Supplementary Information

Table S1. Single crystal refinement details for $Cs_2TiCu_3F_{12}$ at room temperature and 125 K.

Parameter	Room temperature	125 K
formula	$Cs_2TiCu_3F_{12}$	
crystal system	Rhombohedral	
space group	$R\bar{3}m$	$R\bar{3}$
a (Å)	7.1014(14)	14.163(3)
c (Å)	19.955(2)	19.865(6)
volume (Å^3)	871.5(2)	3450.88(15)
Z	3	12
wavelength (Å)	0.71073	
ρ (calc.) (g cm^{-3})	4.186	4.229
absorption coefficient (mm^{-1})	12.385	12.511
crystal size (mm)	0.18 × 0.15 × 0.03	0.31 × 0.26 × 0.10
θ range for data collection (°)	3.1–27.5	2.0–27.5
reflections collected	3063	10,280
independent reflections	280	1410
max. & min. transmission	1, 0.425	1, 0.416
data/restraints/parameters	280/0/24	1410/0/101
goodness-of-fit on F2	0.808	0.895
R indices [$I > 2\sigma$ (I)], R1, wR2	0.033, 0.094	0.044, 0.117
R indices (all data), R1, wR2	0.039, 0.102	0.062, 0.110
largest diff. peak & hole (e Å^{-3})	1.01, −2.259	1.56, −1.13

Table S2. Atomic parameters for $Cs_2TiCu_3F_{12}$ as derived from SCXD and corresponding parameters previously reported for $Cs_2SnCu_3F_{12}$.

Atom	x	y	z	U_{ISO} (Å^2) × 100
$Cs_2TiCu_3F_{12}$ (RT)				
Cs	0	0	0.11080(4)	3.40(7)
Ti	0	0	½	1.39(7)
Cu	½	0	0	1.49(11)
F1	0.2037(3)	−0.2037(3)	0.9808(2)	2.56(15)
F2	0.1252(3)	−0.1252(3)	0.4474(2)	4.22(18)
$Cs_2SnCu_3F_{12}$ [1] (RT)				
Cs	0	0	0.1060(1)	3.2(1)
Sn	0	0	½	1.3(1)
Cu	½	0	0	1.1(1)
F1	0.2042(2)	−0.2042(2)	0.9845(1)	2.2(1)
F2	0.1312(2)	−0.1312(2)	0.4465(1)	3.6(1)
$Cs_2TiCu_3F_{12}$ (125 K)				
Cs1	−0.00012(11)	0.49810(7)	0.11189(5)	2.38(4)
Cs2	−1/3	1/3	0.22104(14)	2.24(6)
Cu1	−0.07962(16)	0.57971(17)	0.32991(6)	1.25(5)
Cu2	−0.25705(13)	0.50021(19)	0.00008(15)	1.29(5)
Ti1	1/3	2/3	1/6	1.16(5)
Ti2	−1/6	2/3	1/6	1.16(5)

Table S2. *Cont.*

Atom	*x*	*y*	*z*	U_{ISO} (Å^2) × 100
$Cs_2TiCu_3F_{12}$ (125 K)				
F1	−0.3058(5)	0.6036(9)	−0.0110(4)	1.86(14)
F2	−0.1237(8)	0.4336(8)	0.3109(5)	2.0(3)
F3	0.0641(9)	0.6167(5)	0.3039(4)	1.86(14)
F4	−0.4093(8)	0.3995(8)	0.0208(6)	2.4(3)
F5	0.2473(7)	0.7043(8)	0.1150(6)	2.6(3)
F6	−0.2137(8)	0.7462(7)	0.1152(4)	2.2(2)
F7	−0.2497(7)	0.5429(8)	0.1137(5)	2.1(2)
F8	−0.0459(6)	0.7077(7)	0.1108(5)	2.4(2)

Table S3. Comparison of atomic parameters for $Cs_2TiCu_3F_{12}$ at room temperature as derived from SCXRD, SXPD and NPD data.

Atom	*x*	*y*	*z*	U_{ISO} (Å^2) × 100
SCXRD				
Cs	0	0	0.11080(4)	3.40(7)
Ti	0	0	½	1.39(7)
Cu	½	0	0	1.49(11)
F1	0.2037(3)	−0.2037(3)	0.9808(2)	2.56(15)
F2	0.1252(3)	−0.1252(3)	0.4474(2)	4.22(18)
SXPD				
Cs	0	0	0.11125(3)	2.895(17)
Ti	0	0	½	0.62(4)
Cu	½	0	0	0.684(16)
F1	0.20373(15)	−0.20373(15)	0.98092(10)	2.87(5)
F2	0.12311(15)	−0.12311(15)	0.44766(9)	2.87(5)
NPD				
Cs	0	0	0.10982(13)	2.16(7)
Ti	0	0	½	1.06(11)
Cu	½	0	0	1.04(4)
F1	0.20277(9)	−0.20277(9)	0.98077(7)	2.52(3)
F2	0.12279(10)	−0.12279(10)	0.44776(7)	2.52(3)

Table S4. Comparison of primitive space group fits ($P2_1/n$ and $P2/n$) to $Cs_2TiCu_3F_{12}$ SXPD data at 100 K.

Space group	χ^2	Fitted		Background	
		wR_p (%)	R_p (%)	wR_p (%)	R_p (%)
$P2_1/n$	5.15	8.03	6.24	6.54	5.54
$P2/n$	5.85	8.56	6.68	7.02	5.98

Table S5. Atomic coordinates ($P2_1/n$ model) for $Cs_2TiCu_3F_{12}$ derived from SXPD data at 100 K. Thermal parameters constrained according to element type. a = 7.75776(5) Å, b = 7.04321(4) Å, c = 10.43444(6) Å, β = 96.8692(4)°.

Atom	*x*	*y*	*z*	U_{ISO} (Å^2) × 100
Cs	0.77484(7)	−0.00380(15)	0.11443(5)	0.502(11)
Cu1	½	0	½	−0.11(2)
Cu2	0.2538(3)	0.2305(2)	0.24322(17)	−0.11(2)
Ti	0	0	½	−0.39(3)
F1	0.4573(7)	0.1705(7)	0.3565(5)	0.01(4)
F2	0.9258(7)	0.7140(7)	0.8949(5)	0.01(4)
F3	0.2464(5)	−0.0298(7)	0.1786(4)	0.01(4)
F4	0.5264(6)	0.3541(7)	0.8570(5)	0.01(4)
F5	0.0575(6)	0.7787(7)	0.4108(5)	0.01(4)
F6	0.2273(5)	0.0473(7)	0.5621(4)	0.01(4)

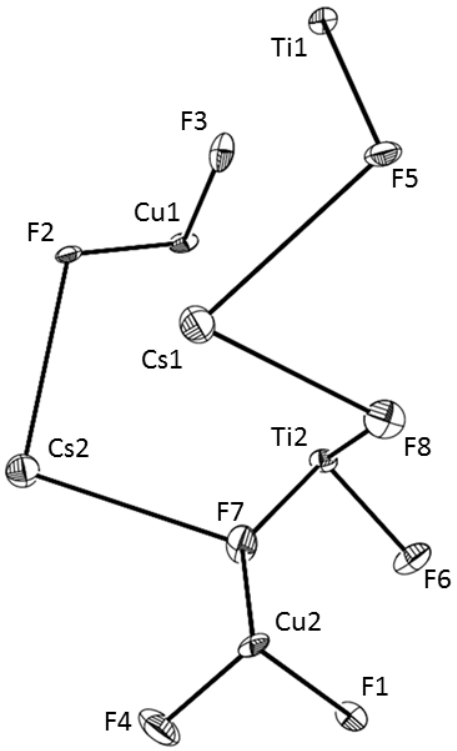

Figure S1. Asymmetric unit of $Cs_2TiCu_3F_{12}$ at 125 K, space group $R\bar{3}$, derived from single crystal data using SHELX.

Table S6. Unit cell parameters for $Cs_2TiCu_3F_{12}$ as a function of temperature as derived from SXPD data.

Temperature (K)	*a* (Å)	*b* (Å)	*c* (Å)	α °	β °	γ °	V (Å^3)
300	7.090323(18)	=*a*	19.91020(9)	90	90	120	866.839(6)
300 (monoclinic equivalent)	7.79768	7.09032	10.53928	90	97.36237	90	577.892
280	7.08882(2)	=*a*	19.89705(10)	90	90	120	865.899(7)
280 (monoclinic equivalent)	7.79349	7.08882	10.53517	90	97.33828	90	577.266
260	7.08613(2)	=*a*	19.87823(11)	90	90	120	864.422(8)
260 (monoclinic equivalent)	7.78734	7.08613	10.52881	90	97.30789	90	576.282
240	7.78574(7)	7.07736(6)	10.51028(14)	90	97.2250(4)	90	574.544(7)
220	7.78215(4)	7.07119(4)	10.49608(7)	90	97.1697(4)	90	573.073(3)
200	7.77779(5)	7.06549(5)	10.48363(7)	90	97.1156(4)	90	571.679(8)
180	7.77302(5)	7.05964(5)	10.47140(7)	90	97.0590(4)	90	571.260(8)
160	7.76895(5)	7.05496(5)	10.46105(7)	90	97.0087(4)	90	569.082(9)
140	7.76513(6)	7.05081(5)	10.45189(9)	90	96.9628(4)	90	568.025(9)
120	7.76151(6)	7.04702(5)	10.44330(8)	90	96.9176(4)	90	567.043(9)
100	7.75776(5)	7.04320(4)	10.43444(6)	90	96.8692(4)	90	566.039(8)

Disagreements between SXPD and NPD Lattice Parameters for $Rb_2TiCu_3F_{12}$

There are small differences in the lattice parameters as reported for $Rb_2TiCu_3F_{12}$ at room temperature for SXPD and NPD data. The purity of the samples needs to be taken into account here as this may complicate analysis. A typical composition is 85.4% $Rb_2TiCu_3F_{12}$, 8.4% Rb_2TiF_6, 4.9% CuO, 1.2% Cu_2O; this may lead to peak overlaps that might obscure or introduce uncertainty into the main phase. The lattice parameters of these phases also differ in both techniques (see Tables S7 and S8). It should also be noted that differences could also be the result of temperature errors and diffractometer offsets.

Table S7. Lattice parameters for main phase and selected impurities in $Rb_2TiCu_3F_{12}$ derived from NPD data.

Phase	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)
$Rb_2TiCu_3F_{12}$	10.3710(12)	10.3541(14)	10.3374(11)	83.729(13)	83.641(10)	83.936(6)
Rb_2TiF_6	5.9215(5)	=*a*	4.8105(8)	90	90	120
CuO	4.715(5)	3.423(3)	5.235(5)	90	100.78(5)	90

Table S8. Lattice parameters for main phase and selected impurities in $Rb_2TiCu_3F_{12}$ derived from SXPD data.

Phase	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)
$Rb_2TiCu_3F_{12}$	10.3529(7)	10.3506(8)	10.3440(3)	83.838(7)	83.832(7)	83.9111(14)
Rb_2TiF_6	5.9325(4)	=*a*	4.8082(6)	90	90	120
CuO	4.6857(2)	3.42384(12)	5.1309(2)	90	99.529(3)	90

Table S9. Triclinic model used for $Rb_2TiCu_3F_{12}$ powder data refinement; the model is derived from the $Rb_2SnCu_3F_{12}$ model [2] using the ISODISTORT program [3] with the removal of disorder at some of the fluoride sites, and no further structural refinement.

Atom	***x***	***y***	***z***
Rb	0.3999	0.8933	0.8991
Rb	0.8991	0.3999	0.8933
Rb	0.8933	0.8991	0.3999
Rb	0.6020	0.6020	0.6020
Cu	0.7628	0.7401	0.0017
Cu	0.0017	0.7628	0.7401
Cu	0.7401	0.0017	0.7628
Cu	0.5285	0.7530	0.2492
Cu	0.2492	0.5285	0.7530
Cu	0.7530	0.2492	0.5285
Ti	½	½	0
Ti	0	½	½
Ti	½	0	½
Ti	0	0	0
F	0.8195	0.5856	0.1049
F	0.1049	0.8195	0.5856
F	0.5856	0.1049	0.8195
F	0.8848	0.6803	0.8666
F	0.8666	0.8848	0.6803
F	0.6803	0.8666	0.8848
F	0.6686	0.8217	0.1412
F	0.1412	0.6686	0.8217
F	0.8217	0.1412	0.6686
F	0.0633	0.9370	0.8337
F	0.8337	0.0633	0.9370
F	0.9370	0.8337	0.0633
F	0.4004	0.5948	0.8668
F	0.8668	0.4004	0.5948
F	0.5948	0.8668	0.4004
F	0.5336	0.6644	0.0525
F	0.0525	0.5336	0.6644
F	0.6644	0.0525	0.5336
F	0.6484	0.5084	0.8717
F	0.8717	0.6484	0.5084
F	0.5084	0.8717	0.6484
F	0.3928	0.6842	0.3619
F	0.3619	0.3928	0.6842
F	0.6842	0.3619	0.3928

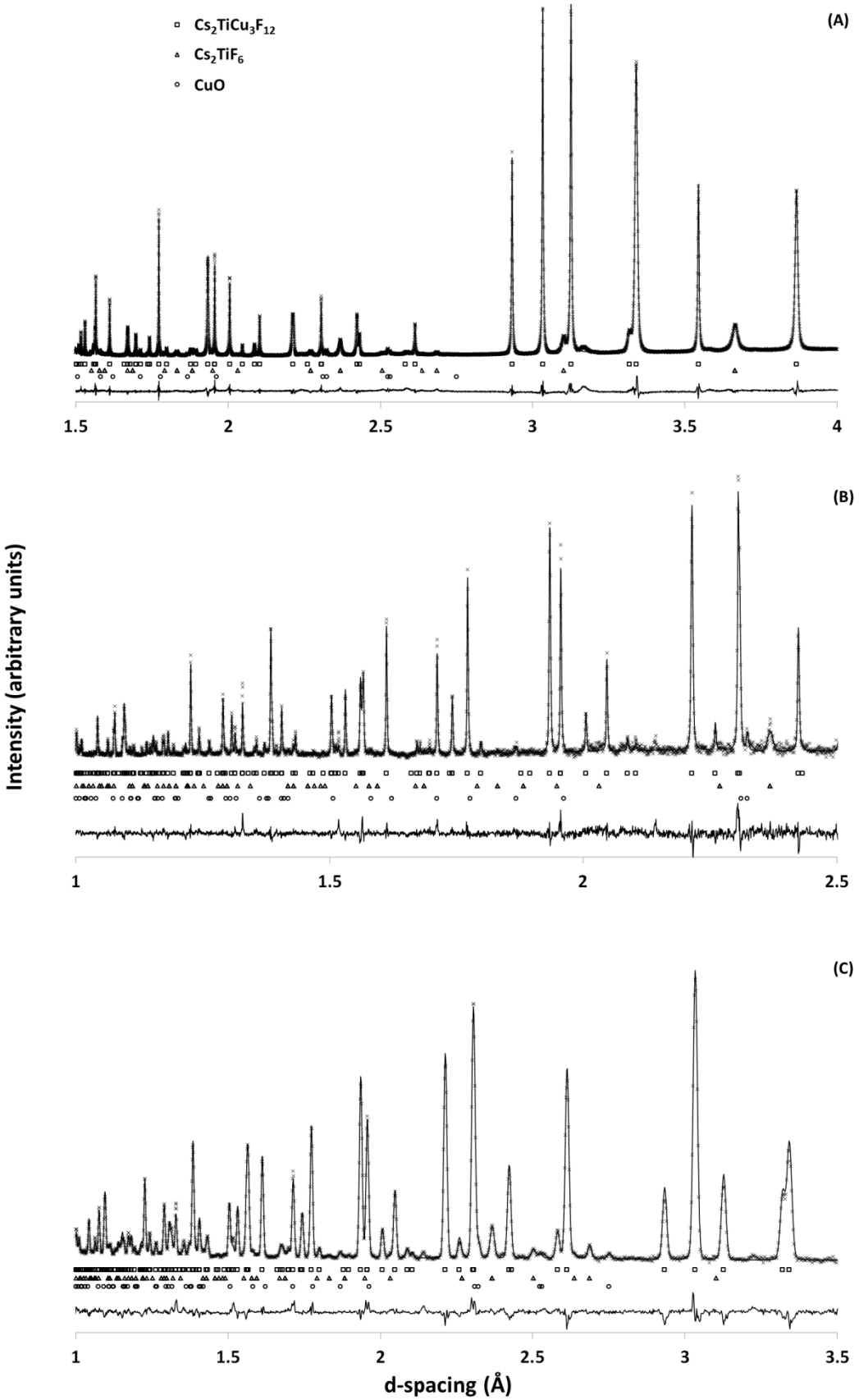

Figure S2. Rietveld fits for $Cs_2TiCu_3F_{12}$ at 300 K; (**A**) SXPD; (**B**) NPD backscattering bank and (**C**) NPD 90 °bank. SXPD performed at I11, Diamond Light Source, NPD performed at HRPD, ISIS.

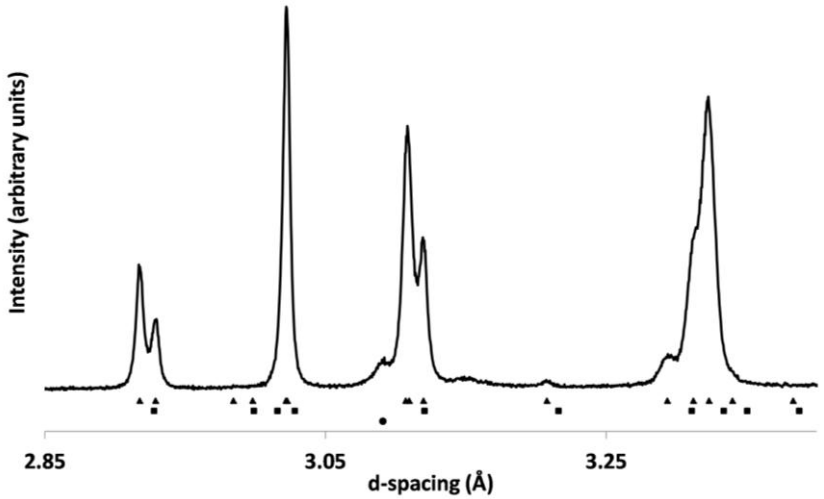

Figure S3. SXPD pattern for $Cs_2TiCu_3F_{12}$ at 100 K; triangles are reflections permitted for the monoclinic ($P2_1/n$) unit cell, squares for the doubled rhombohedral ($R\bar{3}$) unit cell and circles mark the impurity Cs_2TiF_6.

Table S10. Unit cell parameters for $Rb_2TiCu_3F_{12}$ as a function of temperature on cooling.

Temperature (K)	*a* (Å)	*b* (Å)	*c* (Å)	α°	β°	γ°	*V* (Å^3)
300	10.3520(9)	10.3481(10)	10.3405(4)	83.865(8)	83.865(8)	83.954(2)	1090.11(15)
280	10.3486(7)	10.3426(7)	10.3310(4)	83.870(6)	83.869(6)	84.005(2)	1088.29(11)
260	10.3363(5)	10.3488(4)	10.3182(4)	83.834(4)	83.872(4)	84.100(2)	1086.40(8)
240	10.3316(4)	10.3473(4)	10.3074(4)	83.799(3)	83.890(3)	84.177(2)	1084.71(7)
220	10.3260(4)	10.3446(4)	10.2987(4)	83.784(3)	83.905(3)	84.240(2)	1083.04(7)
200	10.3209(4)	10.3410(4)	10.2908(4)	83.785(3)	83.927(3)	84.295(2)	1081.44(7)
180	10.3151(4)	10.3373(4)	10.2843(4)	83.791(3)	83.949(3)	84.343(2)	1079.88(7)
160	10.3102(4)	10.3335(4)	10.2783(4)	83.797(3)	83.974(3)	84.381(2)	1078.47(7)
140	10.3054(4)	10.3298(4)	10.2730(4)	83.809(2)	84.002(3)	84.415(2)	1077.16(7)
120	10.3003(4)	10.3256(4)	10.2683(4)	83.826(3)	84.027(3)	84.441(2)	1075.81(7)
100	10.2956(4)	10.3220(4)	10.2642(4)	83.845(3)	84.057(3)	84.459(2)	1074.64(7)
85	10.2924(4)	10.3190(4)	10.2614(4)	83.861(3)	84.080(3)	84.468(2)	1073.79(7)

Table S11. Unit cell parameters for $Rb_2TiCu_3F_{12}$ as a function of temperature on heating.

Temperature (K)	*a* (Å)	*b* (Å)	*c* (Å)	α°	β°	γ°	*V* (Å^3)
300	10.3537(7)	10.3486(8)	10.3398(4)	83.849(6)	83.849(6)	83.956(2)	1090.22(12)
280	10.3416(4)	10.3532(4)	10.3275(3)	83.830(4)	83.849(4)	84.0437(18)	1088.26(7)
260	10.3365(4)	10.3519(4)	10.3157(3)	83.792(3)	83.863(3)	84.1321(19)	1086.44(7)
240	10.3313(4)	10.3498(4)	10.3059(3)	83.776(3)	83.878(3)	84.1986(19)	1084.76(7)
220	10.3253(3)	10.3457(3)	10.2976(3)	83.773(2)	83.901(3)	84.255(2)	1082.96(5)
200	10.3204(4)	10.3425(4)	10.2904(4)	83.772(2)	83.924(3)	84.306(2)	1081.48(7)
180	10.3149(4)	10.3385(4)	10.2841(4)	83.779(2)	83.948(3)	84.349(2)	1079.95(7)
160	10.3097(4)	10.3339(4)	10.2787(4)	83.793(2)	83.977(3)	84.380(2)	1078.49(7)
140	10.3053(4)	10.3298(4)	10.2732(4)	83.804(2)	84.003(3)	84.415(2)	1077.15(7)
120	10.3000(4)	10.3259(4)	10.2690(4)	83.823(3)	84.030(3)	84.438(2)	1075.88(7)
100	10.2956(4)	10.3219(4)	10.2644(4)	83.845(3)	84.059(3)	84.460(2)	1074.64(7)

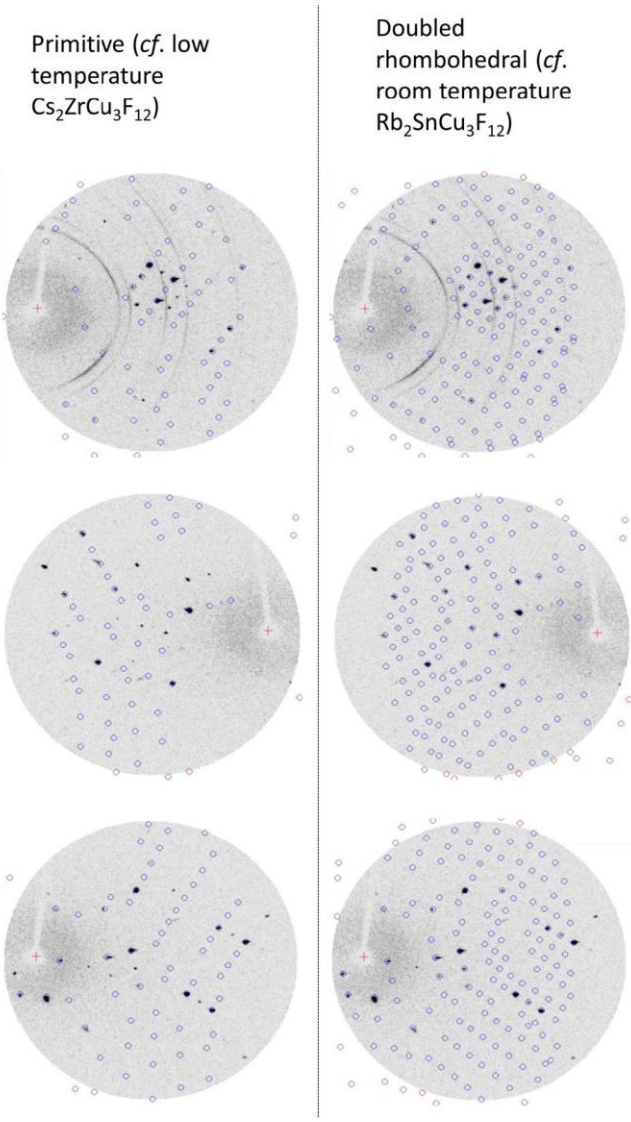

Figure S4. Single crystal diffraction images (from Rigaku CrystalClear 2.0), with indexed peaks circled. The monoclinic unit cell is indicated on the left and the doubled rhombohedral cell on the right. Note the inadequacy of the former to account for the observed reflections.

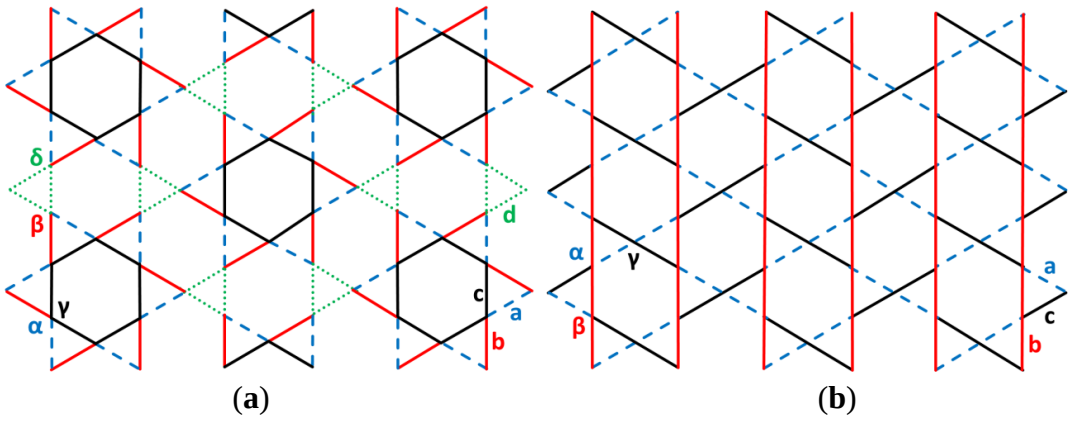

Figure S5. Schematic models of the Cu ··Cu kagome networks in $Cs_2TiCu_3F_{12}$ for the $R\bar{3}$ model (**a**) and $P2_1/n$ model (**b**).

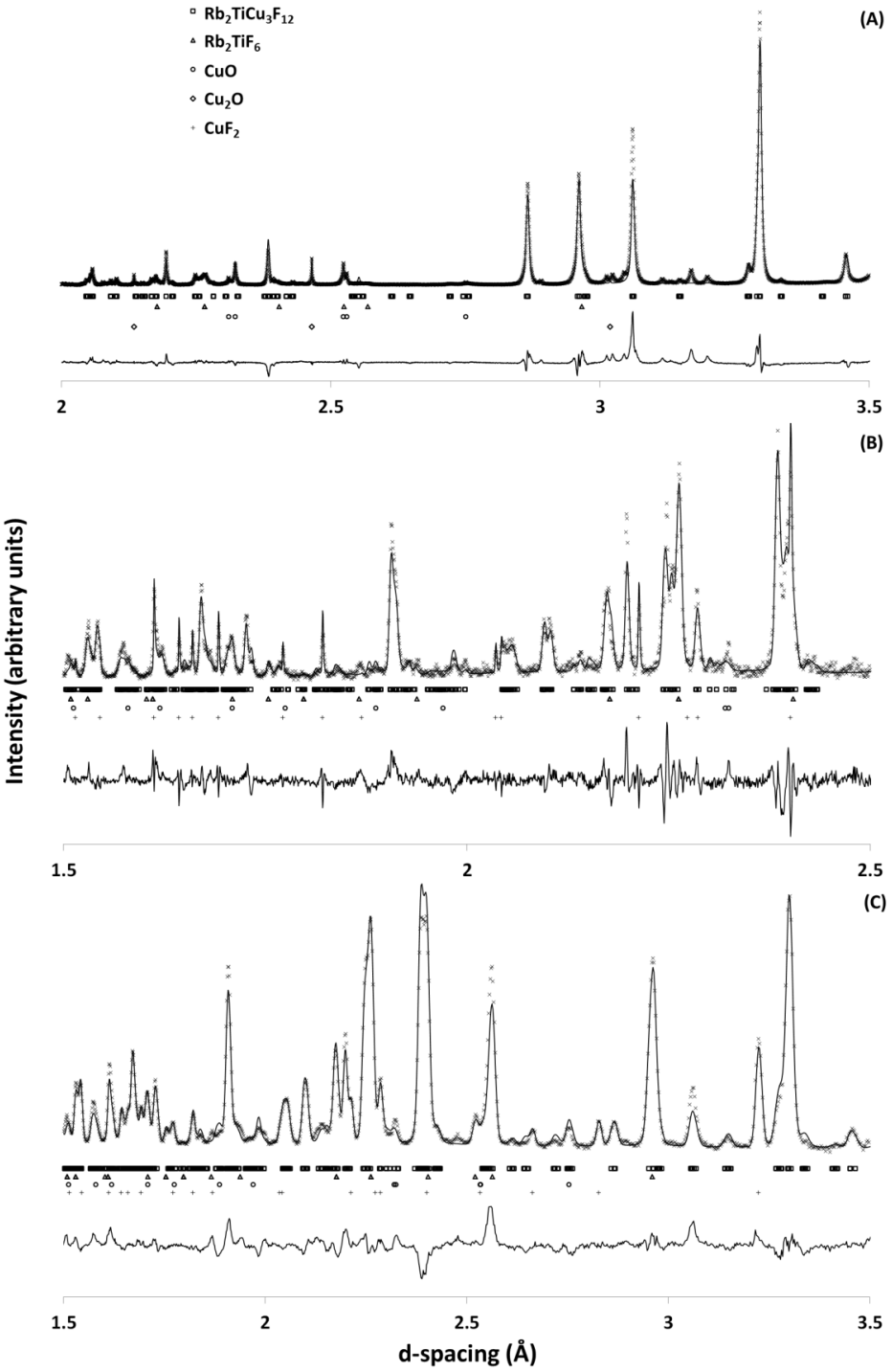

Figure S6. Rietveld fits for $Rb_2TiCu_3F_{12}$ at 300 K; (**A**) SXPD; (**B**) NPD backscattering bank, (**C**) NPD 90 °bank (atomic coordinates not refined).

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