Electronic supplementary information (ESI)

Atomic-Scale Phonon Scatterers in Thermoelectric Colusites with a Tetrahedral Framework Structure

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Table S1 Chemical compositions and lattice parameters a for $Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ ($-0.3 \leq x \leq 1.2$) samples hot-press sintered at 873 K and 973 K. The compositions were obtained by averaging the energy-dispersive spectroscopy data for 30 randomly selected spots. Here, the total composition of Cu, Nb, and Sn was assumed to be 34. The standard deviation of the composition is given in the parentheses. As a result, the samples were found to contain two phases: one phase with a nearly stoichiometric ratio of cations and the other phase with a Cu-poor, Sn-rich composition. The two phases are (modified) ordered-structure phases with $a \approx 1.1$ nm and disordered-structure phases with $a \approx 0.54$ nm, respectively (see text). Notably, the $x = -0.3$ sample sintered at 973 K has a lower sulfur content than the sample sintered at 873 K.

□	Temp.	(Modified) ordered-structure phase					
x	**/K**	**Cu**	**Nb**	**Sn**	**S**	**Spots**	***a*/nm**
1.2	973	–	–	–	–	0	–
0.6	973	25.6(3)	1.7(2)	6.7(2)	28.9(4)	16	1.0871(5)
0	973	25.9(2)	1.9(2)	6.2(3)	28.5(5)	22	1.0891(6)
−0.3	973	26.1(4)	2.0(2)	5.9(2)	28.1(6)	30	1.0895(5)
−0.3	873	25.7(3)	2.0(3)	6.3(3)	29.1(8)	28	1.0816(6)

□	Temp.	Disordered-structure phase					
x	**K**	**Cu**	**Nb**	**Sn**	**S**	**Spots**	***a*/nm**
1.2	973	24.6(3)	2.0(2)	7.4(3)	29.9(6)	28	0.5433(1)
0.6	973	24.8(3)	2.0(2)	7.2(2)	30.0(6)	14	0.5433(3)
0	973	25.0(3)	2.1(2)	6.9(4)	29.6(3)	8	0.5435(3)
−0.3	973	–	–	–	–	0	–
−0.3	873	–	–	–	–	0	0.5423(3)*

*XRD pattern was obtained as a superposition of patterns for the ordered-structure phase and the disordered-structure phase.

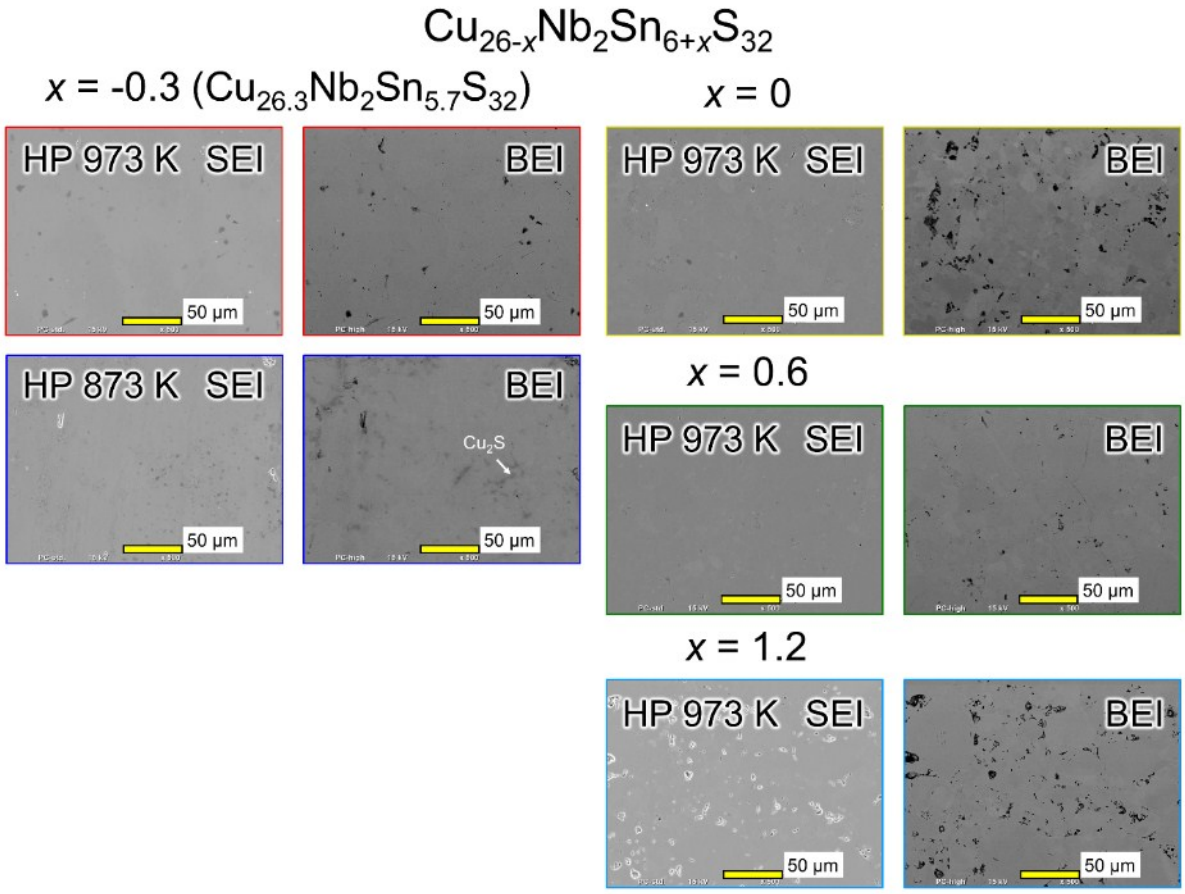

Fig. S1 Scanning electron microscope images for samples of $Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ (x = −0.3, 0, 0.6, 1.2) hot-press sintered at 873 K and 973 K. The secondary electron images (SEIs) and backscattered electron images (BEIs) are shown in the left and right panels, respectively.

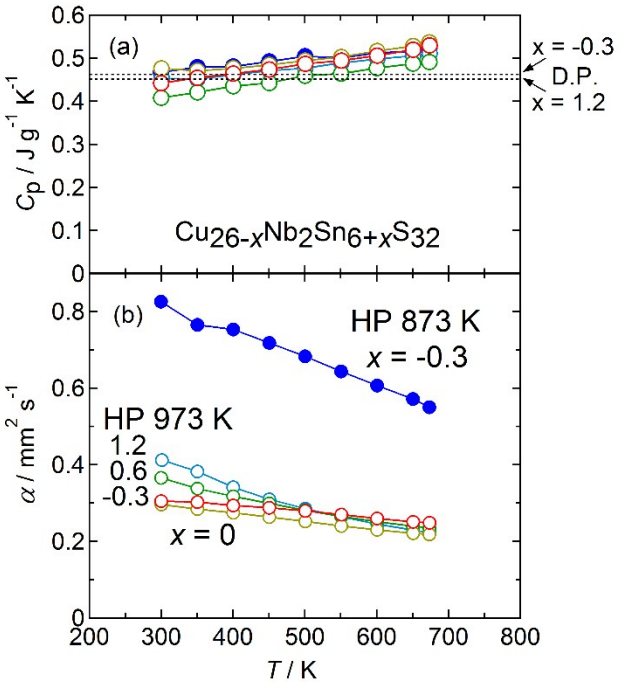

Fig. S2 (a) Specific heat C_p and (b) thermal diffusivity α for $Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ (x = −0.3, 0, 0.6, 1.2) samples hot-press sintered at 873 K and 973 K. Dulong-Petit (D.P.) values of the specific heat for x = −0.3 and 1.2 are drown in (a).

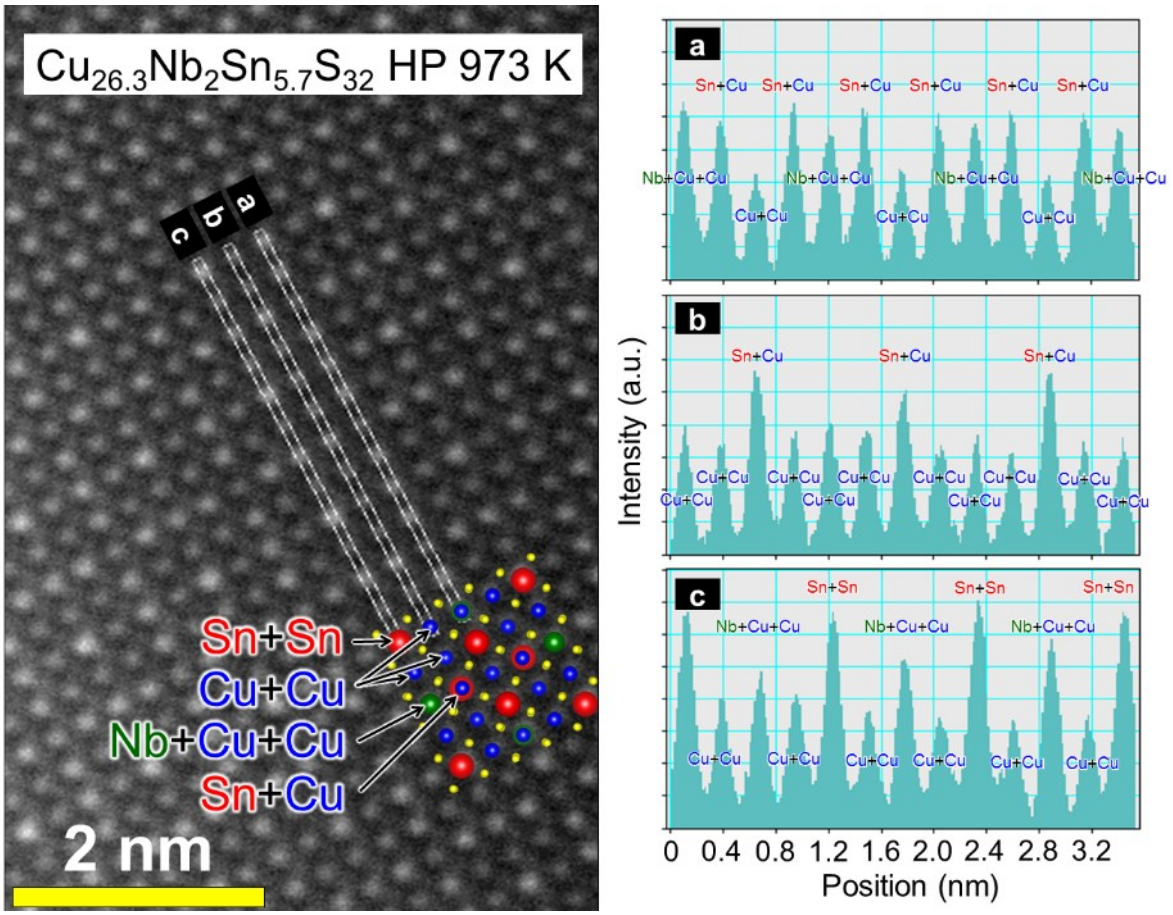

Fig. S3 An annular dark-field scanning transmission electron microscopy (ADF-STEM) image along the 100 direction for the $Cu_{26.3}Nb_2Sn_{5.7}S_{32}$ ($Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ with $x = -0.3$) samples hot-press sintered at 973 K is shown in the left panel. Because the whiteness (intensity) is proportional to the square of the atomic number Z (29 for Cu, 41 for Nb, 50 for Sn, 16 for S), the columns for cations (Cu, Nb, Sn) are visible in the image. The relative intensities of the columns shown in the right panel are expected to be highest for Sn+Sn, followed in order by Nb+Cu+Cu and Sn+Cu (almost equal), and Cu+Cu, consistent with the ordered cation arrangement (Figure 1a). The crystal structure contains interstitial cations (see text), which could not be confirmed from the ADF-STEM image.

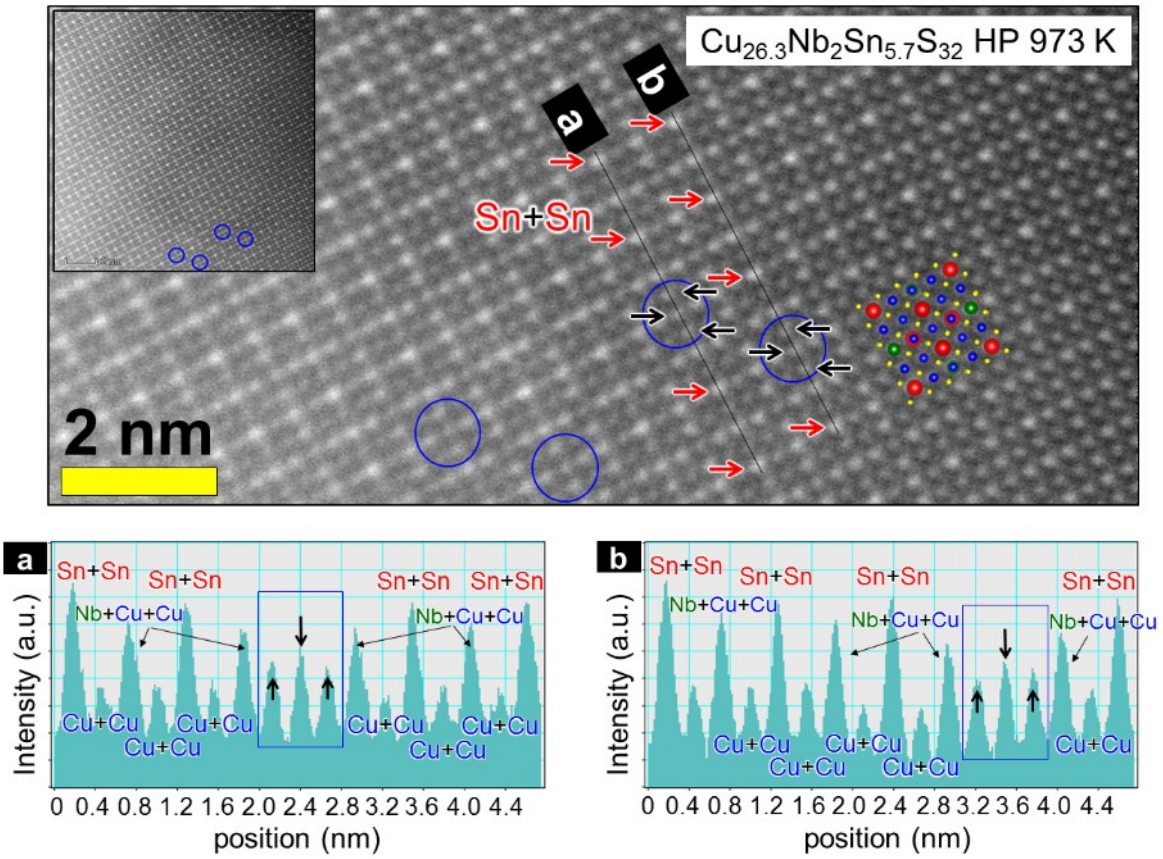

Fig. S4 An annular dark-field scanning transmission electron microscopy (ADF-STEM) image along the 100 direction for the $Cu_{26.3}Nb_2Sn_{5.7}S_{32}$ ($Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ with $x = -0.3$) samples hot-press sintered at 973 K is shown at in the top panel. The relative intensities between columns composed of Cu, Nb, and Sn along lines (a) and (b) are shown at the bottom. Intensities of the Sn+Sn columns circled by blue lines decrease, and simultaneously those of the neighboring Cu+Cu columns increase compared with the other region. The intensities of these "modified" columns are approximately equal, indicating exchange between Sn and Cu or a random (disordered) cation arrangement.

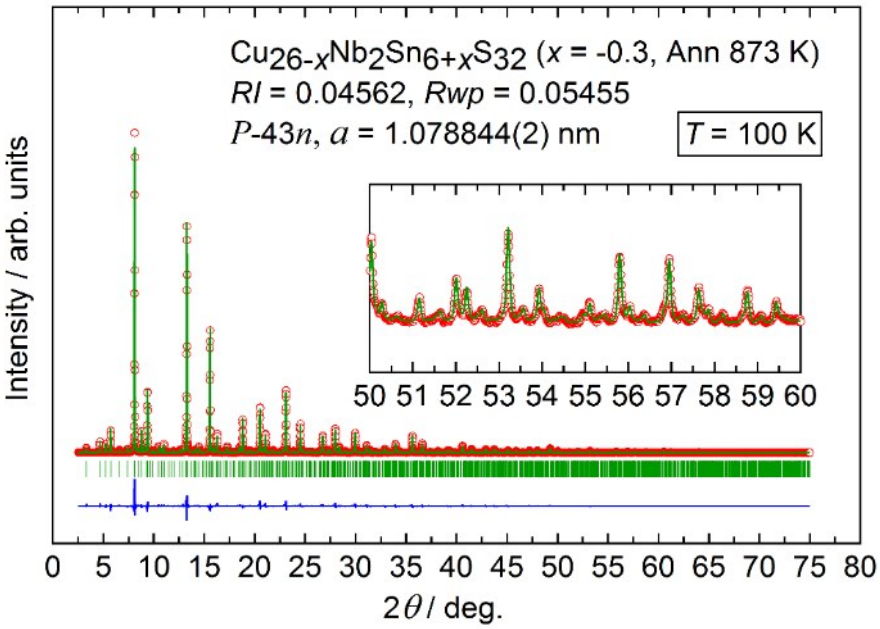

Fig. S5 Rietveld refinement result of synchrotron X-ray diffraction data collected at 100 K for the $Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ sample with $x = -0.3$ before heating (annealed at 873 K). The XRD pattern was fitted by a superposition of patterns for colusite with ordered structure (main phase) and patterns for the colusite with disordered structure and a binary phase Cu_2S (impurity phases). Peak intensities for the impurity phases are less than 1% of those for the main phase. The vertical bars below the calculated pattern indicate Bragg peak positions for the main phase. Reliability factors based on Bragg intensities, *RI*, and on the weighted profile, *Rwp*, of the analysis are 0.04562 and 0.05455, respectively. The refined crystallographic information is listed in Table S2.

Table S2 Refined atomic coordinates and isotropic/anisotropic atomic displacement parameters U_{iso}/U_{ij} at 100 K for the $Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ sample with $x = -0.3$ before heating (annealed at 873 K). The space group, lattice parameter *a*, and reliability factors based on Bragg intensities, *RI*, and on the weighted profile, *Rwp*, are also presented.

P-43*n*, *a* = 1.078844(2) nm, *RI* = 0.04562, *Rwp* = 0.05455

Atom	Position	Occ.	*x*	*y*	*z*	$U_{iso}\times10^2$/nm^2
Nb	2*a*	1	0	0	0	—
Cu(1)	12*f*	0.979(3)	0.25722(8)	0	0	0.0057(2)
Cu(2)	8*e*	0.982(4)	0.2506(13)	*x*	*x*	—
Cu(3)	6*d*	1	0.25	0	0.5	0.0059(3)
Sn	6*c*	0.971(3)	0.25	0.5	0	—
S(1)	8*e*	0.914(8)	0.1242(5)	*x*	*x*	—
S(2)	24*i*	1	0.3775(2)	0.3694(3)	0.1267(2)	0.0068(3)

Atom	$U_{11}\times10^2$/nm^2	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Nb	0.0020(5)	U_{11}	U_{11}	0	0	0
Cu(2)	0.0084(7)	U_{11}	U_{11}	0.0034(8)	U_{12}	U_{12}
Sn	0.0058(6)	0.0045(6)	U_{22}	0	0	0
S(1)	0.0020(10)	U_{11}	U_{11}	−0.0010(10)	U_{12}	U_{12}

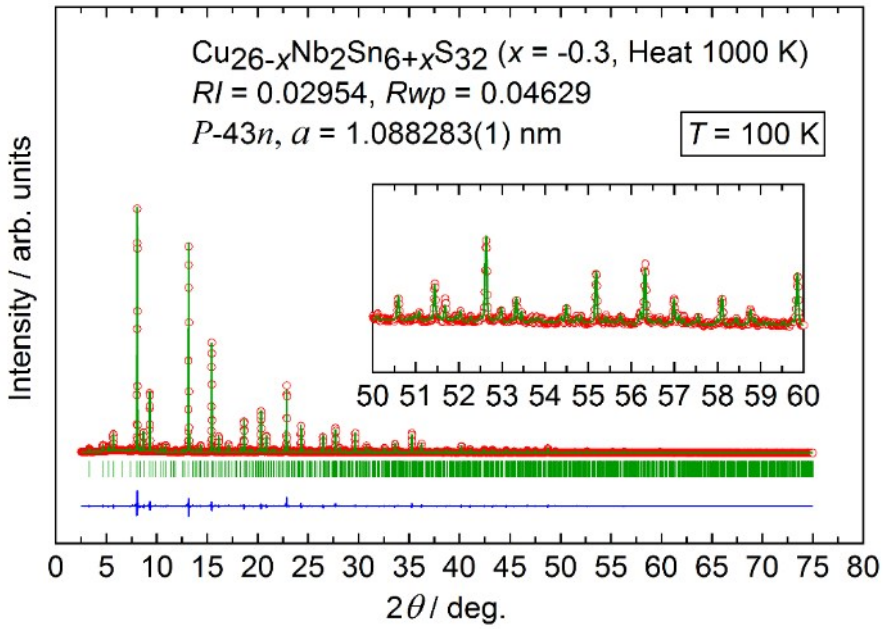

Fig. S6 Rietveld refinement result for synchrotron X-ray diffraction data collected at 100 K for the $Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ sample with $x = -0.3$ after a heating at 1073 K. Reliability factors based on Bragg intensities, *RI*, and on the weighted profile, *Rwp*, of the analysis are 0.02954 and 0.04629, respectively. The refined crystallographic information is listed in Table S3.

Table S3 Refined atomic coordinates and isotropic/anisotropic atomic displacement parameters U_{iso}/U_{ij} at 100 K for the $Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ sample with $x = -0.3$ after a heating at 1073 K. Space group, lattice parameter *a*, and reliability factors based on Bragg intensities, *RI*, and on the weighted profile, *Rwp*, are also presented. Site (4), "interstitial site", was assumed to be occupied by Cu. Furthermore, the exchange between Cu and Sn was assumed for the Cu/Sn(3)-6*d* and Sn/Cu-6*c* sites.

P-43*n*, $a = 1.088283(1)$ nm, $RI = 0.02954$, $Rwp = 0.04629$

Atom	Position	Occ.	*x*	*y*	*z*	$U_{iso}\times10^2$/nm^2
Nb	2*a*	1	0	0	0	—
Cu(1)	12*f*	1	0.25812(11)	0	0	—
Cu(2)A	8*e*	0.464(4)	0.240(3)	*x*	*x*	—
Cu(2)B	8*e*	0.536(4)	0.246(2)	*x*	*x*	—
Cu/Sn(3)	6*d*	0.95/0.05	0.25	0	0.5	—
Cu(4)	24*i*	0.127(5)	0.255(3)	0.215(3)	0.032(3)	0.0038
Sn/Cu	6*c*	0.95/0.05	0.25	0.5	0	—
S(1)	8*e*	0.905(8)	0.1248(6)	*x*	*x*	—
S(2)	24*i*	0.937(4)	0.3774(3)	0.3697(2)	0.1260(3)	0.0040(4)

Atom	$U_{11}\times10^2$/nm^2	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Nb	0.0037(8)	U_{11}	U_{11}	0	0	0
Cu(1)	0.0058(7)	0.0078(14)	0.0161(17)	0	0.0041(8)	0
Cu(2)A	0.035(10)	U_{11}	U_{11}	0.032(8)	U_{12}	U_{12}
Cu(2)B	0.009(5)	U_{11}	U_{11}	−0.003(3)	U_{12}	U_{12}
Cu/Sn(3)	0.009(4)	0.006(4)	U_{22}	0	0	0
Sn/Cu	0.013(3)	0.010(3)	U_{22}	0	0	0
S(1)	0.008(3)	U_{11}	U_{11}	−0.002(3)	U_{12}	U_{12}

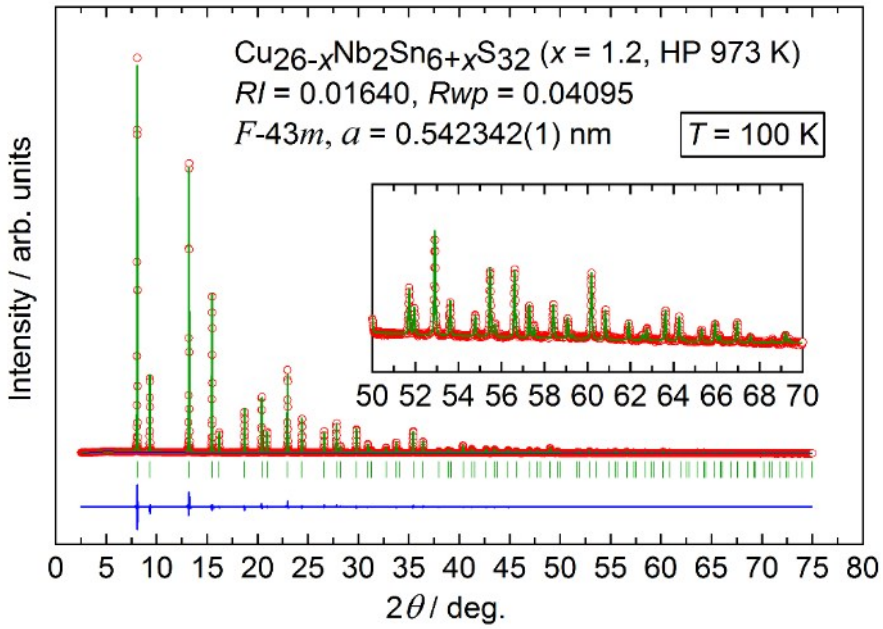

Fig. S7 Rietveld refinement result for synchrotron X-ray diffraction data collected at 100 K for the $Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ sample with x = 1.2 hot-press sintered at 973 K. Reliability factors based on Bragg intensities, *RI*, and on the weighted profile, *Rwp*, of the analysis are 0.01640 and 0.04095, respectively. The refined crystallographic information is listed in Table S4.

Table S4 Refined atomic coordinates and isotropic atomic displacement parameter U_{iso} at 100 K for the $Cu_{26-x}Nb_2Sn_{6+x}S_{32}$ sample with x = 1.2 and sintered at 973 K. Space group, lattice parameter a, and reliability factors based on Bragg intensities, *RI*, and on the weighted profile, *Rwp*, are also presented.

F-43*m*, a = 0.542342(1) nm, *RI* = 0.01640, *Rwp* = 0.04095

Atom	Position	Occ.	x	y	z	$U_{iso}\times10^2$/nm^2
Nb	4*a*	0.0625	0.5	0.5	0	0.0026(3)
Cu	4*b*	0.775	0	0	0.5	0.0087(1)
Sn	4*b*	0.225	0	0	0.5	0.0087(1)
S	4*c*	1	0.25	x	x	0.0063(1)