Supplementary Material:

High-temperature decomposition of Cu_2BaSnS_4 with Sn loss reveals newly identified compound $Cu_2Ba_3Sn_2S_8$

José A. Márquez[1*], Jon-Paul Sun[2], Helena Stange[1], Hasan Ali, Leo Choubrac[1], Stefan Schäfer, Klaus Leifer, Thomas Unold[1], David B. Mitzi[2,4] and Roland Mainz[1*]

[1]*Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany*

[2]*Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708, United States*

[3] *Division of Applied Materials Sciences, Department of Engineering Sciences, Angstrom Laboratory, Uppsala University, SE-752 37 Uppsala, Sweden*

[4]*Department of Chemistry, Duke University, Durham, North Carolina 27708, United States*

*jose.marquez_prieto@helmholtz-berlin.de

*roland.mainz@helmholtz-berlin.de

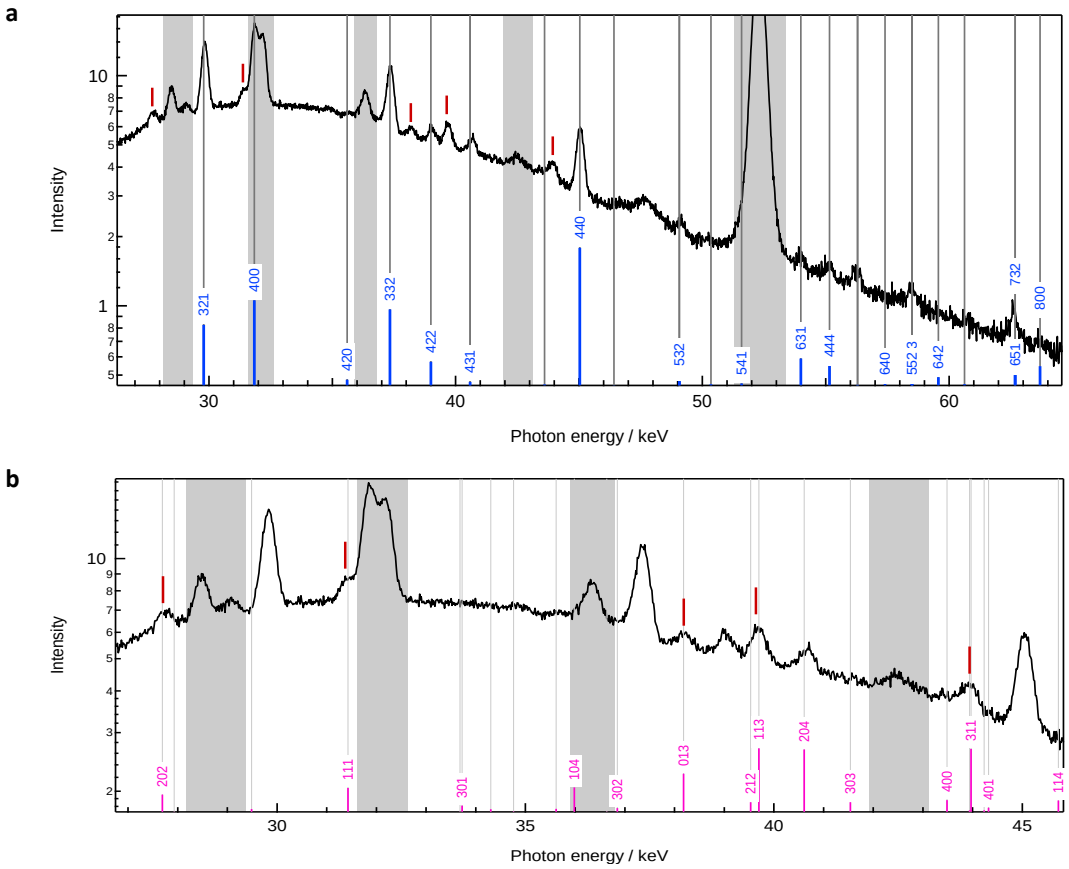

Figure 1S. EDXRD spectrum at 560°C with reference lines for (a) $Cu_2Ba_3Sn_2S_8$ (space group $I\bar{4}3d$) and (b) $BaCu_4S_3$ (space group Pnma).The shaded areas show the peaks coming from either the fluorescence signals or from the diffraction signals of the Mo back contact. The red lines indicate the signals that could not be explained by the precence of only CBTS and/or $BaCu_4S_3$.

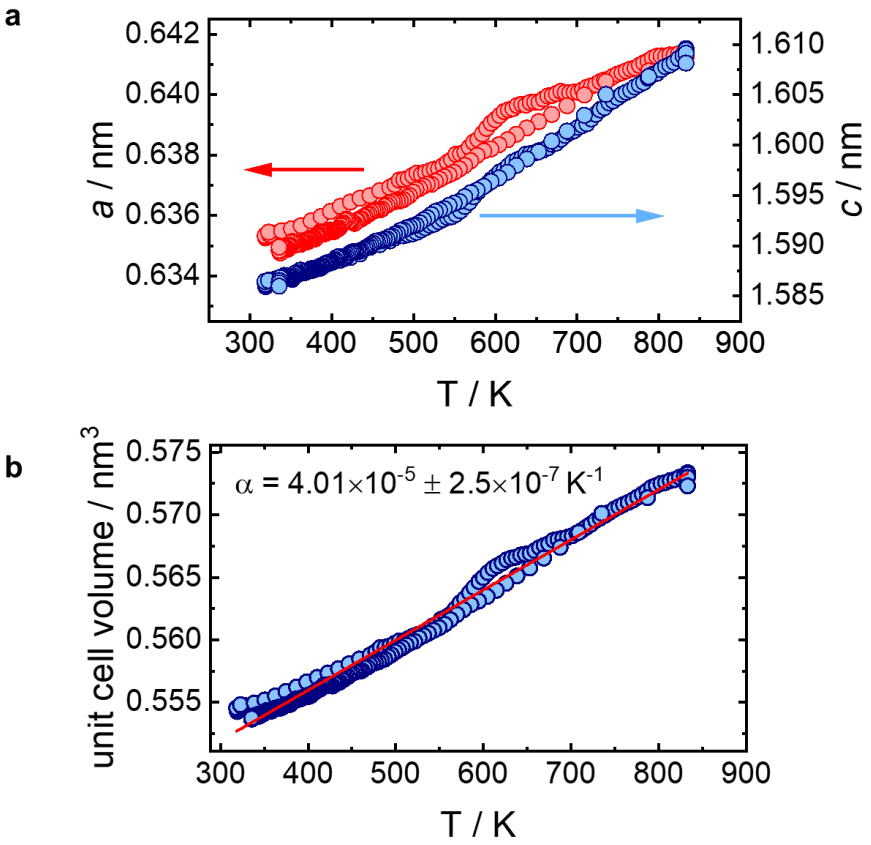

Figure 2S. (a) Evolution of the lattice parameters *a* (red circles) and *c* (blue circles) as a function of temperature of the CBTS phase (space group $P3_1$) derived from the *in-situ* EDXRD data acquired on the process with the "S-anneal" conditions. (b) Temperature dependence of the unit cell volume of CBTS. The red line is a linear fit used to derive a linear thermal expanstion coefficient α of $4.01 \times 10^{-5}\,K^{-1}$ from the slope.