SUPPORTING INFORMATION

Table S1. Crystallographic data for SnSe from NPD data at 473 K.

Crystal data

Orthorhombic	**Space group: *Pnma***
Hall symbol: -P 2ac 2n	Constant Wavelength Neutron Diffraction radiation, λ = 1.594 Å
a = 11.5524 (9) Å	T = 473 K
b = 4.1777 (3) Å	Particle morphology: powder
c = 4.4261 (3) Å	
V = 213.62 (3) Å^3	
Z = 4	Specimen preparation: arc melting from Sn+Se

Refinement: Rietveld	**72 parameters**
R_p = 2.28%	
R_{wp} = 3.04%	
R_{exp} = 1.81%	
R_{Bragg} = 3.03%	
χ^2 = 2.81	
3198 data points	Background function: Linear interpolation between a set of background points with refinable heights.
Excluded region(s): 0	Preferred orientation correction: Yes
Profile function: pseudo Voigt	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	***y***	***z***	U_{iso}*/U_{eq}	**Occ. (<1)**
Sn1	0.11839 (17)	0.25000	0.0957 (3)	0.0249 (13)	0.998 (8)
Se1	0.35525 (13)	0.25000	0.0191 (3)	0.0197 (7)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.0254 (16)	0.0223 (12)	0.0269 (11)	0.00000	−0.0036 (8)	0.00000
Se1	0.0154 (9)	0.0185 (6)	0.0251 (7)	0.00000	−0.0016 (6)	0.00000

Table S2. Crystallographic data for SnSe from NPD data at 573 K.

Crystal data

Orthorhombic	**Space group: *Pnma***
Hall symbol: -P 2ac 2n	Constant Wavelength Neutron Diffraction radiation, λ =1.594 Å
a = 11.5925 (11) Å	T = 573 K
b = 4.2006 (3) Å	Particle morphology: powder
c = 4.4081 (4) Å	
V = 214.65 (3) Å^3	
Z = 4	Specimen preparation: arc melting from Sn+Se

Refinement: Rietveld	**72 parameters**
R_p = 2.15**%**	
R_{wp} = 2.95**%**	
R_{exp} = 1.82**%**	
R_{Bragg} = 3.33%	
χ^2 = 1.82	
3198 data points	Background function: Linear interpolation between a set of background points with refinable heights
Excluded region(s): 0	Preferred orientation correction: Yes
Profile function: pseudo Voigt	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	***y***	***z***	U_{iso}*/U_{eq}	**Occ. (<1)**
Sn1	0.11902 (19)	0.25000	0.0894 (4)	0.0312 (16)	0.997 (9)
Se1	0.35599 (16)	0.25000	0.0198 (3)	0.0248 (9)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.0308 (19)	0.0283 (15)	0.0344 (13)	0.00000	−0.0009 (10)	0.0000
Se1	0.0195 (10)	0.0244 (7)	0.0305 (8)	0.00000	−0.0026 (7)	0.0000

Table S3. Crystallographic data for SnSe from NPD data at 673 K.

Crystal data

Orthorhombic	**Space group: *Pnma***
Hall symbol: -P 2ac 2n	Constant Wavelength Neutron Diffraction radiation, λ = 1.594 Å
a = 11.6310 (12) Å	T = 673 K
b = 4.2302 (4) Å	Particle morphology: powder
c = 4.3805 (4) Å	
V = 215.53 (3) Å^3	
Z = 4	Specimen preparation: arc melting from Sn+Se

Refinement: Rietveld	**72 parameters**
R_p = 2.11%	
R_{wp} = 2.88%	
R_{exp} = 1.83%	
R_{Bragg} = 3.52%	
χ^2 = 2.58	
3198 data points	Background function: Linear interpolation between a set of background points with refinable heights.
Excluded region(s): 0	Preferred orientation correction: Yes
Profile function: pseudoVoigt	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	***y***	***z***	U_{iso}*/U_{eq}	**Occ. (<1)**
Sn1	0.1205 (2)	0.25000	0.0784 (5)	0.0379 (19)	0.995 (10)
Se1	0.35653 (17)	0.25000	0.0175 (4)	0.0321 (10)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.039 (2)	0.0340 (17)	0.0409 (16)	0.00000	0.0008 (13)	0.0000
Se1	0.0293 (12)	0.0306 (10)	0.0364 (10)	0.00000	−0.0005 (10)	0.0000

Table S4a. Crystallographic data for SnSe from NPD data at 773 K, *Pnma* phase.

Crystal data

Orthorhombic	**Space group: Pnma**
Hall symbol: -P 2ac 2n	Constant Wavelength Neutron Diffraction radiation, λ = 1.594 Å
a = 11.68526 (15) Å	T = 773 K
b = 4.27880 (5) Å	Particle morphology: powder
c = 4.33321 (6) Å	
V = 216.656 (5) Å^3	
Z = 4	Specimen preparation: arc melting from Sn+Se

Refinement: Rietveld	**75 parameters**
R_p = 1.99%	
R_{wp} = 2.64%	
R_{exp} = 1.82%	
R_{Bragg} = 4.77%	
χ^2 = 2.16	
3198 data points	Background function: Linear interpolation between a set of background points with refinable heights.
Excluded region(s): 0	Preferred orientation correction: Yes
Profile function: pseudo Voigt	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	***y***	***z***	U_{iso}*/U_{eq}
Sn1	0.1217 (2)	0.25000	0.0565(8)	0.052 (2)
Se1	0.35675 (18)	0.25000	0.0093 (6)	0.0359 (13)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.053 (2)	0.053 (2)	0.0500 (19)	0.00000	0.0010 (20)	0.00000
Se1	0.0280 (16)	0.0379 (13)	0.0419 (11)	0.00000	−0.0002(18)	0.00000

Table S4b. Crystallographic data for SnSe from NPD data at 773 K, *Cmcm* phase.

Crystal data

Orthorhombic	**Space group: *Cmcm***
Hall symbol: -C 2c 2	Constant Wavelength Neutron Diffraction radiation, λ = 1.594 Å
a = 4.3086 (2) Å	T = 773 K
b = 11.6997 (8) Å	Particle morphology: Powder
c = 4.29280 (19) Å	
V = 216.40 (2) Å^3	Specimen preparation: arc melting from Sn+Se

Refinement: Rietveld	**75 parameters**
R_p = 1.99%	
R_{wp} = 2.64%	
R_{exp} = 1.82%	
R_{Bragg} = 3.40%	
χ^2 = 8.02	
3198 data points	Background function: Linear interpolation between a set of background points with refinable heights.
Excluded region(s): 0	Preferred orientation correction: Yes
Profile function: pseudo Voigt	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	***y***	***z***	U_{iso}*/U_{eq}
Sn1	0.00000	0.3726 (3)	0.25000	0.0671 (9)
Se1	0.00000	0.1427 (4)	0.25000	0.091 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.0823 (7)	0.0705 (13)	0.04856 (6)	0.00000	0.00000	0.00000
Se1	0.052 (2)	0.177 (14)	0.0435 (2)	0.00000	0.00000	0.00000

Table S5. Crystallographic data for SnSe from NPD data at 873 K.

Crystal data

Orthorhombic	**Space group: *Cmcm***
Hall symbol: -C 2c 2	Constant Wavelength Neutron Diffraction radiation, λ = 1.594 Å
a = 4.3062 (5) Å	T = 873 K
b = 11.7243 (14) Å	Particle morphology: powder
c = 4.3178 (5) Å	
V = 217.99 (4) Å^3	
Z = 4	Specimen preparation: arc melting from Sn+Se

Refinement: Rietveld	**83 parameters**
R_p = 2.16%	
R_{wp} = 3.00%	
R_{exp} = 1.83%	
R_{Bragg} = 4.07%	
χ^2 = 2.81	
3198 data points	Background function: Linear interpolation between a set of background points with refinable heights.
Excluded region(s): 0	Preferred orientation correction: Yes
Profile function: pseudo Voigt	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	***y***	***z***	U_{iso}*/U_{eq}	**Occ. (<1)**
Sn1	0.00000	0.3767 (3)	0.25000	0.069 (3)	0.998 (12)
Se1	0.00000	0.1429 (2)	0.25000	0.0481 (19)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.087 (3)	0.075 (4)	0.046 (3)	0.00000	0.00000	0.00000
Se1	0.0477 (15)	0.0526 (18)	0.044 (2)	0.00000	0.00000	0.00000

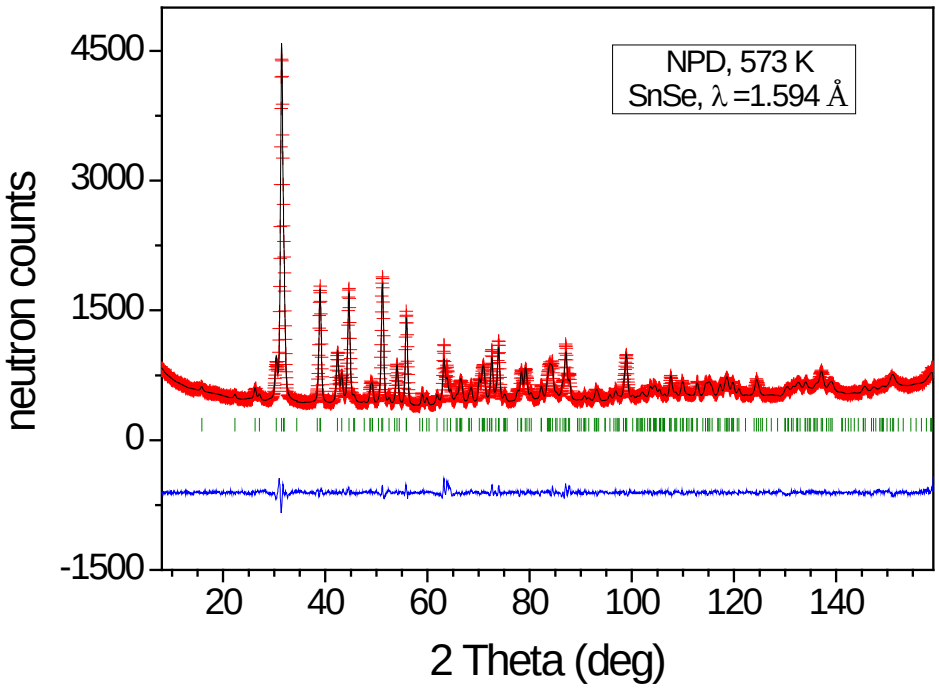

Fig. S1

Rietveld plot for SnSe at 573 K.

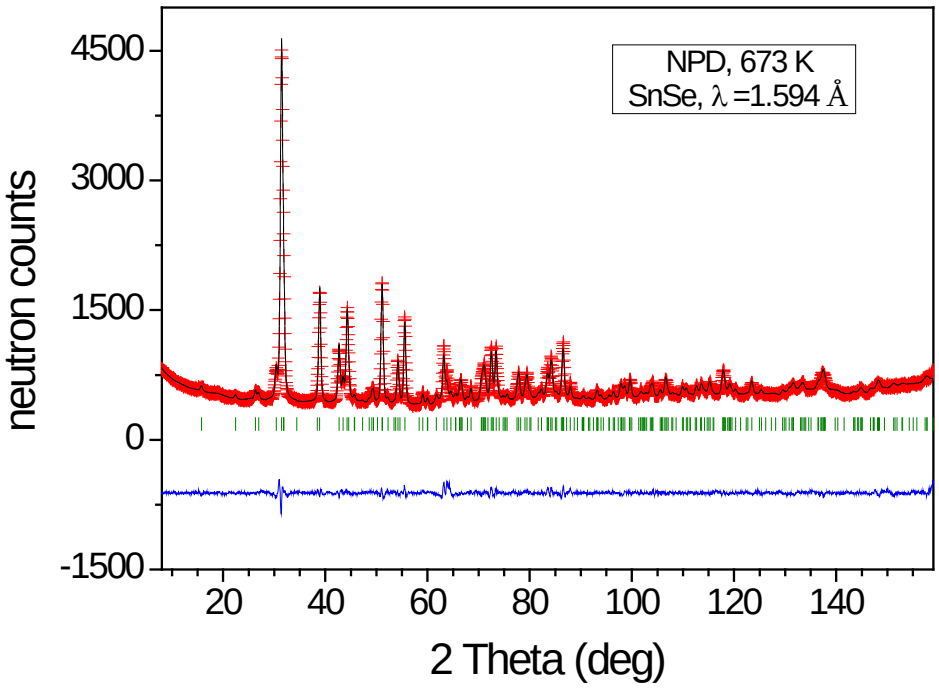

Fig. S2

Rietveld plot for SnSe at 673 K.

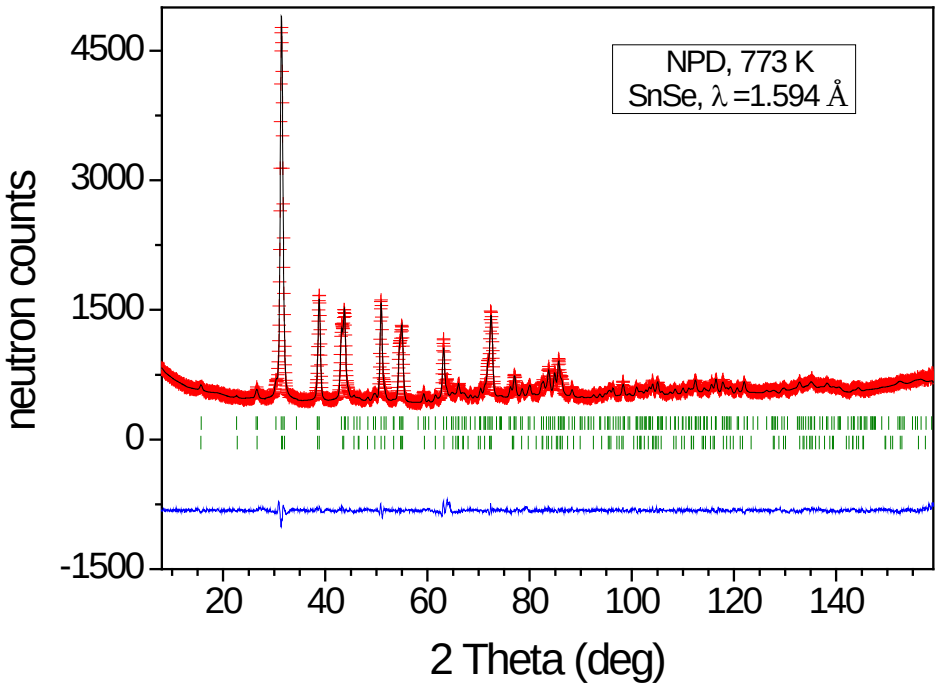

Fig. S3

Rietveld plot for SnSe at 773 K. The two series of Bragg positions correspond to the *Pnma* and *Cmcm* phases, coexisting at this temperature.