Supplementary data

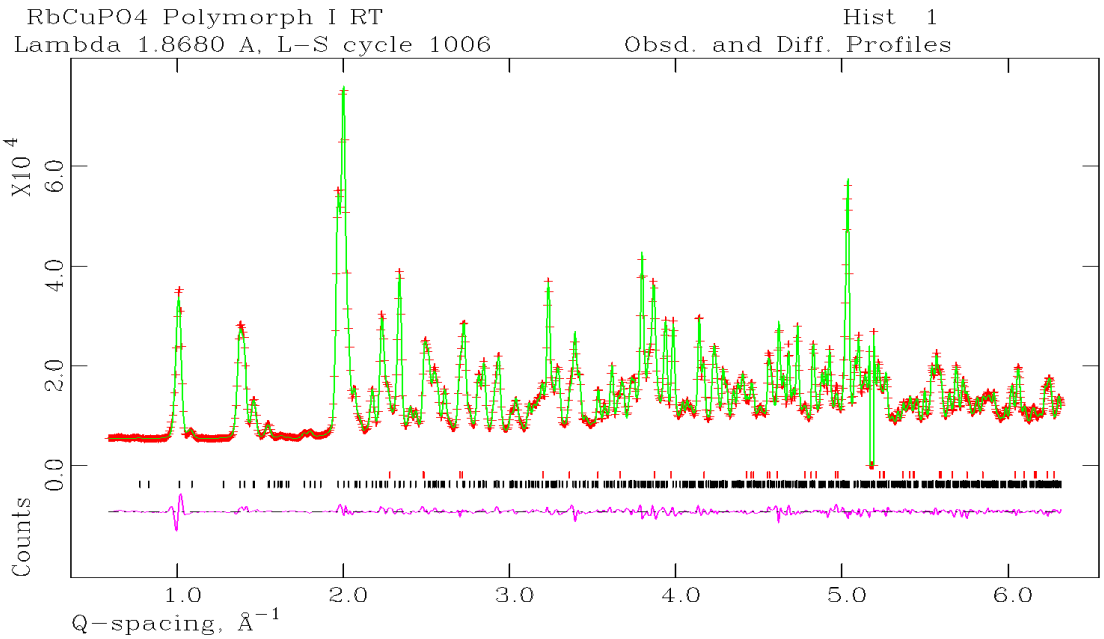

Figure S1 Final Rietveld refinement profile for the 1.87 Å incident wavelength D20 PND data for $RbCuPO_4$ polymorph **II**. The observed data are crosses, the calculated pattern a solid line, the tick marks show the allowed reflections and the lower solid line is the difference plot; R_{wp} = 2.92 %, R_p = 2.10 % and $R_{F^{**}2}$ = 1.75 % for 790 observations. The excluded region is caused by unstable detector cells during the data collection.

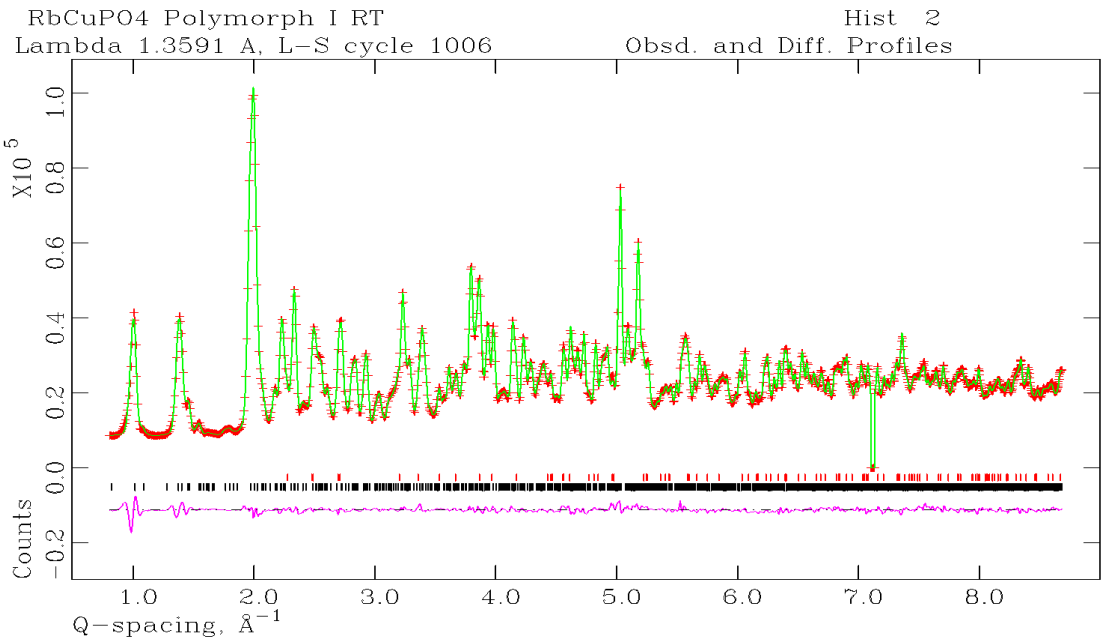

Figure S2 Final Rietveld refinement profile for the 1.36 Å incident wavelength D20 PND data for $RbCuPO_4$ polymorph **I**. The observed data are crosses, the calculated pattern a solid line, the tick marks show the allowed reflections and the lower solid line is the difference plot; R_{wp} = 2.50 %, R_p = 1.69 % and $R_{F^{**}2}$ = 2.26 % for 2041 observations. The excluded region is caused by unstable detector cells during the data collection.

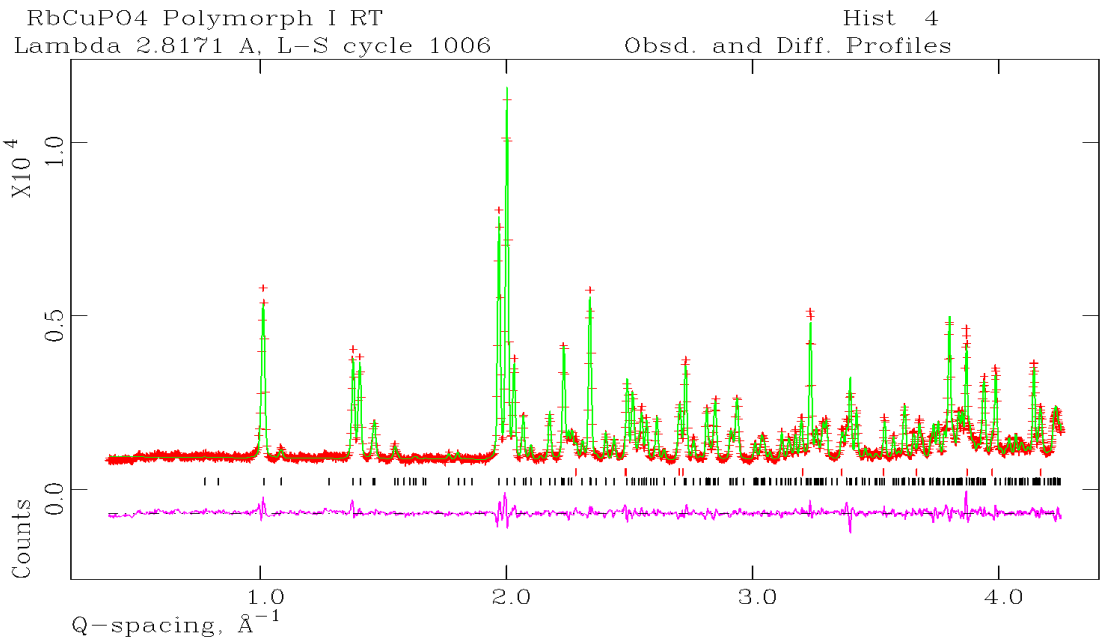

Figure S3 Final Rietveld refinement profile for the 2.82 Å incident wavelength E9 PND data for $RbCuPO_4$ polymorph **I**. The observed data are crosses, the calculated pattern a solid line, the tick marks show the allowed reflections and the lower solid line is the difference plot; R_{wp} = 5.24 %, R_p = 4.10 % and R_{F**2} = 4.23 % for 233 observations.

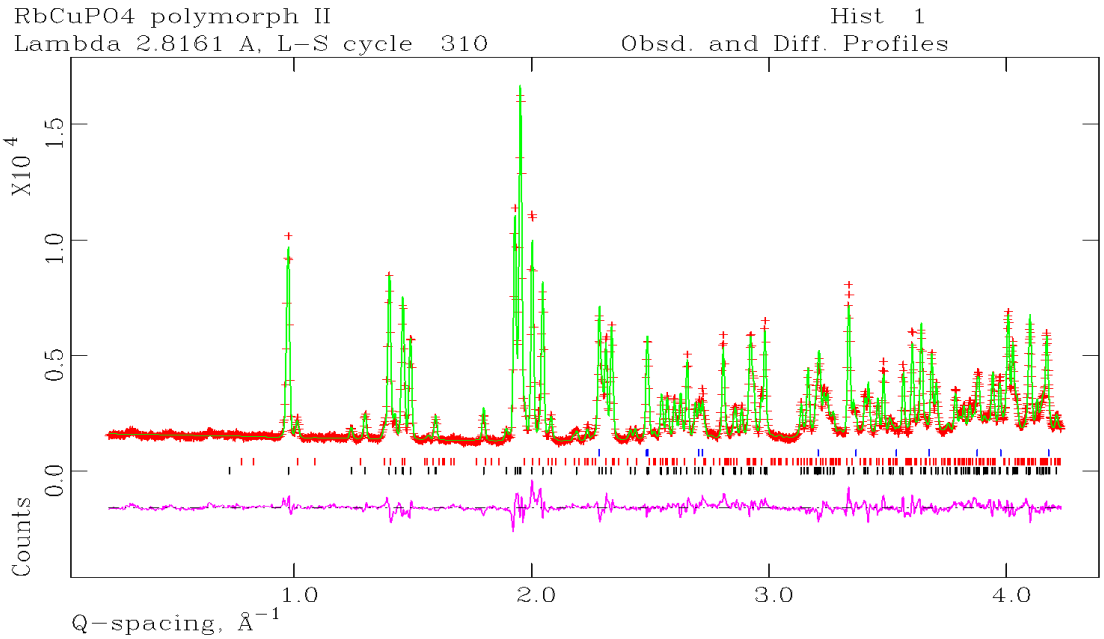

Figure S4 Final Rietveld refinement profile for the 2.82 Å incident wavelength E9 PND data for $RbCuPO_4$ polymorph **II**. The observed data are crosses, the calculated pattern a solid line, the tick marks show the allowed reflections (upper **I**, middle CuO and lower **II**) and the lower solid line is the difference plot; R_{wp} = 6.00 %, R_p = 4.68 % and $R_{F^{**}2}$ = 6.42 % for 416 observations.

Table S1 Bond valence sums for polymorph **I** and **II**.

Polymorph **I**		Polymorph **II**	
Atom	bvs	Atom	bvs
Rb(1)	1.23	Rb(1)	1.32
Rb(2)	1.17	Rb(2)	1.14
Cu(1)	2.03	Cu(1)	2.06
Cu(2)	1.99	Cu(2)	2.04
P(1)	4.91	P(1)	4.84
P(2)	4.93	P(2)	4.77
O(1)	2.00	O(1)	2.06
O(2)	2.11	O(2)	2.07
O(3)	1.96	O(3)	1.87
O(4)	2.08	O(4)	2.07
O(5)	2.04	O(5)	2.07
O(6)	1.97	O(6)	1.99
O(7)	2.07	O(7)	2.05
		O(8)	2.02

Table S2 Bond valence sums for Rb(1) and Rb(2) using different bond length cutoffs.

	Polymorph **I**				Polymorph **II**			
Cut off / Å	Rb(1)	Coord. Num.	Rb(2)	Coord. Num.	Rb(1)	Coord. Num.	Rb(2)	Coord. Num.
3.0	0.93	5	0.77	4	1.02	5	0.71	3
3.15	1.12	7	1.09	7	1.25	7	0.97	5
3.50	1.23	9	1.17	8	1.32	8	1.14	8
4.0	1.23	9	1.20	10	1.36	10	1.14	8

Bond valence sum calculations (bvs) are determined with respect to reference bond lengths from crystal structures that are based on simplifying assumptions, which can limit their applicability. Of particular relevance to the rubidium bvs calculations in the above tables is the use of the universal value of *b* of 0.37, which does not take into account the softness of the anions. For a full account of the effect of calculating the value of *b* explicitly for alkali metal chalcogenides see Adams, 2001. The effect is to overestimate the bvs, particularly in the case of highly asymmetric coordination geometries, using standard cut-off distances for bond contributions.

References

Bvs calculations:
Brown & Altermatt (1985), *Acta Crystallogr.* **B41**, 244.247. (empirical)
Brese & O'Keeffe (1991), *Acta Crystallogr.* **B47**, 192-197. (extrapolated)
In each case, all the values except phosphorus are taken from Brown & Altermatt (1985).

Adams, S. (2001). *Acta Crystallogr.* **B57**, 278-287.

Table S3 Bond lengths within the Rb coordination polyhedra (to 4Å) for **I** and **II**.

Polymorph **I**		Polymorph **II**	
Bond	Length / Å	Bond	Length / Å
Rb(1) - O(1) × 2	2.9004(32)	Rb(1) - O(1)	2.796(8)
Rb(1) - O(1) × 2	3.1223(32)	Rb(1) - O(2)	3.004(10)
Rb(1) - O(2) × 2	2.9001(33)	Rb(1) - O(3)	2.949(9)
Rb(1) - O(3) × 2	3.3356(31)	Rb(1) - O(3)	3.816(9)
Rb(1) - O(4)	2.843(5)	Rb(1) - O(4)	2.912(10)
		Rb(1) - O(4)	3.200(9)
Rb(2) - O(2)	2.8098(33)	Rb(1) - O(5)	3.141(9)
Rb(2) - O(2)	3.6887(29)	Rb(1) - O(6)	3.710(8)
Rb(2) - O(3)	3.0413(26)	Rb(1) - O(6)	2.789(9)
Rb(2) - O(4)	2.8163(32)	Rb(1) - O(8)	2.839(9)
Rb(2) - O(5)	3.8122(34)		
Rb(2) - O(6)	3.0818(30)	Rb(2) - O(1)	2.779(8)
Rb(2) - O(6)	3.2255(31)	Rb(2) - O(3)	3.005(10)
Rb(2) - O(6)	3.1369(32)	Rb(2) - O(4)	3.657(10)
Rb(2) - O(7)	2.9041(30)	Rb(2) - O(4)	3.816(10)
Rb(2) - O(7)	2.9961(29)	Rb(2) - O(5)	2.793(8)
		Rb(2) - O(6)	3.313(10)
		Rb(2) - O(7)	3.191(10)
		Rb(2) - O(7)	2.819(10)
		Rb(2) - O(8)	3.048(9)