Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

$Co_3M_2S_2$ (M = Sn, In) Shandites as Tellurium-Free Thermoelectrics

Jack Corps, Paz Vaqueiro and Anthony V. Powell*

Institute of Chemical Sciences and the Centre for Advanced Energy Storage and Recovery, Heriot-Watt University, Edinburgh EH14 4AS, UK.

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Experimental Details

Mixtures of elemental cobalt, tin, indium and sulphur, corresponding to stoichometries, $Co_3Sn_{2-x}In_xS_2$ ($0 \leq x \leq 2$), were ground in an agate pestle and mortar and sealed into evacuated ($<10^{-4}$ Torr) fused silica tubes. The tin end-member phase ($x = 0$), was prepared according to our previously reported procedure by heating the reaction mixture at 500°C for 48 hours, followed by a second firing at 700 °C for 48 hours. The sample was ground between firings and cooled to room temperature at 0.5 °C min^{-1} after each firing. The indium end-member of this series ($x = 2$) was prepared by increasing the temperature to 800ºC at 0.5 ºC min^{-1} and holding at this temperature for 96 hours, prior to cooling at the same rate. This procedure was performed three times in total with intermediate re-grinding. All mixed metal compositions were prepared by heating reaction mixtures for three periods of 48 hours at 900ºC with regrinding between firings. Heating and cooling was at the natural rate of the furnace.

Electrical resistivity measurements over the temperature range $100 \leq T/K \leq 300$ were made in 25 K steps, on ingots (*ca.* $6 \times 3 \times 1$ mm^3) cut from hot-pressed pellets. Four 50 μm silver wires were attached using colloidal silver paint and connections made to a TTi QL564P power supply and to a Keithley 2182 nanovoltmeter. The latter was used to measure the voltage drop when a specified current was passed through the ingot. The resistance was then determined using Ohm's law. The sample was mounted in a CF1200 cryostat connected to an Oxford Instruments ITC502 temperature controller. A complete set of resistivity data is provided in Figure S1.

Measurements of the Seebeck coefficient over the temperature range $100 \leq T/K \leq 300$ were made on an ingot (*ca.* $8 \times 4 \times 1$ mm^3), also cut from a hot-pressed pellet. This was mounted on a copper holder using silver adhesive. The holder incorporates a small heater (120 Ω strain gauge) located close to one end of the sample and is attached to the hot stage of a closed-cycle refrigerator (DE-202, Advanced Research Systems), controlled by a Lakeshore LS-331 temperature controller. Two 50 μm copper wires were attached to the ends of the sample using silver paint and connections made to a Keithley 2182A nanovoltmeter. Two Au: 0.07% Fe *vs.* chromel thermocouples were placed close to the sample at the hot and cold ends, and connected to a second Lakeshore LS-331 temperature controller. The Seebeck coefficient at a given temperature was determined by applying a temperature gradient, ΔT, across the sample and measuring the corresponding thermal voltage, ΔV. The slope of the line, $\Delta V/\Delta T$, was used to determine the Seebeck coefficient. The data were corrected for contributions due to the copper wires. A complete set of Seebeck coefficient data is provided in Figure S2.

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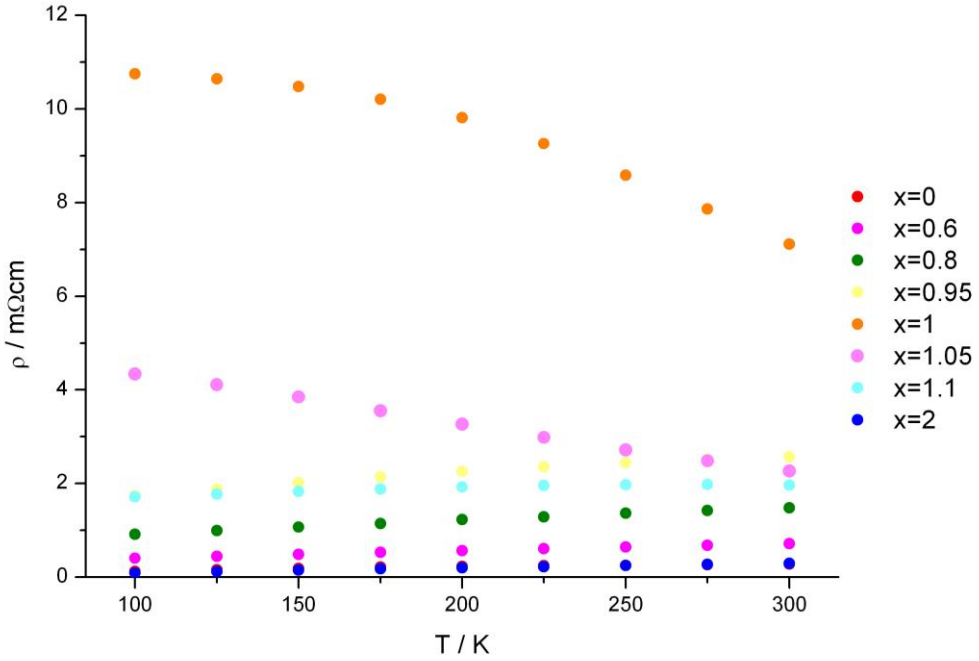
(a)



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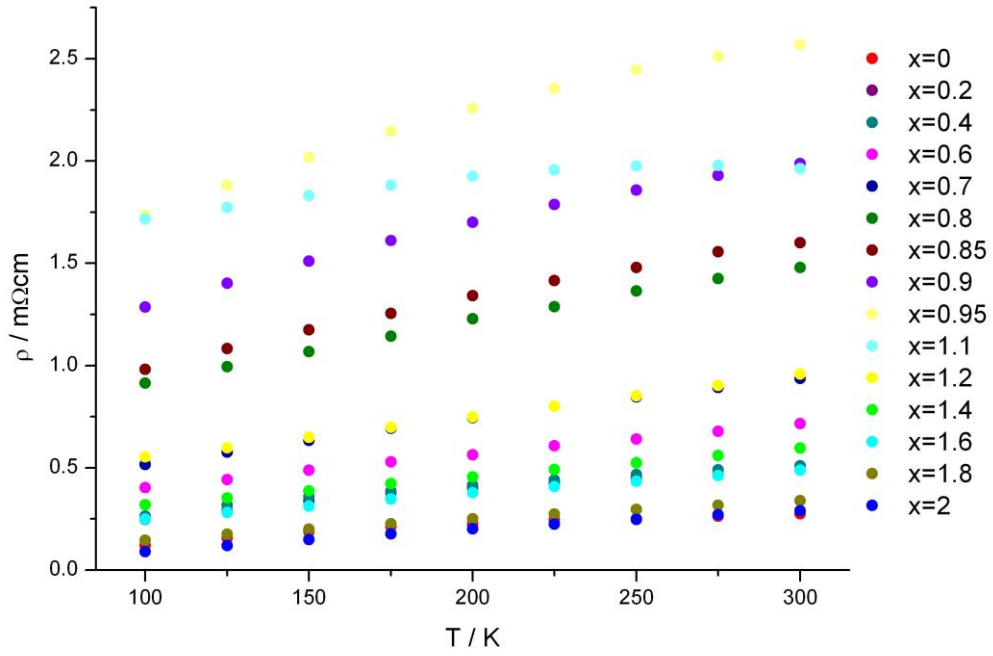

Figure S1: Electrical resistivity data in the range 100 to 300K for $Co_3Sn_{2-x}In_xS_2$ ($0 \leq x \leq 2$) phases.

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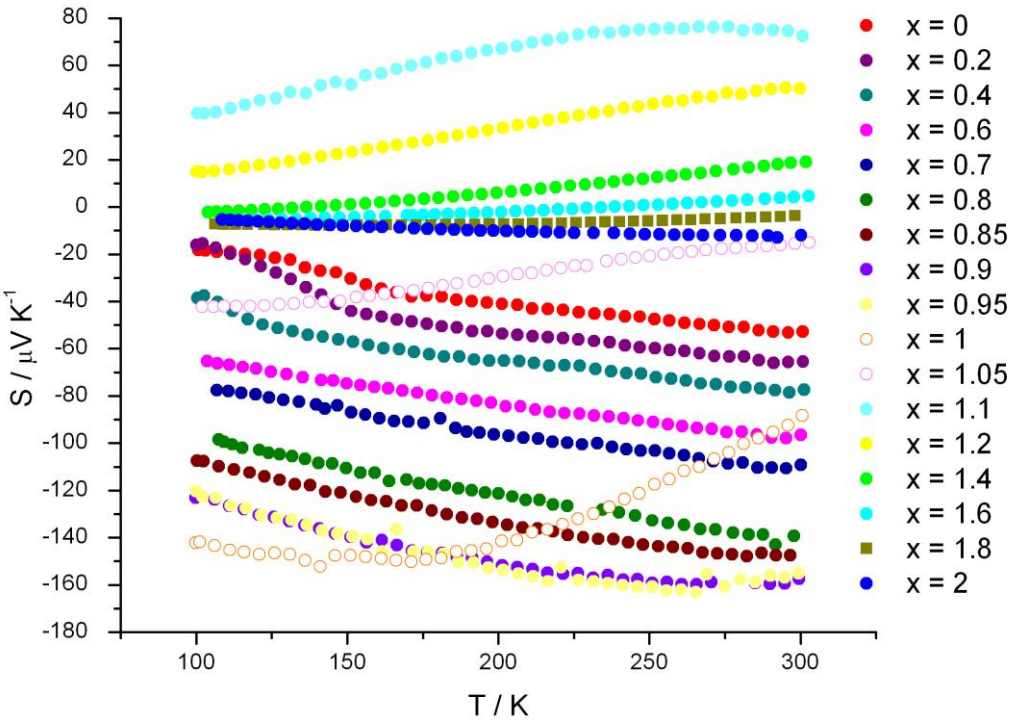

Figure S2 Seebeck coefficient data in the range 100 to 300K for $Co_3Sn_{2-x}In_xS_2$ ($0 \leq x \leq 2$) phases.

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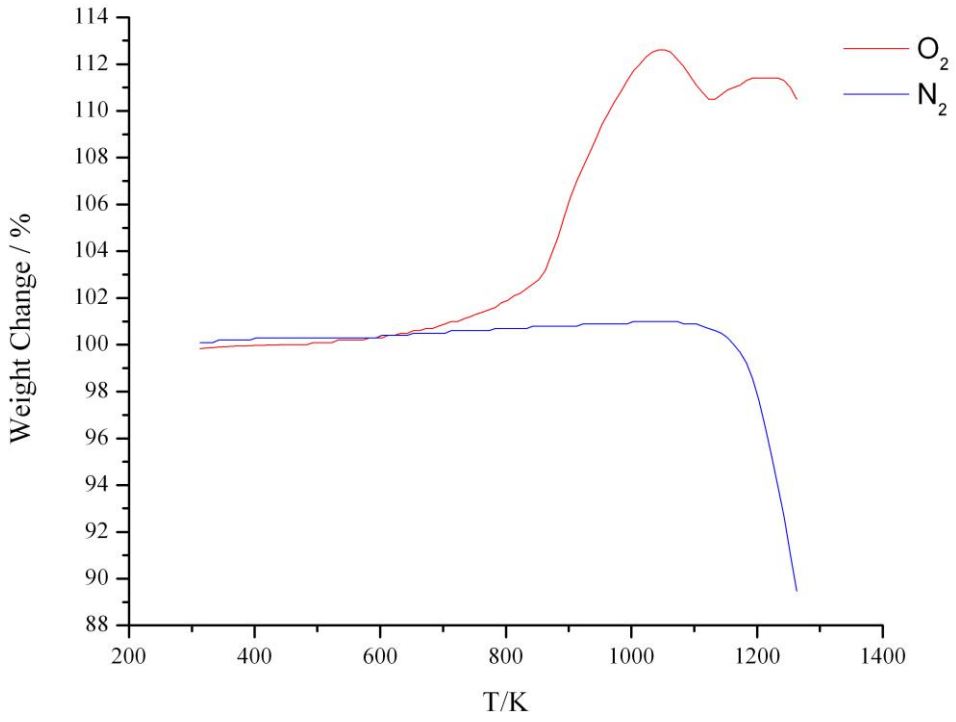

Figure S3: Thermogravimetric analysis data for Co_3SnInS_2 heated in a flow of O_2 or N_2 gas.

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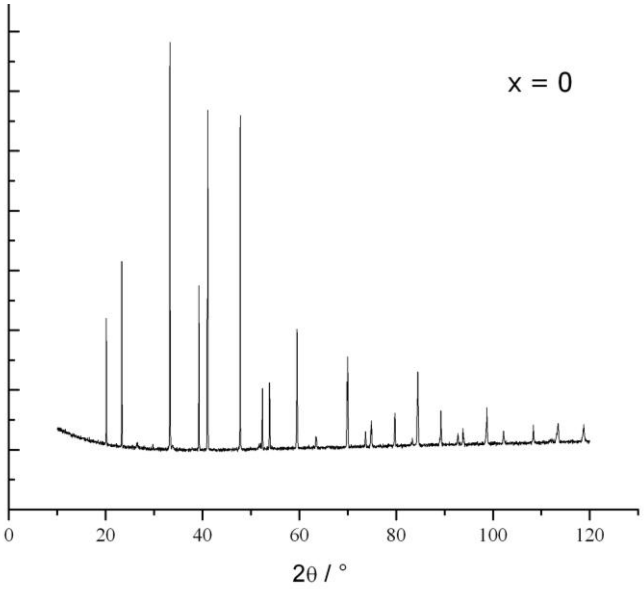

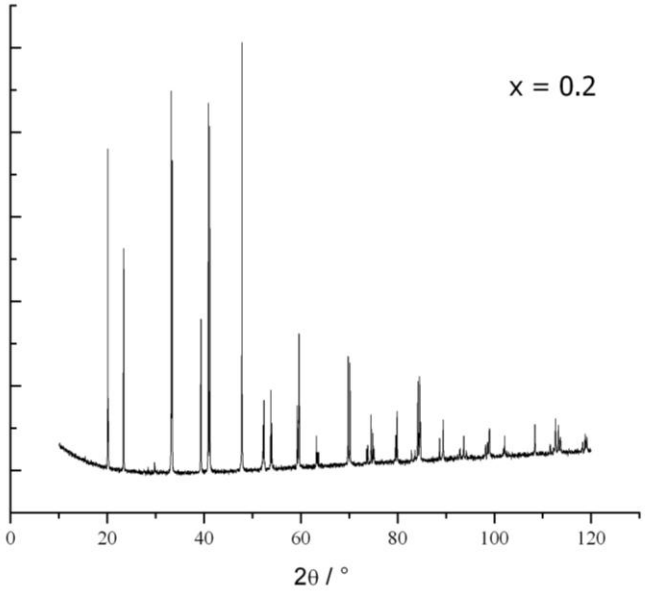

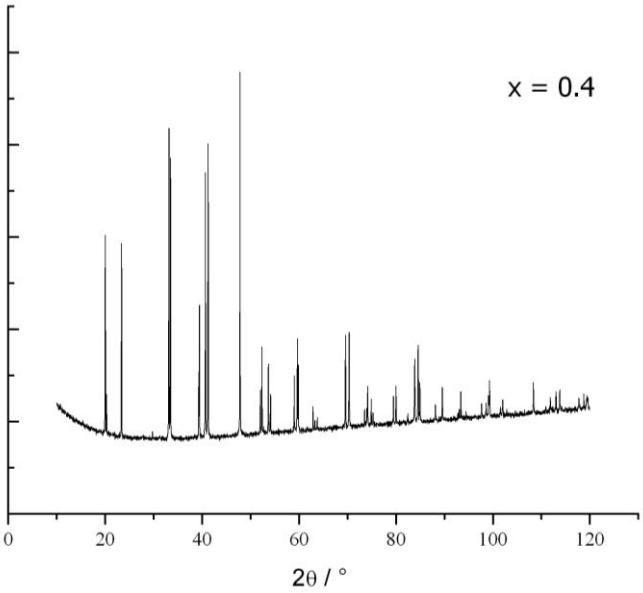

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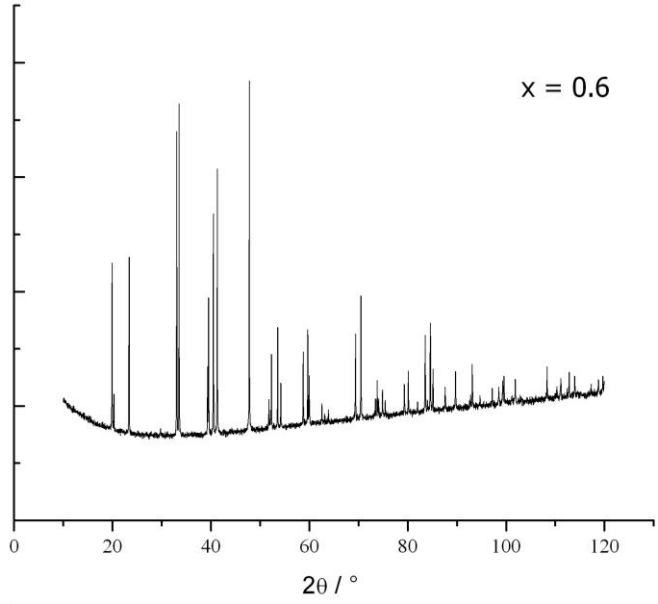

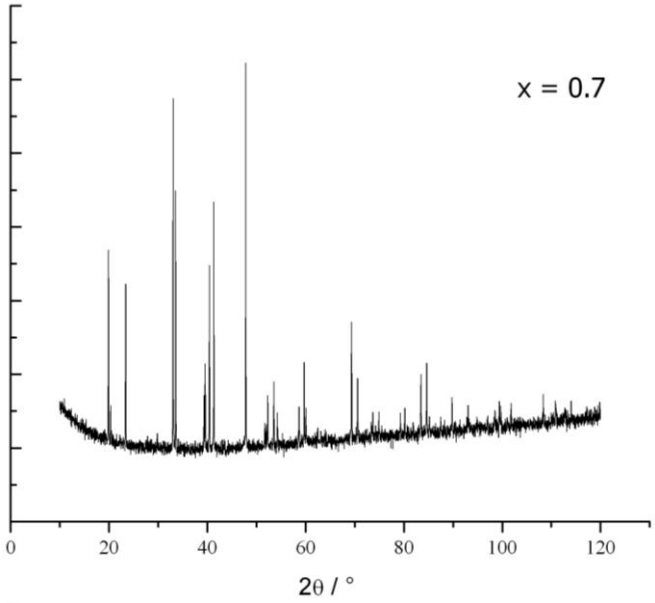

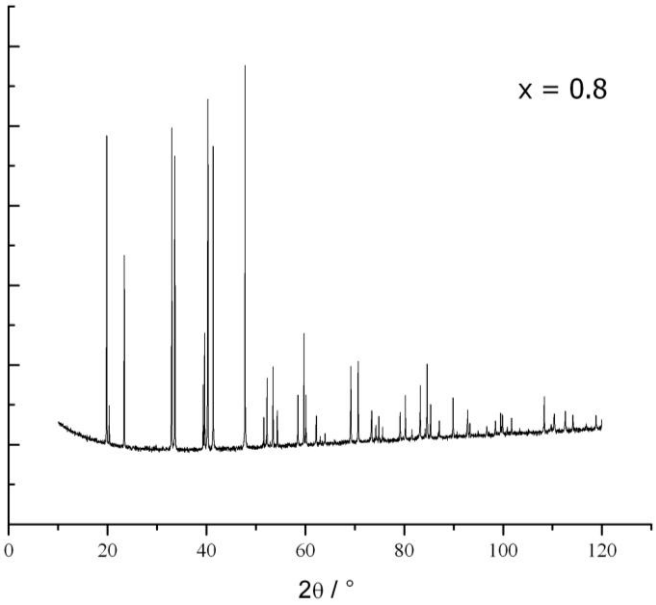

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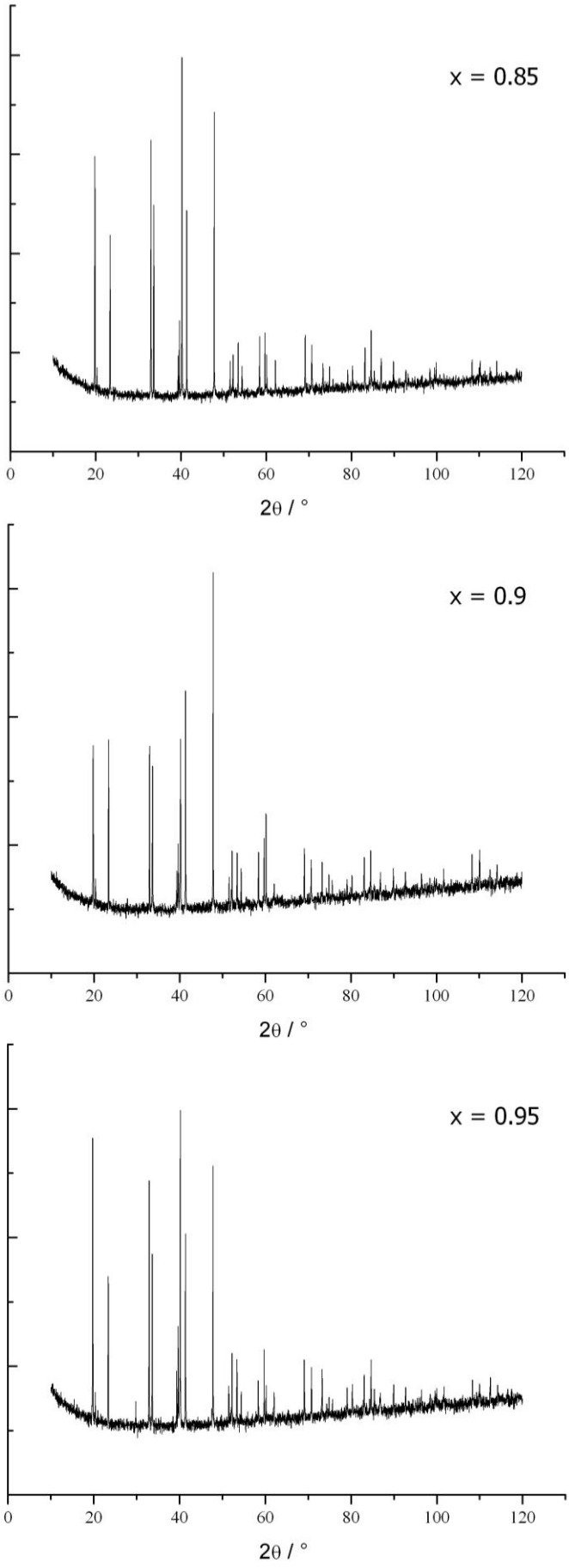

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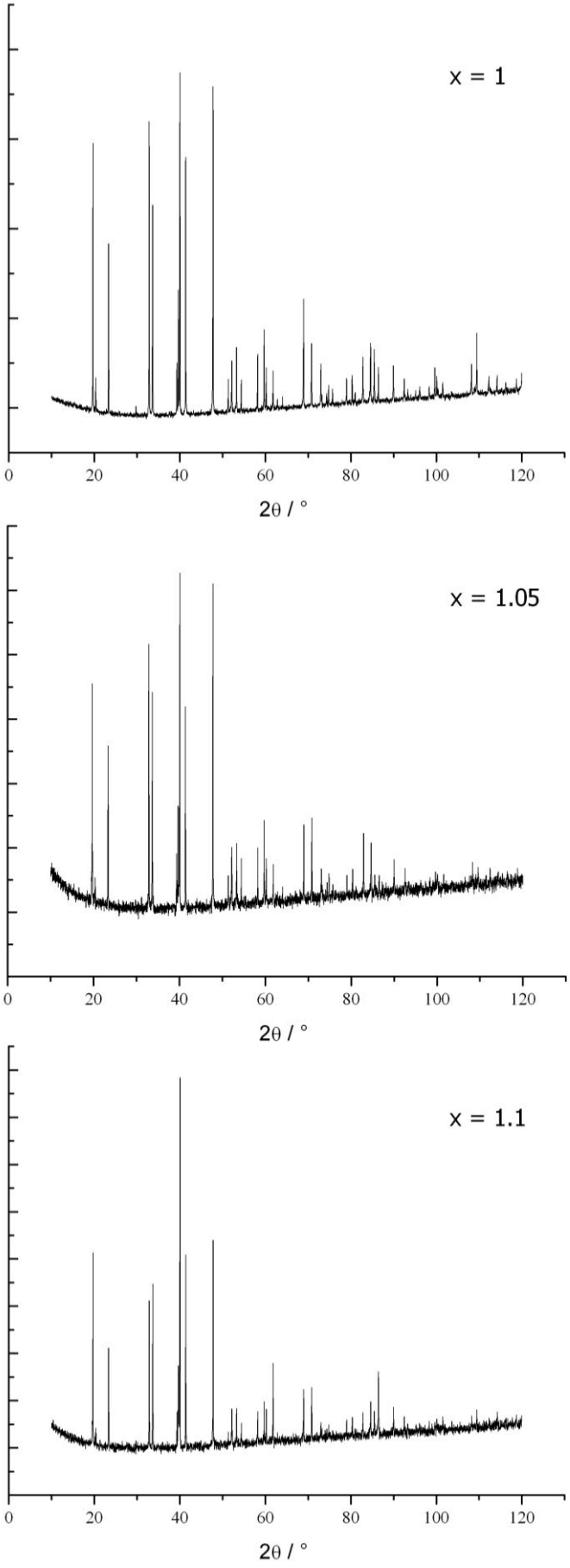

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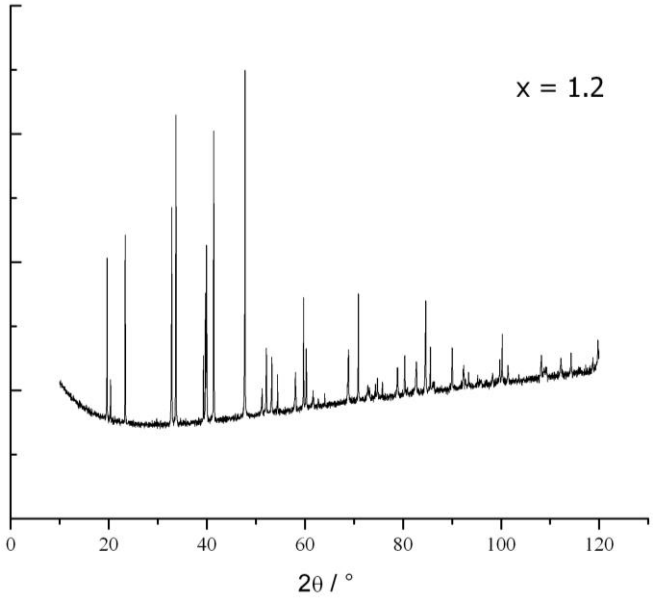

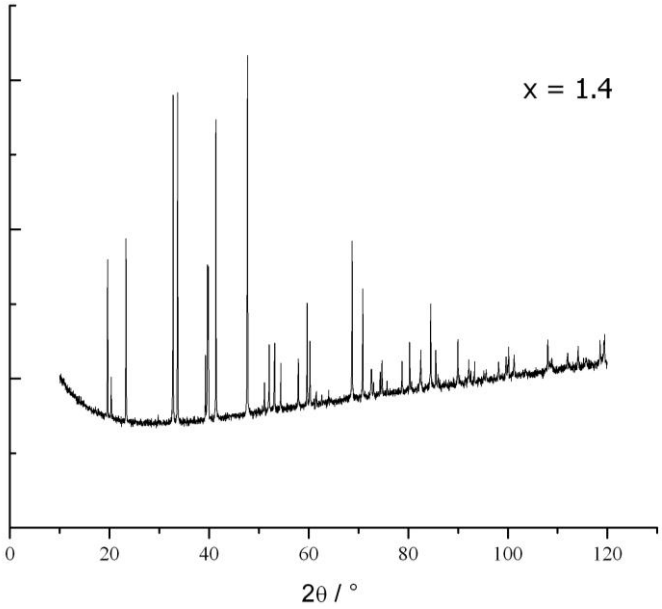

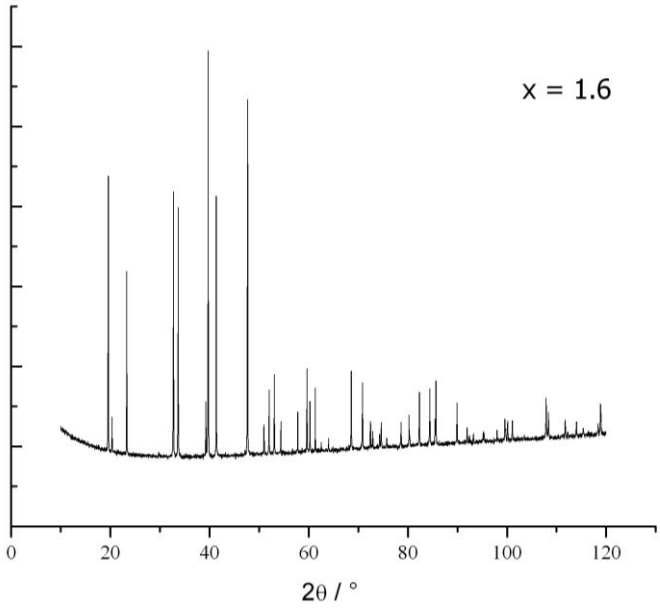

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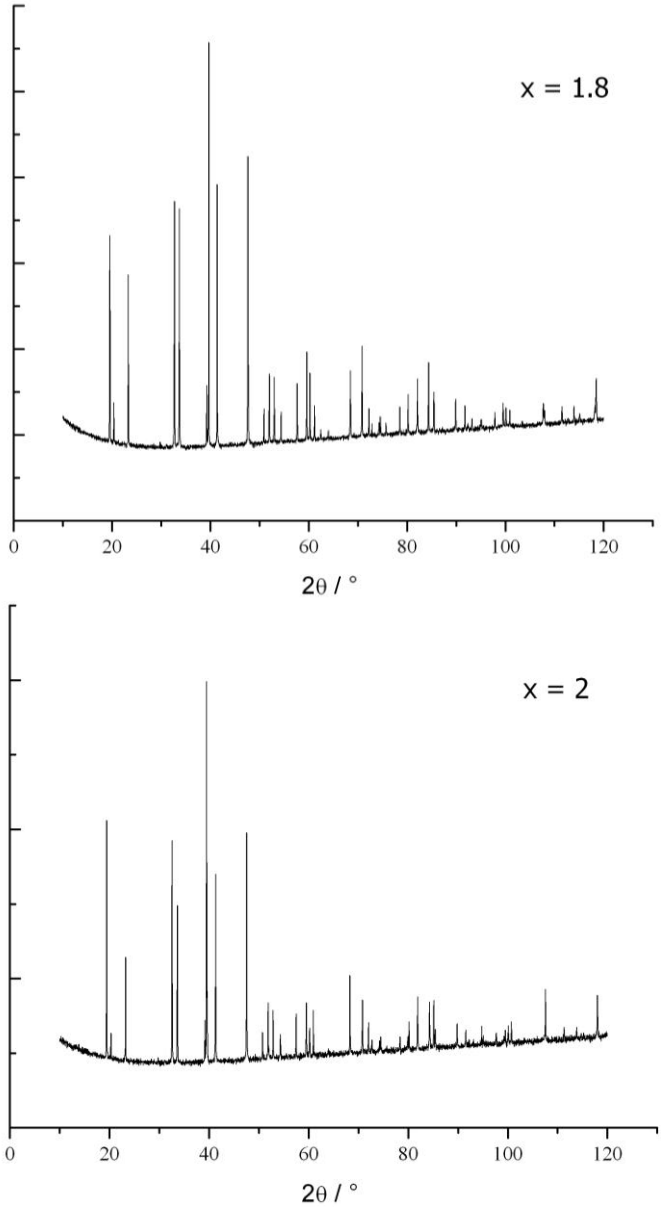

Figure S4. Powder X-Ray diffraction patterns of the series $Co_3Sn_{2-x}In_xS_2$ ($0 \leq x \leq 2$).

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Table S1. Compositional variation of the lattice parameters (Space Group *R*-3*m*: hexagonal setting) determined by powder X-ray diffraction for the series $Co_3Sn_{2-x}In_xS_2$ ($0 \leq x \leq 2$) using the TOPAS3 software package.

x	a/Å	c/Å
0.0	5.3755(6)	13.1886(12)
0.2	5.3575(4)	13.2176(10)
0.4	5.3464(3)	13.2795(15)
0.6	5.3371(5)	13.3567(16)
0.7	5.3321(4)	13.3728(7)
0.8	5.3284(4)	13.4245(11)
0.85	5.3247(3)	13.4299(6)
0.9	5.3223(3)	13.4418(9)
0.95	5.3203(2)	13.4534(8)
1.0	5.3145(4)	13.4882(13)
1.05	5.3161(3)	13.4851(8)
1.1	5.3144(3)	13.4932(8)
1.2	5.3163(6)	13.5447(16)
1.4	5.3170(7)	13.5696(19)
1.6	5.3167(4)	13.5985(13)
1.8	5.3209(9)	13.6385(14)
2.0	5.3171(5)	13.6561(14)