SUPPLEMENTARY INFORMATION

Subtle symmetry breaking in averievite-type compounds, (*MX*)$Cu_5O_2(VO_4)_2$ (*MX* = CsBr, CsI, RbBr, RbI and KI)

Ilya V. Kornyakov,[*ab] *Alexey A. Kalinichev,*[a] *Marina V. Likholetova,*[a] *and Sergey V. Krivovichev*[ab]

[a] St. Petersburg State University, University Emb. 7/9, 199034, St. Petersburg, Russia. E-mail: i.kornyakov@spbu.ru;

[b] Nanomaterials Research Centre, Kola Science Centre, Russian Academy of Sciences, Fersmana 14, 184209, Apatity, Russia.

Synthesis and X-ray diffraction analysis of $(CsI)Cu_5O_2(PO_4)_2$

Single crystal of $(CsI)Cu_5O_2(PO_4)_2$ were obtained by means solid state reactions in low vacuum following the same method, utilized by Kornyakov *et al*. for synthesis of other phosphates of averievite family.[1] There are two significant distinctions: the use of CsI reagent (CsI, 99%, Sigma-Aldrich) and the maximal temperature of the synthesis which did not exceed 600 °C.

Single crystals of the $(CsI)Cu_5O_2(PO_4)_2$ compound were investigated by single-crystal X-ray diffraction. The measurements were performed using a Rigaku XtaLAB Synergy-S diffractometer equipped with a monochromatic microfocus MoKα source (PhotonJet-S, $\lambda = 0.71073$ Å, 50 kV, 1.0 mA) and a HyPix-6000HE hybrid photon counting detector at 300 and 100 K.

CrysAlisPro software was used for the integration and correction of diffraction data for polarization, background and Lorentz effects, a numerical absorption correction based on Gaussian integration over a multifaceted crystal model, and an empirical absorption correction based on spherical harmonics implemented in the SCALE3 ABSPACK algorithm.[2] The unit cell parameters were refined using a least-squares technique. The structure was solved by a dual-space algorithm and refined using SHELX programs,[3,4] which were incorporated in the *OLEX*2 program package.[5]

References

1. I. V. Kornyakov, V. V. Vladimirova, O. I. Siidra and S. V. Krivovichev, *Molecules*, 2021, **26**, 1833.
2. *CrysAlis Pro, Version 1.171.42.102a*, Rigaku Oxford Diffraction, 2023.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv*., 2015, **71**, 3–8.
4. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem*., 2015, **71**, 3–8.
5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Pushmann, *J. Appl. Crystallogr*., 2009, **42**, 339–341.

Table S1. Selected unit-cell, data collection, and refinement parameters for averievite-type compounds.

T, K	Formula	Space Group	a, Å	c, Å	V, Å^3	Reflections collected	Unique reflections in total	$\sin\theta/\lambda$, Å^{-1}	R_{int}	R_σ	R_1	wR_2	ρ_{max}, e$^-$·Å^{-3}	ρ_{min}, e$^-$·Å^{-3}	CCDC
100	$(KI)Cu_5O_2(VO_4)_2$	$P31m$	11.0737(1)	8.3989(1)	891.946(19)	49302	4357	0.940	5.44	2.39	2.45	6.43	1.50	–1.12	2450785
120			11.0752(1)	8.3980(1)	892.092(19)	49339	4358	0.940	5.56	2.45	2.52	6.63	1.63	–1.08	2450786
140			11.0771(1)	8.3976(1)	892.355(19)	49331	4358	0.940	5.46	2.42	2.54	6.79	1.85	–1.05	2450787
160			11.0805(1)	8.3974(1)	892.882(19)	49389	4359	0.940	5.66	2.53	2.57	6.85	1.66	–1.07	2450788
180			11.0828(1)	8.3957(1)	893.072(19)	49392	4360	0.939	5.65	2.47	2.65	7.10	1.66	–0.94	2450789
200			11.0857(1)	8.3959(1)	893.561(19)	49427	4363	0.941	5.62	2.46	2.48	6.67	1.30	–0.96	2450790
220			11.0882(1)	8.3952(1)	893.889(19)	49457	4366	0.940	5.69	2.49	2.56	6.88	1.16	–1.04	2450791
240			11.0911(1)	8.3954(1)	894.378(19)	49480	4366	0.941	5.75	2.55	2.62	7.03	1.14	–1.18	2450792
260			11.0934(1)	8.3944(1)	894.642(19)	49510	4369	0.941	5.72	2.55	2.74	7.33	1.33	–1.20	2450793
280			11.0963(2)	8.3940(1)	895.07(3)	49524	4372	0.941	5.74	2.60	2.78	7.42	1.52	–1.28	2450794
300			11.0993(2)	8.3940(1)	895.55(3)	49551	4373	0.941	5.87	2.68	2.84	7.36	1.53	–1.36	2450795
320			11.1026(2)	8.3948(1)	896.17(3)	49604	4376	0.940	5.83	2.61	2.91	8.22	1.78	–1.54	2450796
340			11.1063(2)	8.3936(1)	896.64(3)	49634	4380	0.941	5.88	2.65	3.09	8.70	1.87	–1.54	2450797
360			11.1108(2)	8.3940(1)	897.41(3)	49659	4383	0.941	5.87	2.65	3.20	9.16	2.01	–1.68	2450798
380			11.1159(2)	8.3957(1)	898.41(3)	49731	4386	0.941	5.92	2.67	3.33	9.45	2.28	–1.87	2450799
400			11.1188(2)	8.3948(2)	898.79(4)	49769	4389	0.940	5.86	2.68	3.50	10.11	2.46	–2.09	2450784

Table S1 (continued).

T, K	Formula	Space Group	*a*, Å	*c*, Å	*V*, Å³	Reflections collected	Unique reflections in total	$\sin\theta/\lambda$, Å^{-1}	R_{int}	R_σ	R_1	wR_2	ρ_{max}, e$^-$·Å^{-3}	ρ_{min}, e$^-$·Å^{-3}	CCDC
100	$(KI)Cu_5O_2(VO_4)_2$	$P\bar{3}$	11.0737(1)	8.3989(1)	891.946(19)	49302	4101	0.940	5.63	2.36	4.49	10.26	2.36	–3.79	–
120			11.0752(1)	8.3980(1)	892.092(19)	49339	4103	0.940	5.72	2.38	4.27	10.12	2.59	–3.15	–
140			11.0771(1)	8.3976(1)	892.355(19)	49331	4106	0.940	5.68	2.37	4.05	9.59	2.70	–2.87	–
160			11.0805(1)	8.3974(1)	892.882(19)	49389	4107	0.940	5.79	2.44	3.8	9.13	2.19	–2.36	–
180			11.0828(1)	8.3957(1)	893.072(19)	49392	4108	0.939	5.85	2.46	3.55	8.31	1.84	–2.30	–
200			11.0857(1)	8.3959(1)	893.561(19)	49427	4110	0.941	5.84	2.43	3.39	7.97	1.62	–1.70	–
220			11.0882(1)	8.3952(1)	893.889(19)	49457	4114	0.940	5.86	2.44	3.19	7.63	1.40	–1.35	–
240			11.0911(1)	8.3954(1)	894.378(19)	49480	4116	0.941	5.90	2.48	3.08	7.34	1.33	–1.42	–
260			11.0934(1)	8.3944(1)	894.642(19)	49510	4118	0.941	5.85	2.47	3.03	7.48	1.64	–1.30	–
280			11.0963(2)	8.3940(1)	895.07(3)	49524	4119	0.941	5.96	2.51	3.02	7.15	1.81	–1.60	–
300			11.0993(2)	8.3940(1)	895.55(3)	49551	4120	0.941	5.97	2.56	3.00	7.48	2.18	–1.79	–
320			11.1026(2)	8.3948(1)	896.17(3)	49604	4126	0.940	6.00	2.51	3.05	7.66	2.21	–1.93	–
340			11.1063(2)	8.3936(1)	896.64(3)	49634	4129	0.941	6.03	2.54	3.18	8.48	2.55	–2.09	–
360			11.1108(2)	8.3940(1)	897.41(3)	49659	4133	0.941	6.16	2.55	3.23	8.65	2.59	–2.30	–
380			11.1159(2)	8.3957(1)	898.41(3)	49731	4136	0.941	6.09	2.56	3.47	9.22	2.88	–2.36	–
400			11.1188(2)	8.3948(2)	898.79(4)	49769	4138	0.940	6.19	2.55	3.55	9.59	2.86	–2.69	–

Table S1 (continued).

T, K	Formula	Space Group	*a*, Å	*c*, Å	*V*, Å³	Reflections collected	Unique reflections in total	$\sin\theta/\lambda$, Å^{-1}	R_{int}	R_{σ}	R_1	wR_2	ρ_{max}, e$^-$·Å^{-3}	ρ_{min}, e$^-$·Å^{-3}	CCDC
100	$(CsI)Cu_5O_2(VO_4)_2$	$P31m$	11.10846(15)	8.38498(11)	896.07(3)	49404	4347	0.940	5.86	2.86	2.37	5.28	0.79	–0.96	2450921
102			11.10702(15)	8.38437(11)	895.77(3)	49383	4344	0.940	5.82	2.93	2.43	5.52	0.75	–1.19	2450947
104			11.10671(15)	8.3841(1)	895.69(3)	49409	4346	0.940	5.84	2.85	2.48	5.93	1.01	–1.22	2450937
106			11.10826(15)	8.38438(11)	895.97(3)	49408	4344	0.940	5.82	2.85	2.45	5.70	0.99	–1.34	2450944
108			11.10799(15)	8.3845(1)	895.94(3)	49415	4346	0.940	5.76	2.76	2.45	5.78	0.94	–1.14	2450948
110			11.10806(15)	8.38469(11)	895.97(3)	49381	4346	0.940	5.73	2.82	2.45	5.86	0.69	–1.01	2450940
112			11.10857(15)	8.38468(11)	896.05(3)	49420	4347	0.940	5.64	2.78	2.47	5.95	0.72	–1.09	2450942
114			11.10905(16)	8.38449(12)	896.11(3)	49422	4346	0.940	5.62	2.79	2.44	5.83	0.72	–1.08	2450946
116			11.10909(16)	8.38536(12)	896.21(3)	49423	4346	0.940	5.57	2.76	2.38	5.86	0.80	–1.16	2450941
118			11.10914(16)	8.38522(12)	896.2(0)	49394	4346	0.940	5.52	2.72	2.47	6.11	0.87	–0.99	2450939
120			11.1114(2)	8.3861(1)	896.66(3)	49399	4345	0.940	5.48	2.77	2.29	5.56	0.79	–1.07	2450945
122			11.11152(16)	8.38672(12)	896.75(3)	49381	4345	0.940	5.56	2.74	2.39	6.05	0.74	–1.04	2450938
124			11.11154(16)	8.38609(12)	896.68(3)	49371	4344	0.940	5.38	2.78	2.48	6.56	0.84	–1.10	2450943
130		$P\bar{3}m1$	6.4151(1)	8.3878(1)	298.941(10)	16571	821	0.940	5.21	1.47	1.37	3.32	0.73	–1.07	2450936
140			6.4158(1)	8.3874(1)	298.992(10)	16574	822	0.940	5.14	1.48	1.42	3.25	0.78	–1.20	2450929
160			6.4164(1)	8.3868(1)	299.026(10)	16583	821	0.940	4.81	1.38	1.42	3.31	0.93	–1.31	2450928
180			6.4175(1)	8.3877(1)	299.161(10)	16605	822	0.940	4.66	1.37	1.50	3.62	1.31	–1.61	2450930
200			6.4178(1)	8.3883(1)	299.211(10)	16630	822	0.941	4.60	1.37	1.55	3.42	1.33	–1.66	2450933
220			6.4184(1)	8.3885(1)	299.274(10)	16617	821	0.938	4.69	1.37	1.65	3.71	1.48	–1.74	2450923
240			6.4191(1)	8.3882(1)	299.328(10)	16632	822	0.941	4.71	1.38	1.72	3.88	1.61	–1.94	2450926
260			6.4195(1)	8.3884(1)	299.373(10)	16646	822	0.941	4.84	1.41	1.87	4.52	1.60	–2.17	2450932
280			6.4204(1)	8.3889(1)	299.474(10)	16672	823	0.941	5.01	1.47	1.96	4.51	1.92	–2.26	2450935
300			6.4214(1)	8.3909(1)	299.639(10)	16681	823	0.941	5.08	1.49	2.10	4.68	2.00	–2.42	2450924
320			6.4230(1)	8.3913(1)	299.803(10)	16703	823	0.940	5.29	1.58	2.19	5.28	2.03	–2.56	2450925
340			6.4235(1)	8.3913(1)	299.849(10)	16702	823	0.940	5.37	1.57	2.30	5.35	2.19	–2.53	2450934
360			6.4250(1)	8.3926(1)	300.036(10)	16667	822	0.940	5.38	1.57	2.35	5.28	2.52	–2.75	2450927
380			6.4265(1)	8.3924(1)	300.169(10)	16711	823	0.940	5.55	1.63	2.58	5.68	2.43	–2.86	2450931
400			6.4280(1)	8.3947(1)	300.391(10)	16747	825	0.940	5.49	1.60	2.62	5.98	2.55	–2.84	2450922

Table S1 (continued).

T, K	Formula	Space Group	a, Å	c, Å	V, Å^3	Reflections collected	Unique reflections in total	$\sin\theta/\lambda$, Å^{-1}	R_{int}	R_σ	R_1	wR_2	ρ_{max}, e$^-$Å^{-3}	ρ_{min}, e$^-$Å^{-3}	CCDC
100			11.10846(15)	8.38498(11)	896.07(3)	49404	4106	0.940	5.96	2.48	2.22	4.95	0.89	–1.21	–
102			11.10702(15)	8.38437(11)	895.77(3)	49383	4104	0.940	5.93	2.52	2.27	5.02	0.88	–1.30	–
104			11.10671(15)	8.3841(1)	895.69(3)	49409	4106	0.940	6.00	2.48	2.29	5.24	0.94	–1.20	–
106			11.10826(15)	8.38438(11)	895.97(3)	49408	4104	0.940	5.9	2.43	2.26	5.11	1.13	–1.26	–
108			11.10799(15)	8.3845(1)	895.94(3)	49415	4106	0.940	5.87	2.37	2.26	5.20	0.95	–1.15	–
110			11.10806(15)	8.38469(11)	895.97(3)	49381	4106	0.940	5.88	2.4	2.27	5.13	0.89	–1.16	–
112	$(CsI)Cu_5O_2(VO_4)_2$	$P\bar{3}$	11.10857(15)	8.38468(11)	896.05(3)	49420	4107	0.940	5.75	2.36	2.30	5.33	0.93	–1.14	–
114			11.10905(16)	8.38449(12)	896.11(3)	49422	4106	0.940	5.74	2.36	2.20	5.07	0.83	–1.22	–
116			11.10909(16)	8.38536(12)	896.21(3)	49423	4109	0.940	5.67	2.34	2.31	5.78	1.04	–1.45	–
118			11.10914(16)	8.38522(12)	896.2(0)	49394	4109	0.940	5.65	2.31	2.34	5.96	0.90	–1.14	–
120			11.1114(2)	8.3861(1)	896.66(3)	49399	4108	0.940	5.57	2.33	2.30	5.57	0.99	–1.20	–
122			11.11152(16)	8.38672(12)	896.75(3)	49381	4108	0.940	5.67	2.30	2.31	6.24	0.85	–1.15	–
124			11.11154(16)	8.38609(12)	896.68(3)	49371	4107	0.940	5.50	2.33	2.41	6.46	1.04	–1.25	–

Table S1 (continued).

T, K	Formula	Space Group	a, Å	c, Å	V, Å^3	Reflections collected	Unique reflections in total	$\sin\theta/\lambda$, Å^{-1}	R_{int}	R_σ	R_1	wR_2	ρ_{max}, e$^-$·Å^{-3}	ρ_{min}, e$^-$·Å^{-3}	CCDC
100			11.0574(2)	8.3888(1)	888.25(3)	96848	4325	0.939	8.23	3.13	3.20	10.80	2.12	–1.17	2450913
102			11.0572(2)	8.3888(1)	888.22(3)	96870	4326	0.939	8.02	3.03	3.15	10.81	2.14	–1.23	2450912
104			11.05625(15)	8.38489(13)	887.65(3)	96890	4325	0.938	7.70	3.08	3.14	10.19	2.23	–1.09	2450915
106			11.06071(16)	8.3882(1)	888.72(3)	96991	4330	0.939	7.67	3.00	3.13	10.33	2.26	–1.05	2450918
108			11.0562(2)	8.389(0)	888.08(3)	96904	4327	0.939	7.62	2.91	3.09	9.95	2.28	–1.13	2450920
110		$P31m$	11.0598(2)	8.387(0)	888.45(3)	97015	4329	0.939	7.58	2.87	3.17	10.08	2.24	–1.18	2450917
112			11.0573(2)	8.3881(1)	888.16(3)	96912	4325	0.938	7.55	2.71	3.09	9.88	2.19	–1.27	2450910
114			11.056(0)	8.3877(1)	887.91(3)	96898	4326	0.939	7.63	2.86	3.11	10.19	2.16	–1.28	2450914
116			11.0598(2)	8.3881(1)	888.56(3)	96862	4326	0.938	7.49	2.71	3.04	10.06	2.21	–1.27	2450916
118			11.0603(2)	8.3884(1)	888.68(3)	96902	4327	0.938	7.42	2.69	3.10	10.26	2.19	–1.33	2450911
120			11.0574(2)	8.3886(1)	888.23(3)	96824	4325	0.938	7.33	2.59	3.07	10.66	2.18	–1.23	2450919
140			6.3858(1)	8.3842(2)	296.089(12)	16341	810	0.937	6.03	1.82	2.50	6.52	2.16	–2.28	2450896
160	$(CsBr)Cu_5O_2(VO_4)_2$		6.3869(1)	8.3862(2)	296.262(12)	16362	811	0.937	6.55	1.97	2.47	6.44	1.86	–2.10	2450897
180			6.3867(1)	8.3861(2)	296.24(1)	16355	813	0.937	6.46	2.01	2.50	6.49	1.68	–2.20	2450898
200			6.3877(1)	8.3867(2)	296.354(12)	16368	813	0.937	6.24	1.97	2.60	6.72	1.57	–2.23	2450900
220			6.3878(1)	8.3846(2)	296.289(12)	16373	812	0.937	6.64	2.00	2.62	6.92	1.72	–2.29	2450904
240			6.3877(1)	8.3856(2)	296.315(12)	16358	812	0.937	6.69	2.01	2.74	6.91	1.79	–2.41	2450903
260		$P\bar{3}m1$	6.3888(1)	8.3858(2)	296.424(12)	16387	813	0.937	6.99	2.03	2.74	7.09	1.82	–2.47	2450899
280			6.3892(1)	8.3858(2)	296.461(12)	16383	814	0.937	7.27	2.11	2.88	7.59	2.17	–2.68	2450901
300			6.3903(1)	8.3867(2)	296.595(12)	16405	813	0.937	7.27	2.13	2.95	7.49	2.04	–2.72	2450902
320			6.3907(1)	8.3864(2)	296.622(12)	16405	814	0.937	7.35	2.17	3.08	7.90	2.14	–2.88	2450905
340			6.3921(1)	8.3876(2)	296.794(12)	16407	814	0.937	7.51	2.23	3.16	7.93	2.23	–3.02	2450908
360			6.3928(1)	8.3875(2)	296.856(12)	16408	814	0.937	7.49	2.21	3.18	7.92	2.33	–3.09	2450906
380			6.3929(1)	8.3863(2)	296.822(12)	16410	814	0.934	7.80	2.32	3.17	8.27	2.53	–3.08	2450907
400			6.3969(1)	8.3887(2)	297.279(12)	16417	814	0.934	7.55	2.25	3.27	8.45	2.50	–3.09	2450909

Table S1 (continued).

T, K	Formula	Space Group	a, Å	c, Å	V, Å^3	Reflections collected	Unique reflections in total	$\sin\theta/\lambda$, Å^{-1}	R_{int}	R_σ	R_1	wR_2	ρ_{max}, e$^-$·Å^{-3}	ρ_{min}, e$^-$·Å^{-3}	CCDC
100			11.0574(2)	8.3888(1)	888.25(3)	96848	4071	0.939	8.39	2.70	3.06	10.56	2.11	–1.70	–
102			11.0572(2)	8.3888(1)	888.22(3)	96870	4071	0.939	8.19	2.61	3.03	10.52	2.18	–1.69	–
104			11.05625(15)	8.38489(13)	887.65(3)	96890	4070	0.938	7.86	2.63	3.03	10.03	2.30	–1.57	–
106			11.06071(16)	8.3882(1)	888.72(3)	96991	4074	0.939	7.81	2.55	2.98	9.71	2.34	–1.50	–
108			11.0562(2)	8.389(0)	888.08(3)	96904	4072	0.939	7.76	2.48	2.96	9.71	2.27	–1.56	–
110	$(CsBr)Cu_5O_2(VO_4)_2$	$P\bar{3}$	11.0598(2)	8.387(0)	888.45(3)	97015	4073	0.939	7.74	2.44	3.01	9.75	2.20	–1.70	–
112			11.0573(2)	8.3881(1)	888.16(3)	96912	4072	0.938	7.65	2.32	3.12	10.08	2.26	–1.58	–
114			11.056(0)	8.3877(1)	887.91(3)	96898	4071	0.939	7.74	2.43	3.07	10.05	2.08	–1.65	–
116			11.0598(2)	8.3881(1)	888.56(3)	96862	4071	0.938	7.58	2.32	3.07	10.19	2.25	–1.68	–
118			11.0603(2)	8.3884(1)	888.68(3)	96902	4072	0.938	7.52	2.30	3.07	10.14	2.18	–1.59	–
120			11.0574(2)	8.3886(1)	888.23(3)	96824	4069	0.938	7.44	2.22	3.11	10.45	2.26	–1.76	–

Table S1 (continued).

T, K	Formula	Space Group	*a*, Å	*c*, Å	*V*, Å³	Reflections collected	Unique reflections in total	$\sin\theta/\lambda$, Å^{-1}	R_{int}	R_σ	R_1	wR_2	ρ_{max}, e$^-$Å^{-3}	ρ_{min}, e$^-$Å^{-3}	CCDC
100			11.0901(2)	8.3900(1)	893.64(3)	49131	4338	0.939	6.37	3.01	2.33	5.33	1.32	–0.91	2451104
120			11.0926(2)	8.3898(1)	894.02(3)	49136	4340	0.938	6.45	3.11	2.40	5.56	0.99	–0.94	2451085
140			11.0931(2)	8.3878(1)	893.89(3)	49129	4340	0.938	6.63	3.20	2.51	5.95	1.04	–1.12	2451101
160			11.0966(2)	8.3894(1)	894.63(3)	49198	4346	0.938	6.65	3.31	2.67	6.48	1.37	–1.29	2451088
180			11.0986(2)	8.3879(2)	894.79(4)	49191	4348	0.938	6.81	3.41	2.73	6.58	1.42	–1.41	2451099
200			11.1013(2)	8.3884(2)	895.28(4)	49245	4350	0.938	6.85	3.38	2.77	6.78	1.50	–1.45	2451105
220			11.1032(2)	8.3868(2)	895.41(4)	49264	4352	0.938	7.03	3.50	2.78	6.52	0.61	–1.17	2451103
240			11.1060(2)	8.3886(2)	896.06(4)	49268	4354	0.937	7.28	3.64	2.80	6.68	0.63	–1.39	2451086
260			11.1100(2)	8.3884(2)	896.68(4)	49304	4360	0.940	7.51	3.74	2.82	6.78	0.76	–1.54	2451100
280			11.1117(2)	8.3895(2)	897.07(4)	49321	4364	0.940	7.93	3.96	3.05	7.36	0.91	–1.58	2451102
300		$P31m$	11.1145(2)	8.3894(2)	897.51(4)	49323	4366	0.939	8.17	4.35	3.36	8.51	1.29	–1.64	2451098
310			11.1155(2)	8.3879(2)	897.52(4)	49335	4367	0.939	8.26	4.39	3.36	8.63	1.20	–1.69	2451097
320	$(RbI)Cu_5O_2(VO_4)_2$		11.1159(2)	8.3894(2)	897.74(4)	49337	4367	0.939	8.15	4.20	3.32	8.68	1.12	–1.77	2451087
330			11.1166(3)	8.3855(2)	897.44(5)	49337	4369	0.939	8.30	4.52	3.70	9.93	1.36	–2.13	2451090
340			11.1175(3)	8.3864(2)	897.68(5)	49316	4369	0.939	8.38	4.60	3.92	10.96	1.51	–2.14	2451094
350			11.1200(3)	8.3880(2)	898.25(5)	49328	4371	0.939	8.27	4.54	3.93	11.13	1.44	–2.20	2451089
360			11.1228(3)	8.3897(2)	898.89(5)	49290	4371	0.939	8.41	4.70	4.10	12.19	1.58	–2.43	2451093
364			11.1260(3)	8.3926(2)	899.72(5)	49286	4371	0.938	8.49	4.91	4.22	12.92	1.87	–2.66	2451096
368			11.1249(3)	8.3904(2)	899.30(5)	49272	4369	0.938	8.38	4.87	4.39	14.16	2.23	–2.93	2451091
372			11.1252(3)	8.3916(2)	899.48(5)	49238	4368	0.938	8.38	4.82	4.55	14.79	2.39	–2.92	2451095
376			11.1267(3)	8.3922(2)	899.79(5)	49226	4368	0.938	8.41	4.93	4.45	15.26	2.55	–3.05	2451092
378			6.4226(2)	8.3905(2)	299.737(18)	16461	823	0.939	6.87	2.16	3.09	7.09	3.39	–4.07	2451083
380		$P\bar{3}m1$	6.4200(2)	8.3876(2)	299.39(2)	16435	823	0.939	7.13	2.25	2.99	6.72	3.06	–3.82	2451084
390			6.4222(2)	8.3899(2)	299.68(2)	16443	823	0.939	7.25	2.28	2.98	6.83	3.00	–3.74	2451081
400			6.42413(16)	8.3898(2)	299.856(17)	16475	823	0.938	7.22	2.26	2.97	6.72	3.14	–3.90	2451082

Table S1 (continued).

T, K	Formula	Space Group	*a*, Å	*c*, Å	*V*, Å³	Reflections collected	Unique reflections in total	sinθ/λ, Å^{-1}	R_{int}	R_{σ}	R_1	wR_2	ρ_{max}, e$^-$Å^{-3}	ρ_{min}, e$^-$Å^{-3}	CCDC
100			11.0901(2)	8.3900(1)	893.64(3)	49131	4095	0.939	6.63	2.81	7.21	17.58	6.72	–12.87	–
120			11.0926(2)	8.3898(1)	894.02(3)	49136	4098	0.938	6.69	2.89	5.97	14.59	4.78	–10.41	–
140			11.0931(2)	8.3878(1)	893.89(3)	49129	4099	0.938	6.9	2.97	5.12	12.23	4.50	–8.39	–
160			11.0966(2)	8.3894(1)	894.63(3)	49198	4102	0.938	6.98	3.06	4.41	10.2	3.24	–6.81	–
180			11.0986(2)	8.3879(2)	894.79(4)	49191	4103	0.938	7.13	3.15	3.75	8.59	2.85	–4.93	–
200			11.1013(2)	8.3884(2)	895.28(4)	49245	4105	0.938	7.07	3.13	3.3	7.45	1.55	–3.04	–
220			11.1032(2)	8.3868(2)	895.41(4)	49264	4105	0.938	7.36	3.23	2.99	6.65	1.28	–2.03	–
240			11.1060(2)	8.3886(2)	896.06(4)	49268	4110	0.937	7.52	3.35	2.88	6.47	1.31	–1.77	–
260			11.1100(2)	8.3884(2)	896.68(4)	49304	4115	0.940	7.76	3.46	2.81	6.29	1.04	–1.41	–
280			11.1117(2)	8.3895(2)	897.07(4)	49321	4118	0.940	8.24	3.65	2.87	6.21	1.49	–1.64	–
300	$(RbI)Cu_5O_2(VO_4)_2$	$P\bar{3}$	11.1145(2)	8.3894(2)	897.51(4)	49323	4119	0.939	8.55	3.99	3.12	7.04	1.72	–1.79	–
310			11.1155(2)	8.3879(2)	897.52(4)	49335	4122	0.939	8.61	4.02	3.24	7.53	1.77	–2.06	–
320			11.1159(2)	8.3894(2)	897.74(4)	49337	4122	0.939	8.58	3.89	3.21	7.4	1.75	–2.42	–
330			11.1166(3)	8.3855(2)	897.44(5)	49337	4124	0.939	8.74	4.14	3.55	8.45	1.88	–2.36	–
340			11.1175(3)	8.3864(2)	897.68(5)	49316	4121	0.939	8.91	4.2	3.59	8.85	2.00	–2.30	–
350			11.1200(3)	8.3880(2)	898.25(5)	49328	4128	0.939	8.71	4.17	3.66	9.43	2.22	–2.93	–
360			11.1228(3)	8.3897(2)	898.89(5)	49290	4127	0.939	8.95	4.29	3.88	10.43	2.20	–2.79	–
364			11.1260(3)	8.3926(2)	899.72(5)	49286	4127	0.938	9.03	4.49	3.92	11.2	2.42	–3.43	–
368			11.1249(3)	8.3904(2)	899.30(5)	49272	4125	0.938	8.98	4.45	3.96	11.45	2.63	–3.34	–
372			11.1252(3)	8.3916(2)	899.48(5)	49238	4123	0.938	8.97	4.43	4.28	12.9	3.06	–3.54	–
376			11.1267(3)	8.3922(2)	899.79(5)	49226	4124	0.938	9.01	4.42	4.34	13.77	3.32	–3.56	–

Table S1 (continued).

T, K	Formula	Space Group	*a*, Å	*c*, Å	*V*, Å³	Reflections collected	Unique reflections in total	$\sin\theta/\lambda$, Å^{-1}	R_{int}	R_σ	R_1	wR_2	ρ_{max}, e$^-$Å^{-3}	ρ_{min}, e$^-$Å^{-3}	CCDC
100			11.0282(1)	8.3938(1)	884.094(19)	97212	4320	0.940	6.55	2.18	2.70	7.20	1.79	–1.38	2451064
120			11.0295(1)	8.3939(1)	884.313(19)	97222	4319	0.939	6.62	2.21	2.72	7.25	1.66	–1.65	2451060
140			11.0308(1)	8.3918(1)	884.300(19)	97223	4322	0.940	6.63	2.23	2.71	7.14	1.54	–1.25	2451077
160			11.0308(1)	8.392(0)	884.321(19)	97217	4318	0.940	6.73	2.28	2.84	7.53	1.57	–1.17	2451078
180			11.0325(2)	8.3915(1)	884.54(3)	97224	4319	0.939	7.79	2.65	2.84	7.27	1.38	–1.14	2451062
200			11.0344(2)	8.3903(1)	884.72(3)	97239	4319	0.939	6.93	2.36	2.91	7.98	1.31	–1.00	2451065
220			11.0359(2)	8.3905(1)	884.98(3)	97246	4320	0.939	7.07	2.48	3.08	8.47	1.14	–1.10	2451074
240			11.0353(2)	8.3891(1)	884.74(3)	97243	4319	0.939	7.02	2.44	2.92	7.93	1.10	–1.09	2451080
260			11.0385(2)	8.3888(1)	885.22(3)	97215	4320	0.939	7.08	2.47	2.92	7.85	1.16	–1.06	2451067
280			11.0397(2)	8.3898(1)	885.52(3)	97260	4322	0.939	7.32	2.57	3.05	8.40	1.06	–1.19	2451066
300	$(RbBr)Cu_5O_2(VO_4)_2$	*P*31*m*	11.0422(2)	8.3888(1)	885.81(3)	97208	4321	0.939	7.42	2.62	3.12	8.57	1.07	–1.26	2451070
320			11.0436(2)	8.3883(1)	885.98(3)	97198	4322	0.939	7.82	2.77	3.23	8.53	1.26	–1.54	2451068
340			11.0422(5)	8.3865(4)	885.57(9)	96302	4332	0.939	8.17	2.80	3.46	9.61	1.50	–1.76	2451071
360			11.0457(2)	8.3886(2)	886.35(4)	97098	4322	0.939	8.16	3.01	3.52	9.77	1.30	–1.70	2451069
380			11.0480(2)	8.3899(2)	886.86(4)	96986	4325	0.939	8.11	3.04	3.74	11.01	1.31	–1.84	2451073
384			11.0491(2)	8.3882(2)	886.86(4)	96953	4323	0.938	8.46	3.13	3.71	10.74	1.45	–1.97	2451075
388			11.0623(2)	8.3923(2)	889.41(4)	97462	4341	0.938	7.90	2.15	4.31	12.65	1.61	–2.09	2451072
390			11.0524(2)	8.3904(2)	887.62(4)	97014	4326	0.938	8.23	3.10	3.81	10.97	1.52	–1.84	2451061
392			11.0510(2)	8.3892(2)	887.27(4)	96964	4328	0.939	8.20	3.07	3.90	11.42	1.47	–1.83	2451076
396			11.0514(2)	8.3900(2)	887.42(4)	96919	4327	0.939	8.30	3.12	3.94	11.88	1.74	–2.03	2451079
400			11.0645(2)	8.3944(2)	889.99(4)	97165	4338	0.938	8.02	3.10	4.11	12.37	1.75	–2.07	2451063

Table S1 (continued).

T, K	Formula	Space Group	a, Å	c, Å	V, Å³	Reflections collected	Unique reflections in total	$\sin\theta/\lambda$, Å^{-1}	R_{int}	R_{σ}	R_1	wR_2	ρ_{max}, e$^-$·Å^{-3}	ρ_{min}, e$^-$·Å^{-3}	CCDC
100			11.0282(1)	8.3938(1)	884.094(19)	97212	4064	0.940	6.96	2.05	3.01	6.79	1.39	-1.59	–
120			11.0295(1)	8.3939(1)	884.313(19)	97222	4065	0.939	7.04	2.08	2.97	6.58	1.28	-1.92	–
140			11.0308(1)	8.3918(1)	884.300(19)	97223	4066	0.940	7.05	2.10	2.92	6.65	1.32	-1.48	–
160			11.0308(1)	8.392(0)	884.321(19)	97217	4064	0.940	7.23	2.15	2.84	6.39	1.36	-1.55	–
180			11.0325(2)	8.3915(1)	884.54(3)	97224	4064	0.939	8.14	2.47	2.79	6.54	1.38	-1.37	–
200			11.0344(2)	8.3903(1)	884.72(3)	97239	4065	0.939	7.49	2.24	2.65	6.11	1.18	-1.25	–
220			11.0359(2)	8.3905(1)	884.98(3)	97246	4066	0.939	7.8	2.35	2.63	6.06	1.54	-1.28	–
240			11.0353(2)	8.3891(1)	884.74(3)	97243	4066	0.939	7.54	2.33	2.67	6.04	1.46	-1.47	–
260			11.0385(2)	8.3888(1)	885.22(3)	97215	4065	0.939	7.54	2.35	2.72	6.54	1.64	-1.34	–
280			11.0397(2)	8.3898(1)	885.52(3)	97260	4066	0.939	7.84	2.45	2.84	6.72	1.54	-1.56	–
300	$(RbBr)Cu_5O_2(VO_4)_2$	$P\bar{3}$	11.0422(2)	8.3888(1)	885.81(3)	97208	4065	0.939	7.93	2.48	2.96	6.87	1.58	-1.75	–
320			11.0436(2)	8.3883(1)	885.98(3)	97198	4068	0.939	8.33	2.67	3.16	7.64	1.86	-1.98	–
340			11.0422(5)	8.3865(4)	885.57(9)	96302	4076	0.939	8.68	2.71	3.32	8.38	2.04	-2.06	–
360			11.0457(2)	8.3886(2)	886.35(4)	97098	4067	0.939	8.76	2.88	3.47	8.66	2.17	-2.20	–
380			11.0480(2)	8.3899(2)	886.86(4)	96986	4071	0.939	8.73	2.9	3.42	8.92	1.96	-2.47	–
384			11.0491(2)	8.3882(2)	886.86(4)	96953	4067	0.938	9.09	3.05	3.54	9.10	1.99	-2.63	–
388			11.0623(2)	8.3923(2)	889.41(4)	97462	4083	0.938	8.59	2.39	4.10	10.74	2.06	-2.82	–
390			11.0524(2)	8.3904(2)	887.62(4)	97014	4071	0.938	8.88	2.99	3.56	9.42	2.18	-2.51	–
392			11.0510(2)	8.3892(2)	887.27(4)	96964	4072	0.939	8.91	2.97	3.55	9.59	2.12	-2.45	–
396			11.0514(2)	8.3900(2)	887.42(4)	96919	4071	0.939	8.97	3.04	3.61	9.77	2.21	-2.84	–
400			11.0645(2)	8.3944(2)	889.99(4)	97165	4082	0.938	8.91	3.00	3.67	10.29	2.43	-2.65	–

Table S1 (continued).

T, K	Formula	Space Group	a, Å	c, Å	b, Å	β, Å	V, Å³	Reflections collected	Unique reflections in total	$\sin\theta/\lambda$, Å^{-1}	R_{int}	R_σ	R_1	wR_2	ρ_{max}, e$^-$Å^{-3}	ρ_{min}, e$^-$Å^{-3}	CCDC
100	$(CsI)Cu_5O_2(PO_4)_2$	$C2/c$	10.9371(8)	6.3463(5)	16.2846(13)	92.425(6)	1129.31(15)	4059	4059	0.817	*N/A*	3.02	4.16	10.72	2.26	–1.27	2450885
296		$P\bar{3}m1$	6.26222(15)	6.26222(15)	8.2422(2)	–	279.918(15)	10746	510	0.817	1.97	0.69	0.97	2.44	0.42	–0.48	2450886

Table S2. The principal coefficients of the thermal expansion/contraction upon cooling.

T, K	α_{11}, $10^6 \cdot K^{-1}$	α_{33}, $10^6 \cdot K^{-1}$	α_V, $10^6 \cdot K^{-1}$
		CsBr†	
100	1(2)	–1.2(3)	1(5)
200	–2.8(8)	–1.2(3)	–7(2)
300	–6.6(5)	–1.2(3)	–14(1)
400	–10(1)	–1.2(3)	–22(4)
		CsI†	
100	–2.7(8)	0.4(1)	–5(2)
200	–5.2(3)	–1.6(4)	–12.0(8)
300	–7.7(3)	–3.6(4)	–19.1(7)
400	–10.3(8)	–6(1)	–26(2)
		RbBr	
100	–3.9(8)	5.0(9)	–3(2)
200	–5.3(8)	3.2(3)	–7.4(5)
300	–7(2)	1.3(8)	–12(2)
400	–8.1(3)	–1(2)	–17(3)
		RbI‡	
100	–11.1(2)	3(2)	–19.5(9)
200	–11.0(2)	1.0(5)	–19.5(9)
300	–11.0(2)	–1(2)	–22.7(9)
400	–11.0(2)	–2(3)	–24.2(9)
		KI	
100	–10.0(7)	4.7(6)	–15(1)
200	–12.0(3)	2.8(2)	–21.1(4)
300	–14(1)	1.0(4)	–26.8(9)
400	–16(2)	–0.9(8)	–33(2)

† The principal coefficients were calculated for the $P\bar{3}m1$ structure only.

‡ The principal coefficients were calculated for the $P31m$ structure only.

Table S3. Selected refinement parameters and the Hamilton *F*-statistic values calculated for $P\bar{3}$ and $P31m$ structural models.

T, K	Total unique reflections	Number of parameters		R_1 for all observed reflections		R_1 for reflection with $[F^2 > 2\sigma(F^2)]$		*F*		$F_{b,n-m,\alpha}$†
		$P31m$	$P\bar{3}$	$P31m$	$P\bar{3}$	$P31m$	$P\bar{3}$	For R_1 (all data)	For R_1 $[F^2 > 2\sigma(F^2)]$	
CsBr										
100	4071	117	107	0.0443	0.0457	0.0320	0.0306	25.39	–33.84	1.83
102	4071	121	107	0.0440	0.0455	0.0315	0.0303	19.56	–21.09	1.69
104	4070	121	107	0.0431	0.0446	0.0314	0.0303	19.98	–19.42	1.69
106	4074	117	107	0.0423	0.0437	0.0313	0.0298	26.63	–37.02	1.83
108	4072	113	107	0.0420	0.0438	0.0309	0.0296	57.77	–54.35	2.10
110	4073	121	107	0.0430	0.0446	0.0317	0.0301	21.40	–27.78	1.69
112	4072	117	107	0.0423	0.0450	0.0309	0.0312	52.10	7.72	1.83
114	4071	121	107	0.0435	0.0462	0.0311	0.0307	36.11	–7.21	1.69
116	4071	121	107	0.0438	0.0474	0.0304	0.0307	48.29	5.60	1.69
118	4072	121	107	0.0445	0.0478	0.0310	0.0307	43.41	–5.44	1.69
120	4069	121	101	0.0455	0.0498	0.0307	0.0311	39.07	5.18	1.57
CsI										
100	4106	115	102	0.0299	0.0286	0.0237	0.0222	–26.12	–37.63	1.72
102	4104	115	102	0.0305	0.0290	0.0243	0.0227	–29.44	–39.08	1.72
104	4106	115	102	0.0315	0.0294	0.0248	0.0229	–39.57	–45.24	1.72
106	4104	105	102	0.0313	0.0298	0.0245	0.0226	–124.70	–198.73	2.61
108	4106	111	102	0.0314	0.0297	0.0245	0.0226	–46.76	–66.18	1.88
110	4106	101	102	0.0324	0.0308	0.0245	0.0227	*N/A*	*N/A*	*N/A*
112	4107	105	102	0.0332	0.0311	0.0247	0.0230	–163.42	–177.31	2.61
114	4106	115	102	0.0329	0.0305	0.0244	0.0220	–43.16	–57.42	1.72
116	4109	105	102	0.0328	0.0328	0.0238	0.0231	0.00	–77.36	2.61
118	4109	111	102	0.0352	0.0342	0.0247	0.0234	–24.88	–45.53	1.88
120	4108	115	102	0.0338	0.0341	0.0229	0.0230	5.48	2.69	1.72
122	4108	107	96	0.0364	0.0366	0.0239	0.0231	4.01	–23.94	1.79
124	4107	105	96	0.0398	0.0403	0.0248	0.0241	11.24	–24.75	1.88

Table S3 (continued).

T, K	Total unique reflections	Number of parameters		R_1 for all observed reflections		R_1 for reflection with $[F^2 > 2\sigma(F^2)]$		F		$F_{b,n-m,\alpha}$ †
		$P31m$	$P\bar{3}$	$P31m$	$P\bar{3}$	$P31m$	$P\bar{3}$	For R_1 (all data)	For R_1 $[F^2 > 2\sigma(F^2)]$	
RbI										
100	4095	120	103	0.0257	0.0764	0.0320	0.0306	1832.54	2005.13	1.63
120	4098	120	103	0.0272	0.0650	0.0315	0.0303	1102.30	1213.91	1.63
140	4099	122	103	0.0290	0.0565	0.0314	0.0303	585.20	661.63	1.59
160	4102	122	112	0.0314	0.0503	0.0313	0.0298	623.31	687.77	1.83
180	4103	120	112	0.0330	0.0443	0.0309	0.0296	399.35	441.54	1.94
200	4105	122	112	0.0336	0.0405	0.0317	0.0301	180.38	167.00	1.83
220	4105	135	112	0.0353	0.0392	0.0309	0.0312	40.24	27.06	1.53
240	4110	135	112	0.0373	0.0393	0.0311	0.0307	19.03	10.01	1.53
260	4115	135	112	0.0391	0.0397	0.0304	0.0307	5.35	–1.22	1.53
280	4118	131	116	0.0433	0.0426	0.0310	0.0307	–8.52	–30.44	1.67
300	4119	131	116	0.0477	0.0469	0.0307	0.0311	–8.84	–36.62	1.67
310	4122	131	113	0.0490	0.0497	0.0237	0.0222	6.38	–15.55	1.61
320	4122	131	113	0.0509	0.0516	0.0243	0.0227	6.14	–14.44	1.61
330	4124	121	113	0.0560	0.0574	0.0248	0.0229	25.33	–39.74	1.94
340	4121	115	113	0.0610	0.0607	0.0245	0.0226	–19.65	–323.04	3.00
350	4128	117	113	0.0640	0.0656	0.0245	0.0226	50.76	–133.04	2.37
360	4127	117	113	0.0692	0.0721	0.0245	0.0227	85.78	–104.69	2.37
364	4127	117	113	0.0739	0.0764	0.0247	0.0230	68.97	–137.46	2.37
368	4125	117	113	0.0776	0.0816	0.0244	0.0220	105.96	–186.67	2.37
370	4123	117	113	0.0809	0.0843	0.0238	0.0231	85.94	–153.32	2.37
372	4124	117	113	0.0827	0.0869	0.0247	0.0234	104.33	–115.36	2.37
374	4126	117	113	0.0878	0.0917	0.0229	0.0230	91.01	–196.89	2.37
376	4123	125	113	0.0881	0.0962	0.0239	0.0231	64.08	–16.26	1.75

Table S3 (continued).

T, K	Total unique reflections	Number of parameters		R_1 for all observed reflections		R_1 for reflection with $[F^2 > 2\sigma(F^2)]$		F		$F_{b,n-m,\alpha}$ †
		$P31m$	$P\bar{3}$	$P31m$	$P\bar{3}$	$P31m$	$P\bar{3}$	For R_1 (all data)	For R_1 $[F^2 > 2\sigma(F^2)]$	
					RbBr					
100	4064	121	102	0.0307	0.0344	0.0270	0.0301	53.04	50.39	1.59
120	4065	119	102	0.0315	0.0343	0.0272	0.0297	43.10	44.63	1.63
140	4066	119	102	0.0317	0.0340	0.0271	0.0292	34.91	37.38	1.63
160	4064	119	102	0.0333	0.0343	0.0284	0.0284	14.15	0.00	1.63
180	4064	119	102	0.0345	0.0354	0.0284	0.0279	12.27	-8.10	1.63
200	4065	115	108	0.0360	0.0344	0.0291	0.0265	-49.04	-96.33	2.01
220	4066	115	108	0.0386	0.0348	0.0308	0.0263	-105.66	-152.88	2.01
240	4066	125	108	0.0379	0.0365	0.0292	0.0267	-16.81	-38.00	1.63
260	4065	117	108	0.0391	0.0389	0.0292	0.0272	-4.48	-58.03	1.88
280	4066	125	108	0.0417	0.0415	0.0305	0.0284	-2.22	-30.82	1.63
300	4065	125	108	0.0439	0.0442	0.0312	0.0296	3.18	-23.16	1.63
320	4068	121	107	0.0463	0.0490	0.0323	0.0316	33.84	-12.09	1.69
340	4076	121	107	0.0526	0.0545	0.0346	0.0332	20.78	-22.40	1.69
360	4067	125	107	0.0549	0.0572	0.0352	0.0347	18.73	-6.18	1.61
380	4071	125	116	0.0601	0.0607	0.0374	0.0342	8.80	-71.82	1.88
384	4067	125	116	0.0616	0.0647	0.0371	0.0354	45.19	-39.22	1.88
388	4083	125	116	0.0646	0.0661	0.0431	0.0410	20.66	-41.81	1.88
390	4071	125	116	0.0637	0.0654	0.0381	0.0356	23.71	-55.65	1.88
392	4072	125	116	0.0646	0.0650	0.0390	0.0355	5.45	-75.18	1.88
396	4071	121	116	0.0666	0.0695	0.0394	0.0361	70.30	-126.79	2.22
					KI					
100	4101	130	104	0.0257	0.0468	0.0245	0.0449	353.74	360.23	1.50
120	4103	130	104	0.0265	0.0447	0.0252	0.0427	281.97	285.92	1.50
140	4106	130	104	0.0270	0.0428	0.0254	0.0405	231.34	235.87	1.50
160	4107	130	110	0.0277	0.0407	0.0257	0.0380	230.44	235.89	1.57
180	4108	130	110	0.0289	0.0385	0.0265	0.0355	154.09	158.04	1.57
200	4110	136	110	0.0276	0.0376	0.0248	0.0339	130.82	132.75	1.50
220	4114	136	110	0.0291	0.0363	0.0256	0.0319	85.08	84.57	1.50
240	4116	136	110	0.0305	0.0359	0.0262	0.0308	59.00	58.47	1.50
260	4118	134	110	0.0318	0.0355	0.0274	0.0303	40.88	37.00	1.52
280	4119	136	110	0.0335	0.0365	0.0278	0.0302	28.67	27.59	1.50
300	4120	130	110	0.0346	0.0368	0.0284	0.0300	26.18	23.11	1.57
320	4126	126	116	0.0369	0.0390	0.0291	0.0305	46.82	39.41	1.83
340	4129	126	116	0.0392	0.0415	0.0309	0.0318	48.35	23.66	1.83
360	4133	130	116	0.0415	0.0434	0.0320	0.0323	26.78	5.39	1.69
380	4136	126	110	0.0441	0.0464	0.0333	0.0347	26.82	21.52	1.65
400	4138	130	117	0.0476	0.0495	0.0350	0.0355	25.10	8.87	1.72

† The $F_{b,n-m,\alpha}$ was calculated with the significance level $\alpha = 0.05$.

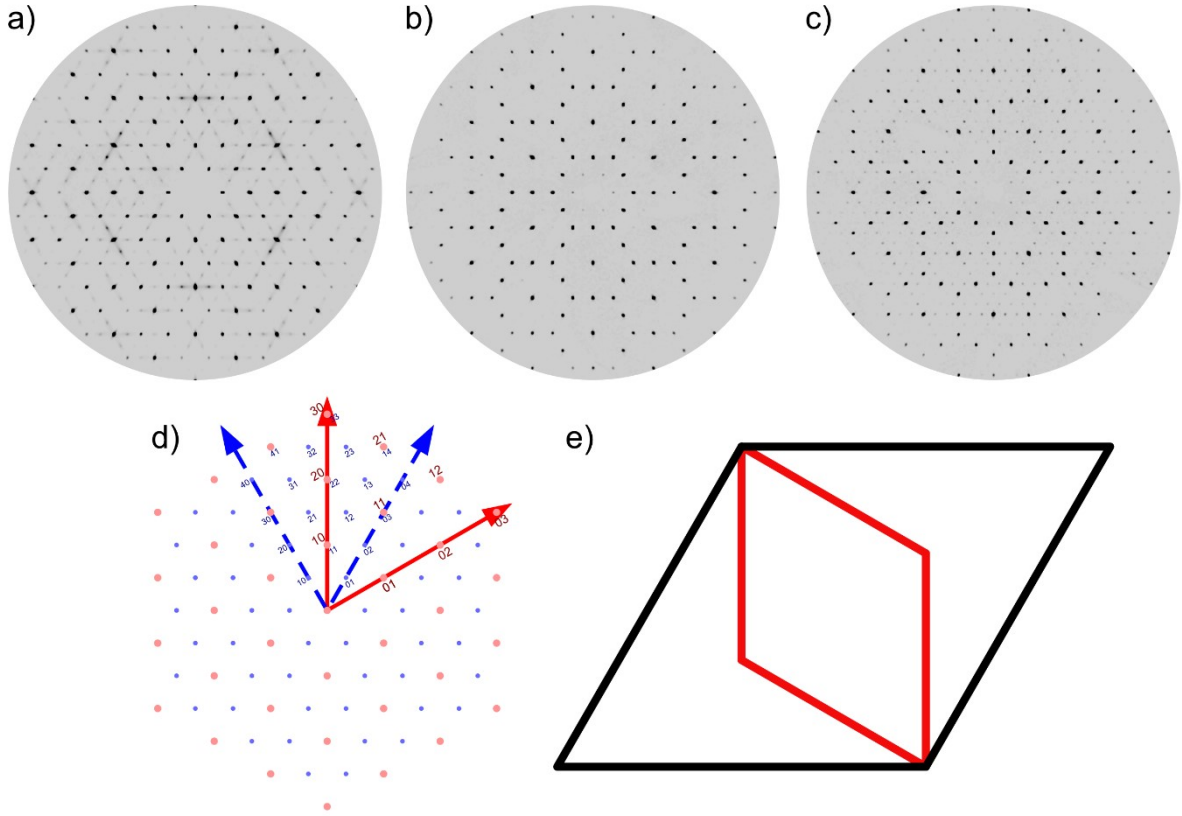

Figure S1 Fragments of precession images of the *hk*0 reciprocal lattice plane of (a) $(CsCl)Cu_5O_2(VO_4)_2$, (b) $(CsI)Cu_5O_2(VO_4)_2$ at 140 K and (c) 100 K; (d) schematic image of the superlattice reflections (blue) of *P*31*m* polymorph and reflections (red) from $P\bar{3}m1$ archetype; (e) relations between unit cells for the *P*31*m* and $P\bar{3}m1$ polymorphs.

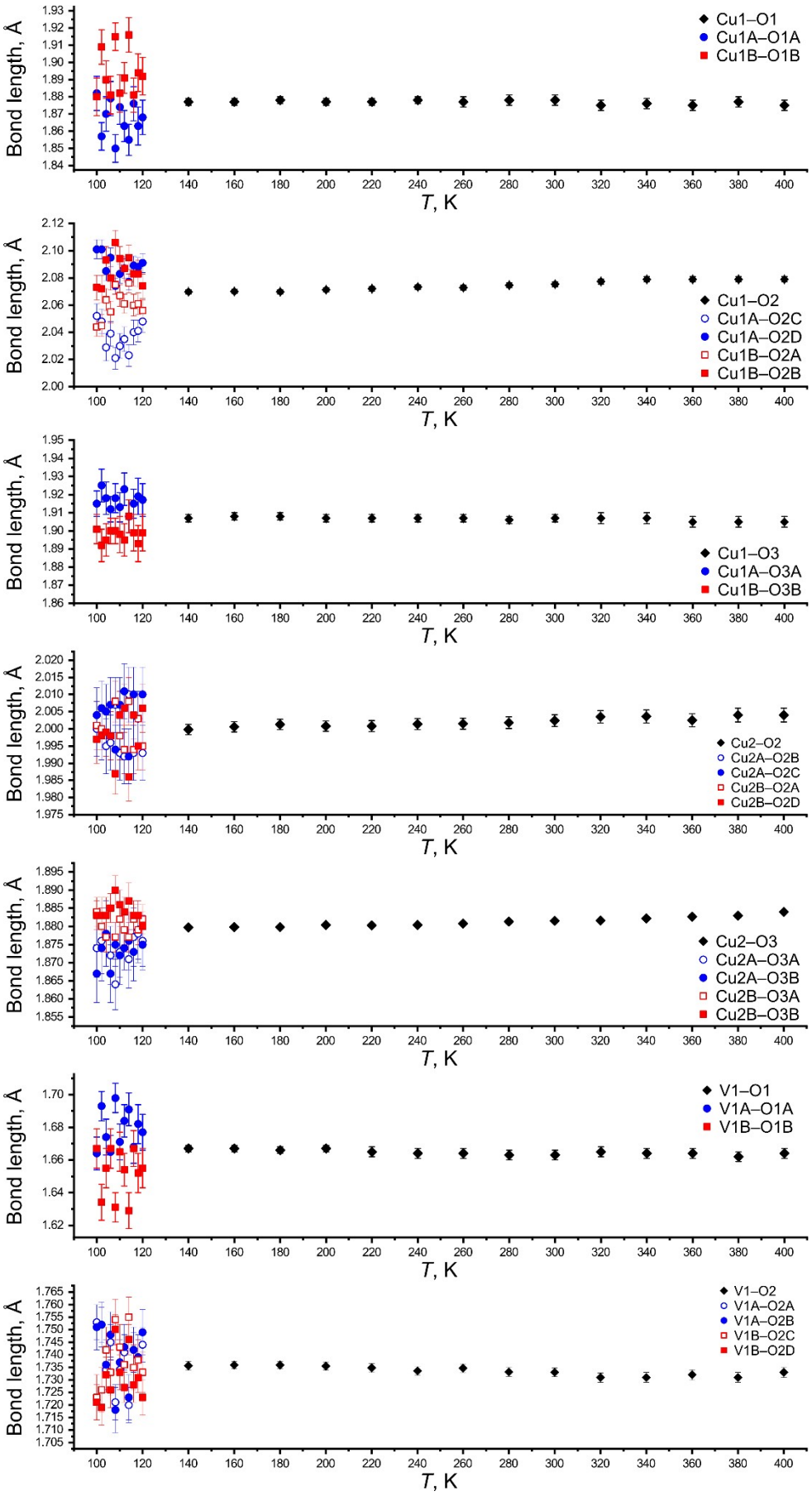

Figure S2 Graphs of selected bond length changing upon cooling in the structure of **CsBr**.

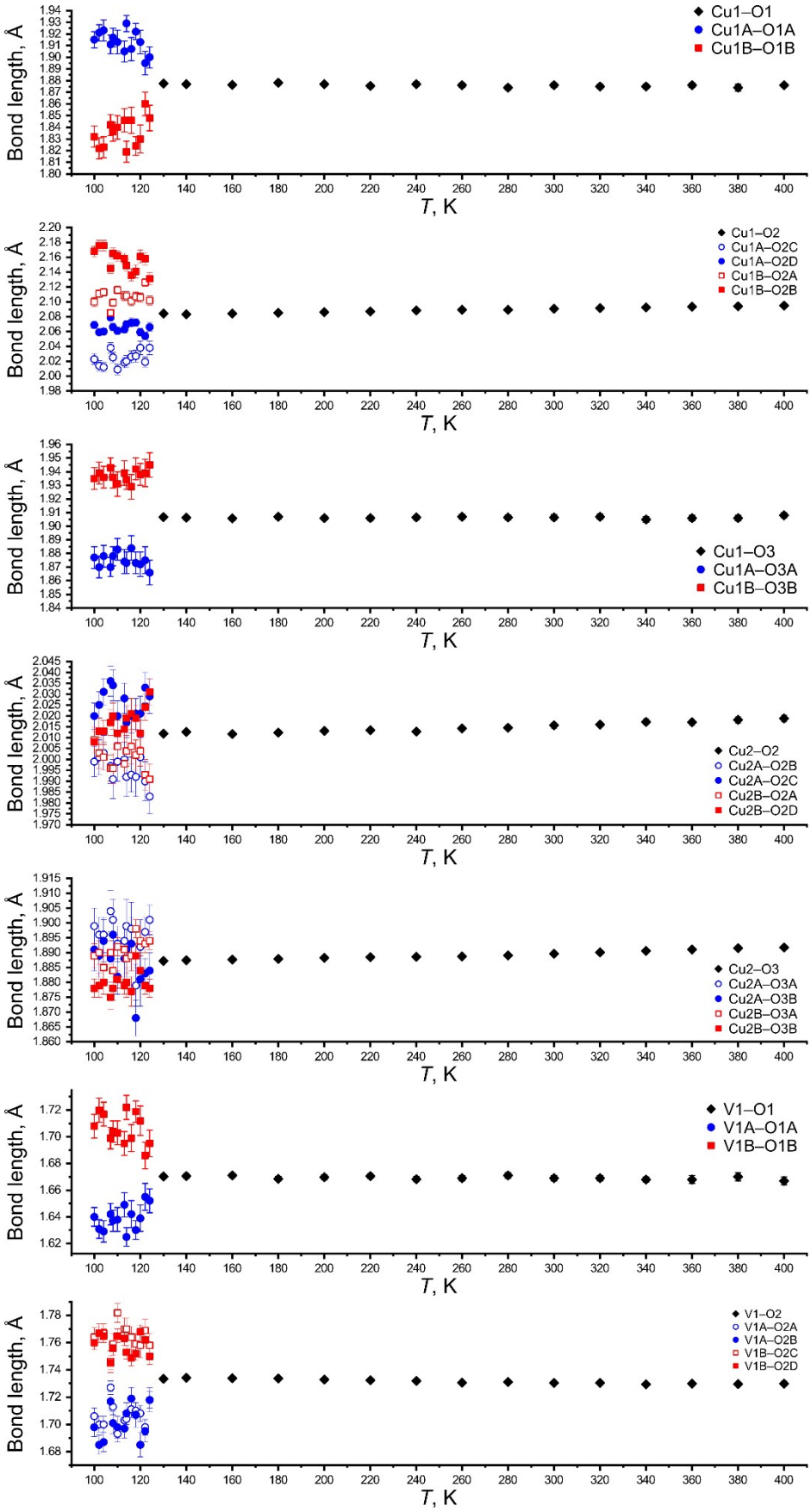

Figure S3 Graphs of selected bond length changing upon cooling in the structure of **CsI**.

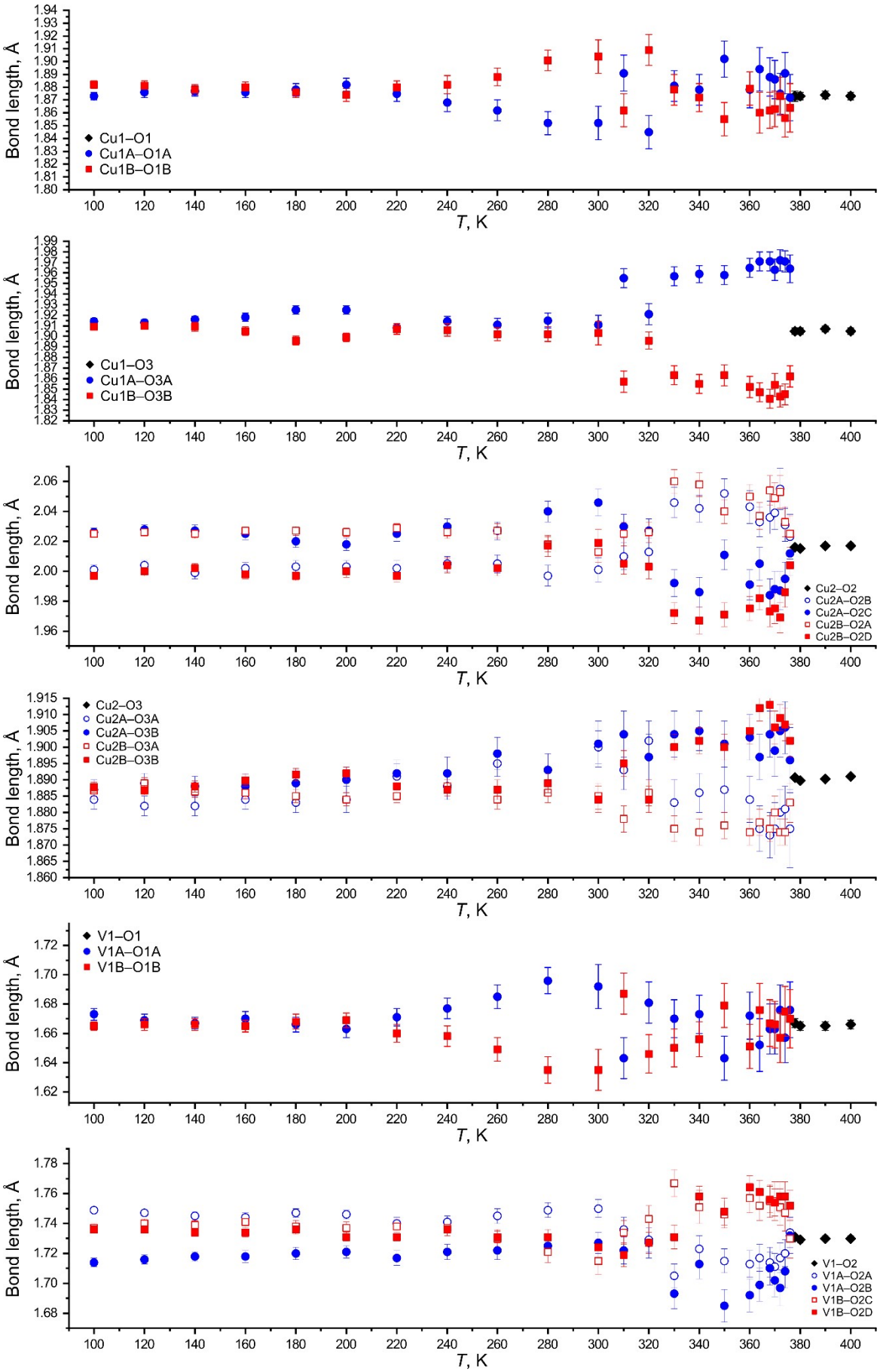

Figure S4 Graphs of selected bond length changing upon cooling in the structure of **RbI**.

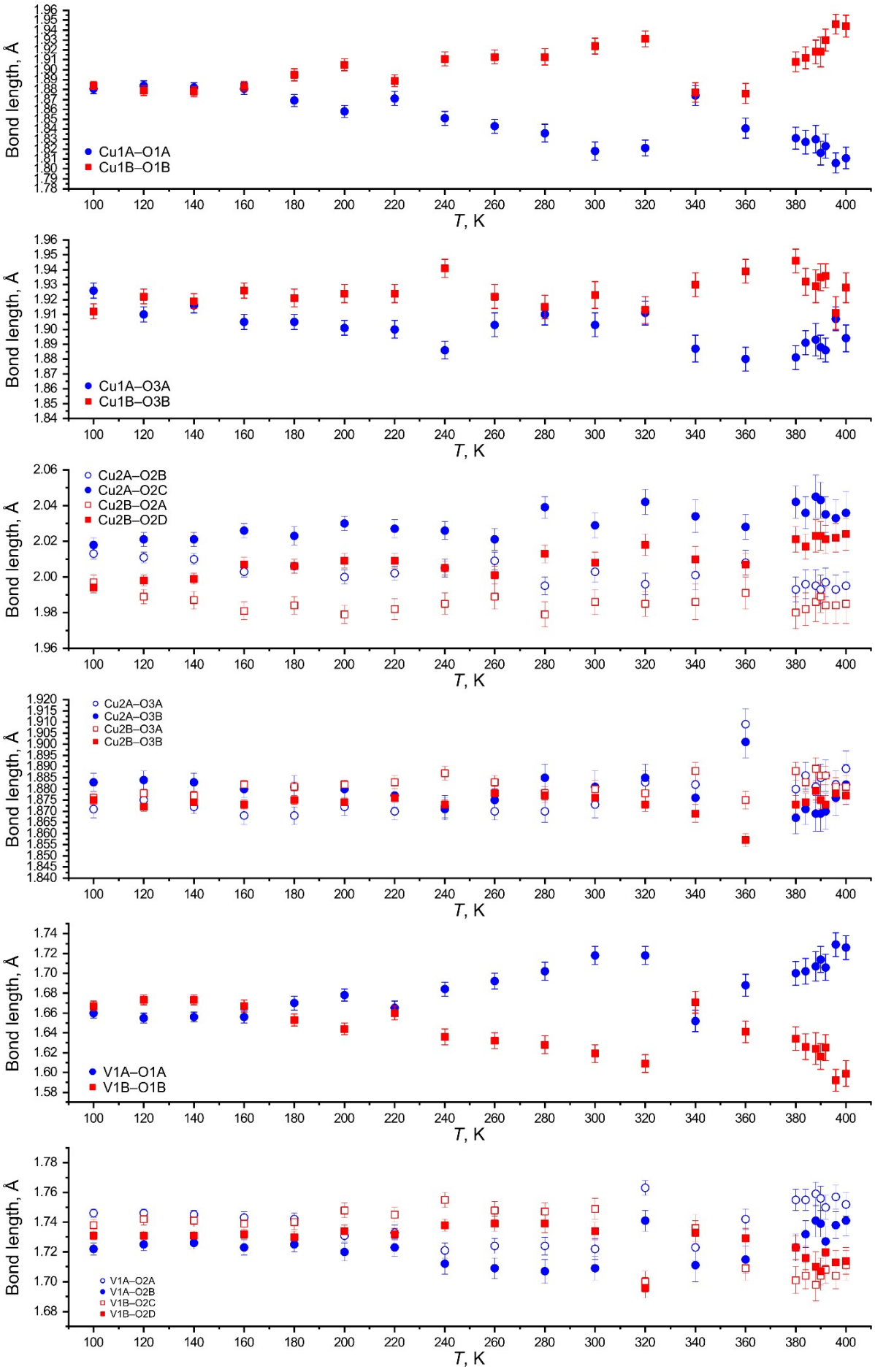

Figure S5 Graphs of selected bond length changing upon cooling in the structure of **RbBr**.

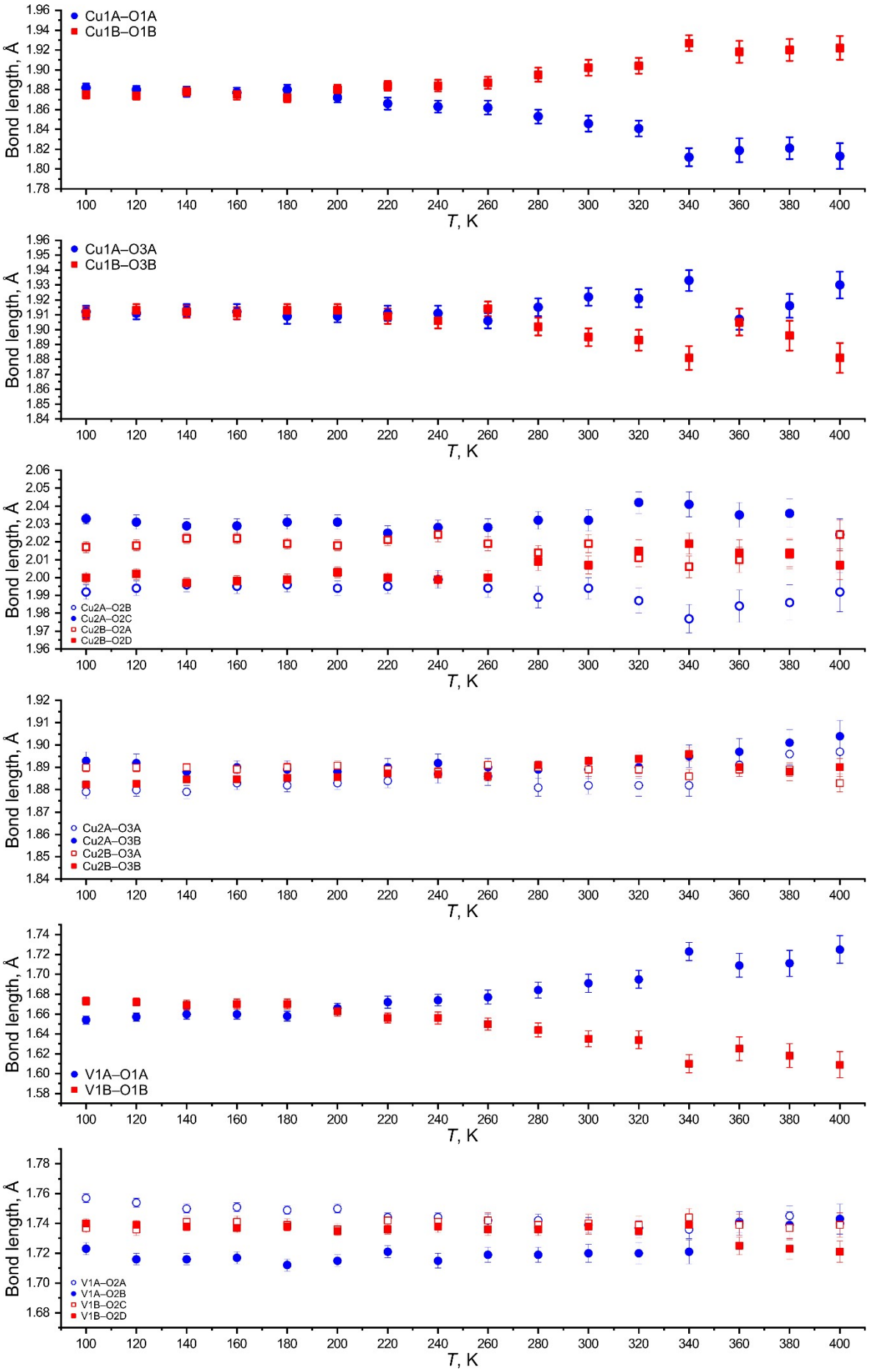

Figure S6 Graphs of selected bond length changing upon cooling in the structure of **KI**.