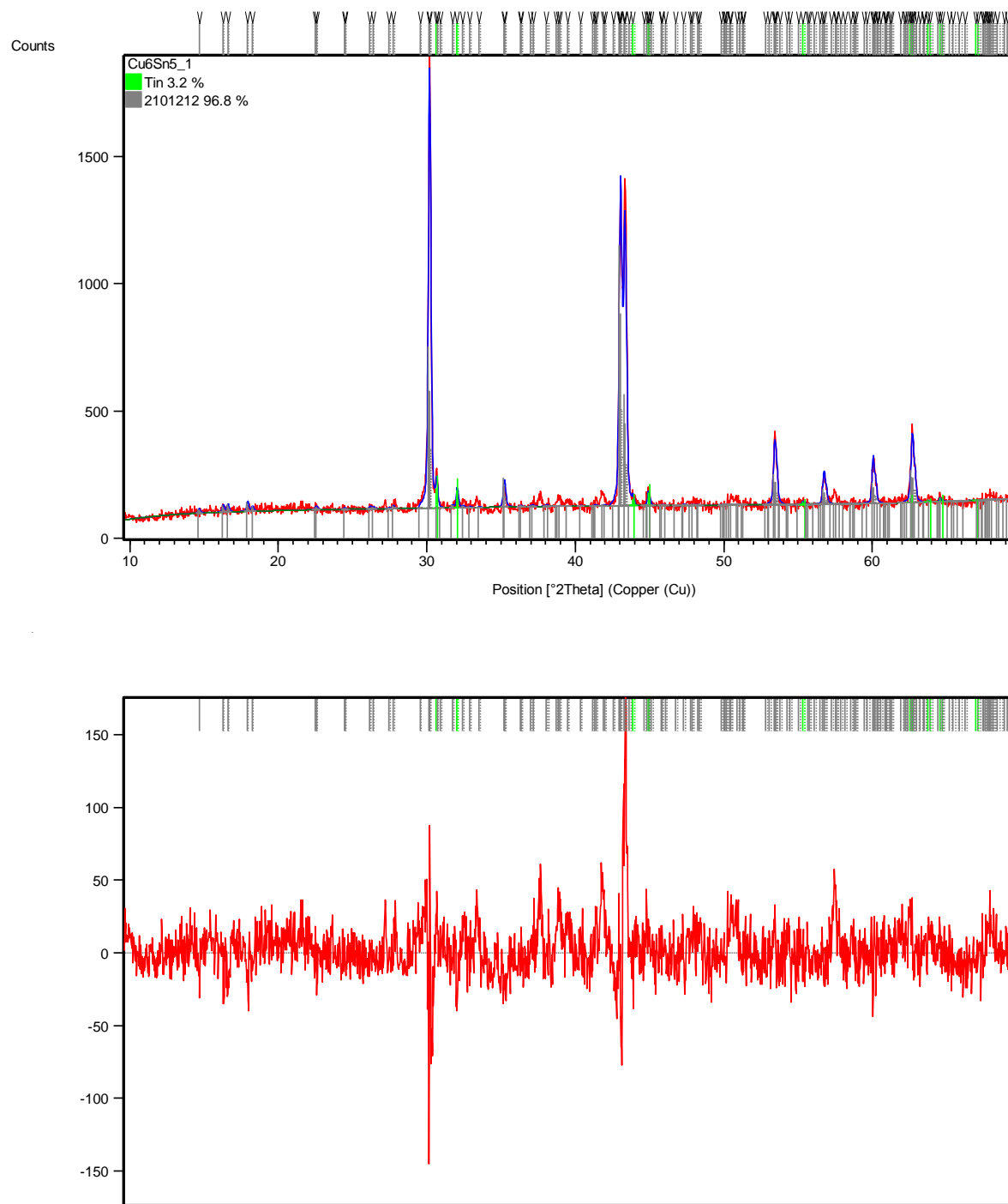


Figure S1. XRD refinement of the starting η' - Cu_6Sn_5 (C2/c) target material.

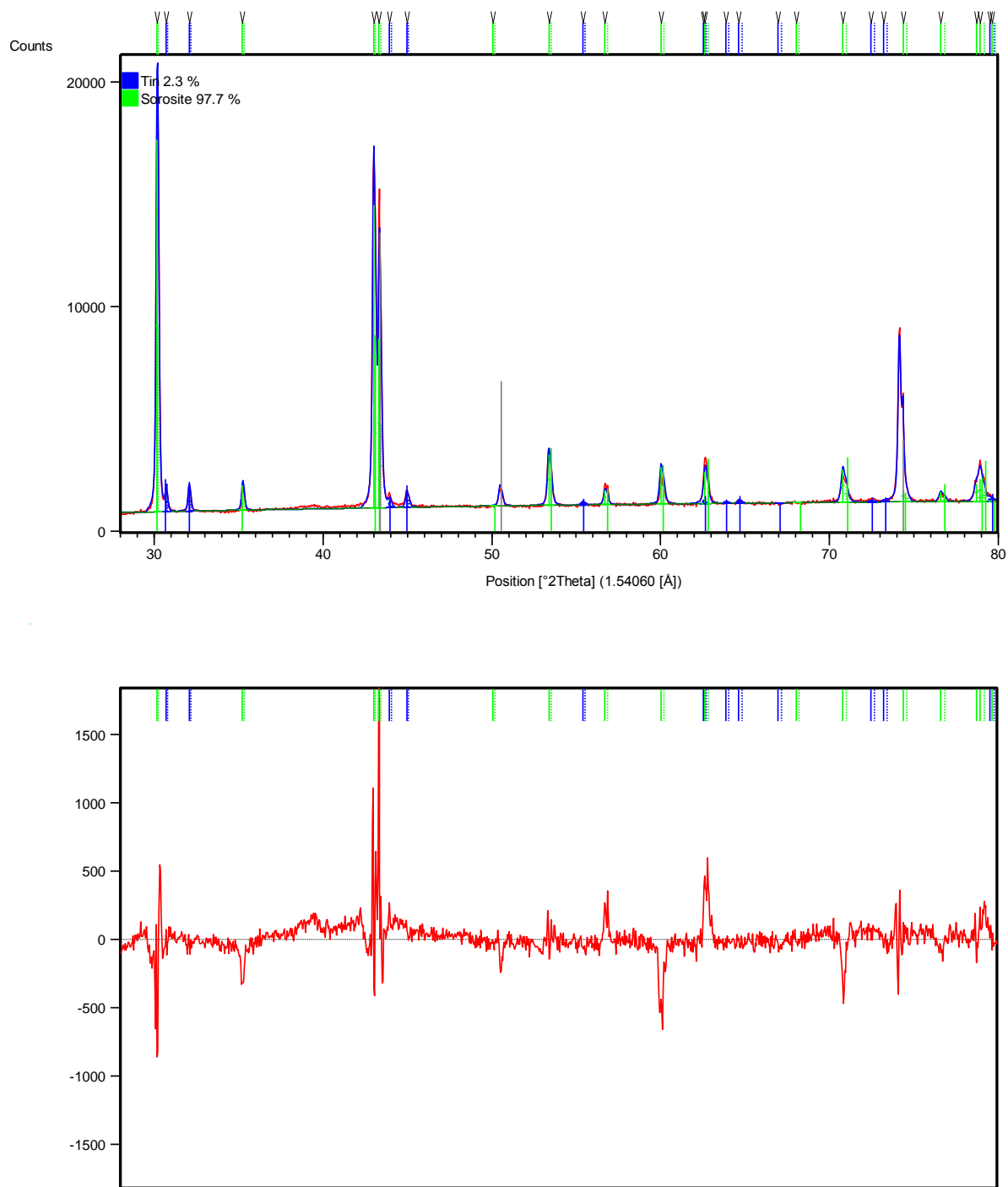


Figure S2. XRD refinement of a representative η -Cu₆Sn₅ (P6₃/mmc) pristine thin film.

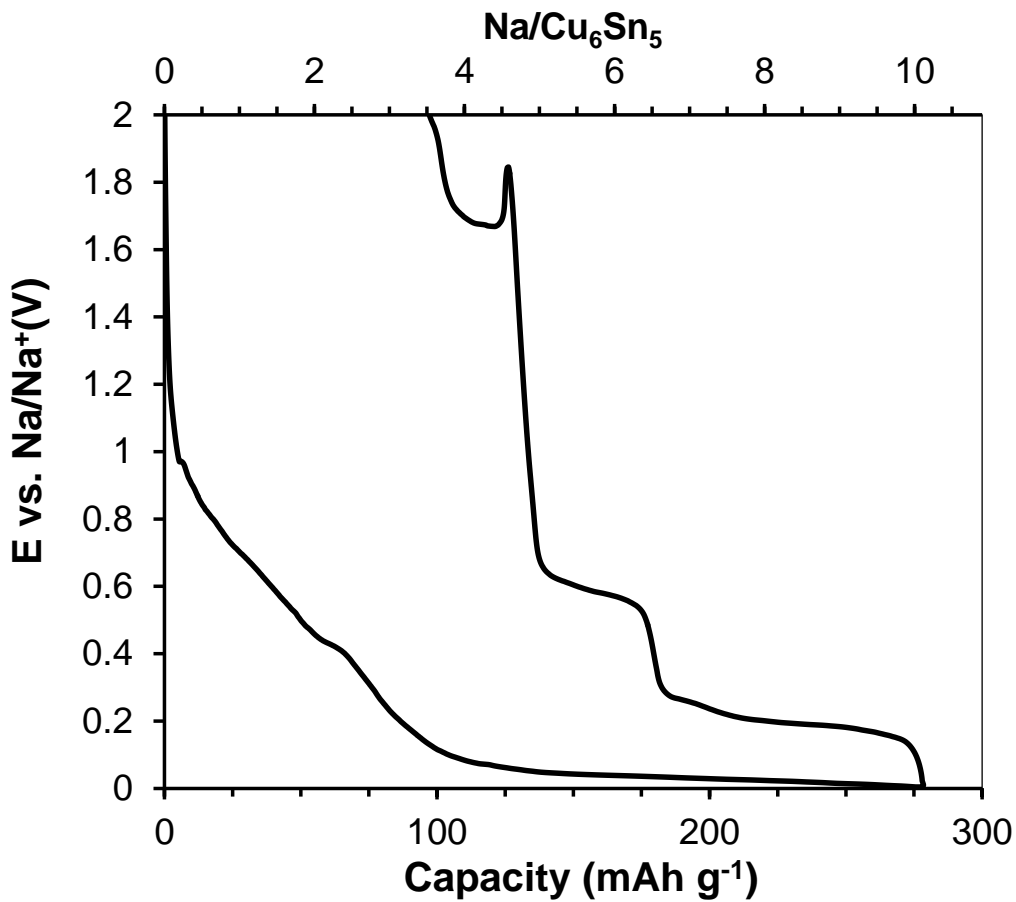


Figure S3. Initial electrochemical potential profile for Na-ion reaction of a $1 \mu\text{m}$ thick electrode at a current of $1.6 \mu\text{A cm}^{-2}$, corresponding to about $C/100$.

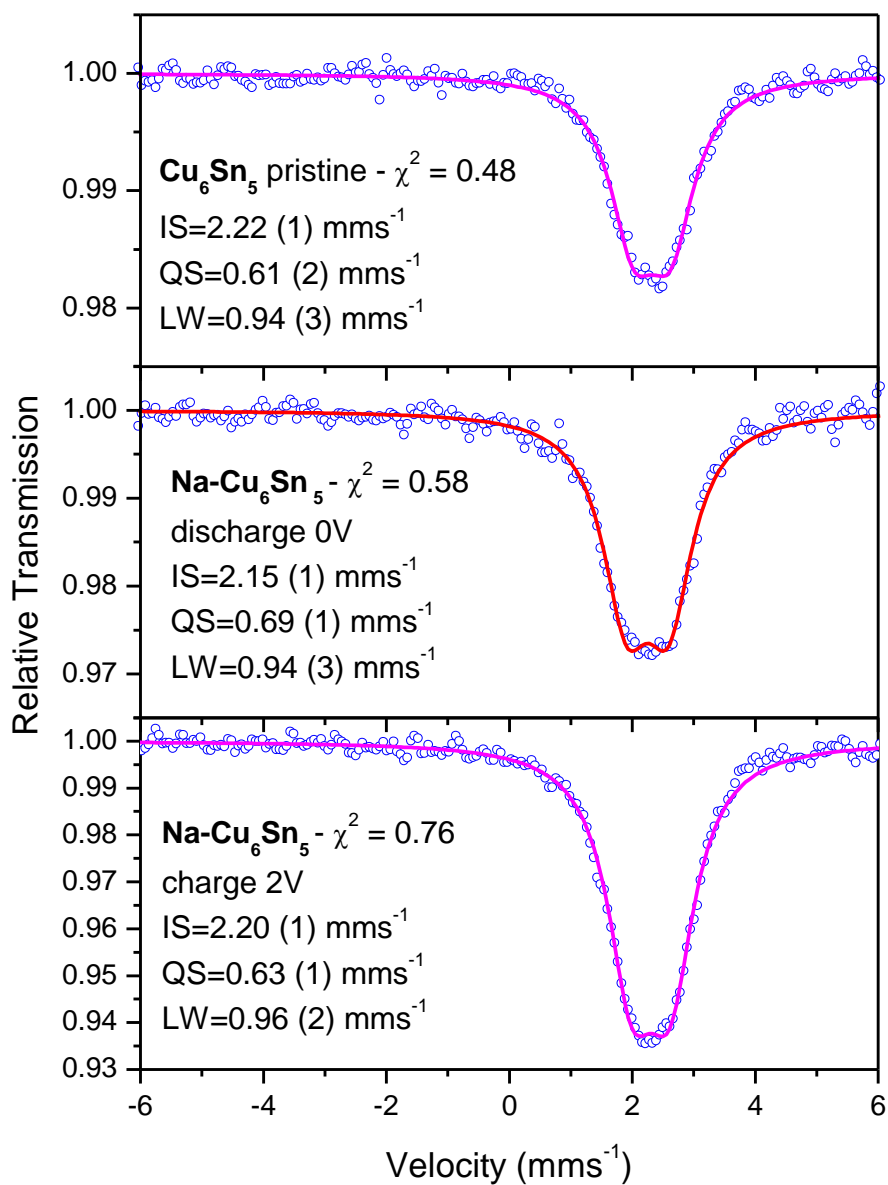


Figure S4. ^{119}Sn Mössbauer spectroscopy data for $\text{Na-Cu}_6\text{Sn}_5$ pristine, fully discharged (short-circuited, 0 V) and fully charged (2 V) electrodes. The hyperfine parameters (isomer shift (IS), quadrupole splitting (QS) and line width (LW)) resulting from fitting with a single contribution are given in the figures.

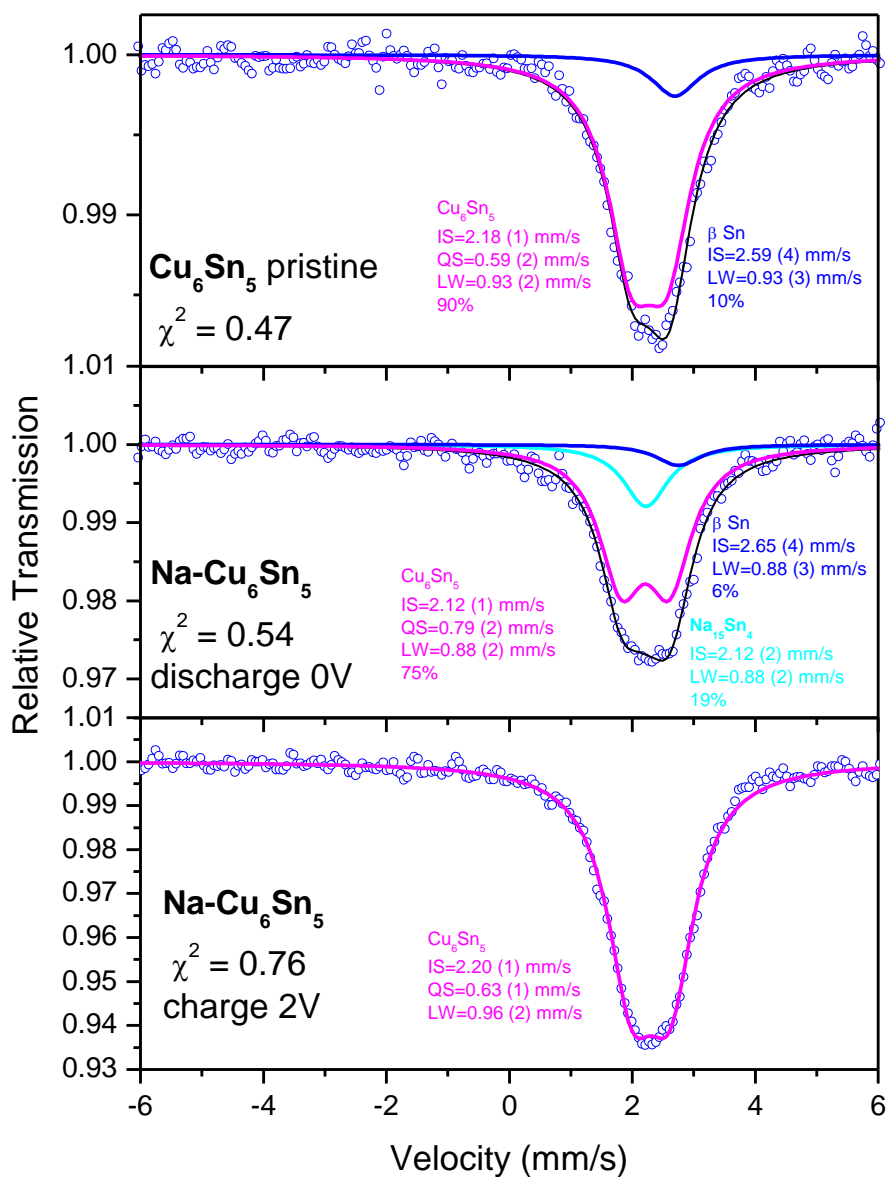


Figure S5. Alternative fits to the ^{119}Sn Mössbauer spectroscopy data including the presence of $\beta\text{-Sn}$ for $\text{Na-Cu}_6\text{Sn}_5$ pristine and fully discharged (short-circuited, 0 V) electrodes, and fully charged (2 V) electrodes. The hyperfine parameters (isomer shift (IS), quadrupole splitting (QS) and line width (LW)) are given in the figures.

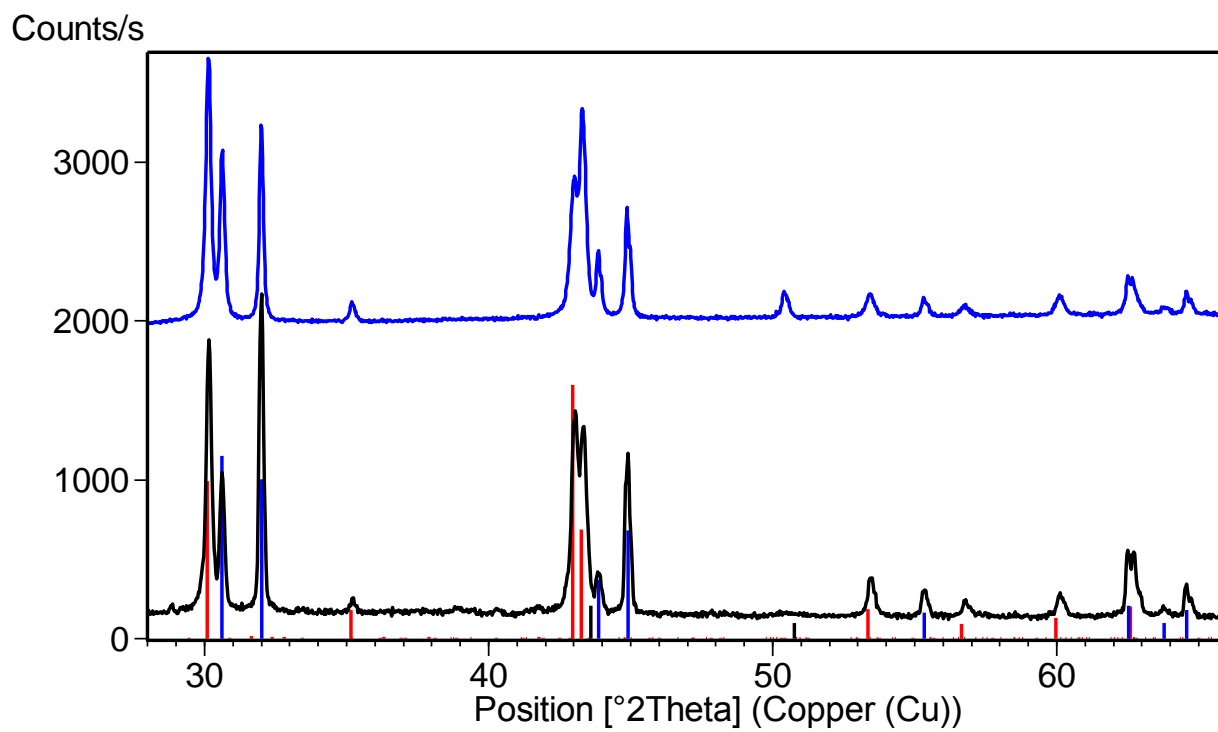


Figure S6. XRD patterns for the starting 'Cu₆Sn₁₀' target material (black) and a representative sputtered thin film (blue). The patterns for Cu (black), Cu₆Sn₅ (red) and Sn (blue) are included as vertical bars.

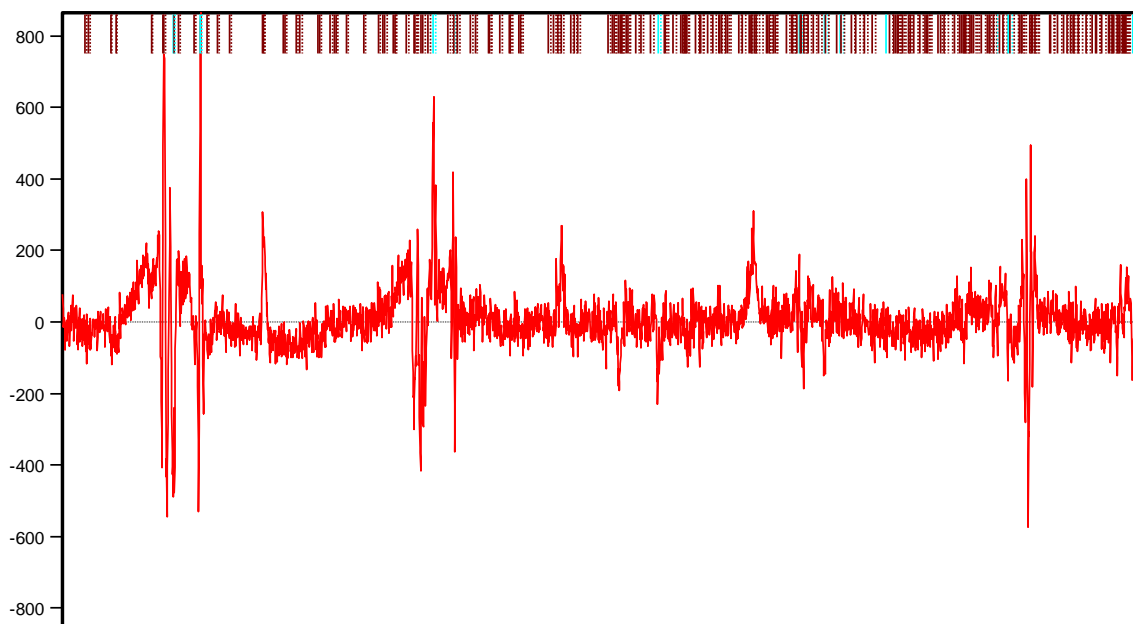
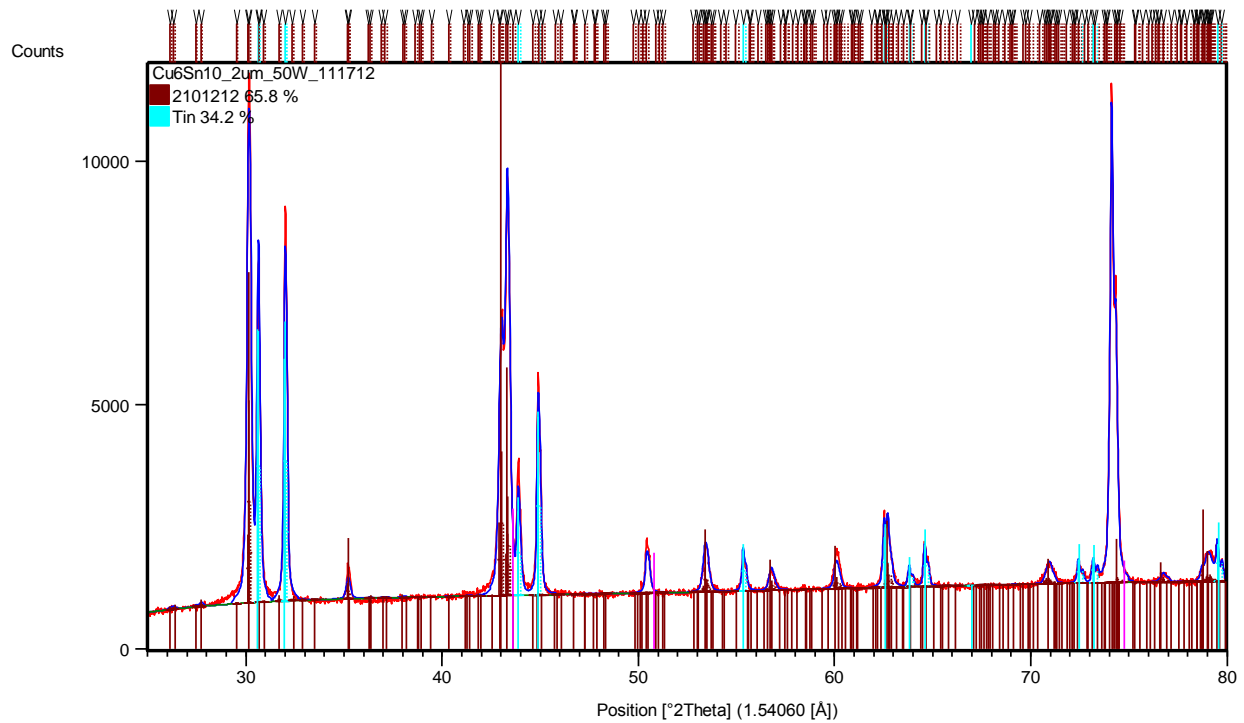


Figure S7. Representative XRD refinement of the starting ' $\text{Cu}_6\text{Sn}_{10}$ ' thin films.