Table 1. Instrument parameters used for X-ray powder diffraction Rietveld refinement.

Geometry: Bragg-Brentano	Divergence slit: fixed = 1.0˚
Radiation source: Cu Kα	Receiving slit: 0.3 mm
Generator: 40 kV, 40 mA	Detector: scintillation counter
Tube: 12 mm long line focus	Step size: 0.02˚
Scan mode: θ/2θ	Time per step: 10 s
Secondary monochromator: graphite	Angular range: 10–140 ˚2θ
Primary and secondary Soller slits: 6.0˚	Mean temperature of measurement: ~22˚C

Table 2.
Summary of the parameters refined and derived for crystal-chemical (C-CH) and standard crystallographic (CRYS) refinement models. Please refer to Table 1 in Mercier *et al* . (2005) for all parameter definitions and symbols, as well as all equations necessary to obtain the parameters derived from those that are refined.

	C-CH	**CRYS**
Parameters refined:	d_{AI-O1}, Δ_{AI-O}, δ_{AI}, α_{AI}, d_{B-O}, τ_{O-B-O}, ρ_{AII}, α_{AII}, d_{AII-O3}, $\phi_{O3-AII-O3}$ (total =10)	a , c , AIz, AIIx, AIIy, Bx, By, O1x, O1y, O2x, O2y, O3x, O3y, O3z (total =14)
Parameters derived:	a , c , ψ_{AI-O1}, η, AIz, AIIx, AIIy, Bx, By, O1x, O1y, O2x, O2y, O3x, O3y, O3z	(AI-O1), $(AI-O1)^{AIz=0}$, Δ_{AI-O}, $\Delta_{AI-O}^{AIz=0}$, δ_{AI}, α_{AI}, <B-O>, $<\tau_{O-B-O}>$, ρ_{AII}, (AII-X), α_{AII}, (AII-O3), $\phi_{O3-AII-O3}$, $\psi_{AI-O1}^{AIz=0}$

Table 3. Optimized structures resulting from *ab initio* total-energy minimization simulations with VASP.

(a) P1*m* 1 models. The results of each simulation are tabulated as separate blocks of data. The first line of data in each simulation block is keyed with the top legend.

	Simulation label	*Ab initio* simulation type*	E_{total} (eV per unit cell)	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	Location of V as per Fig. 1									
	job0079	CC	-305.9671	9.34404	6.86735	9.36455	120.1578	a									
Site occ.:	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	P	F	F	O
x:	0.42962	0.04926	0.31167	0.82653	0.06831	0.81503	0.30015	0.73328	0.39536	0.09275	0.66949	0.69357	0.03218	0.45952	0.06658	0.05874	0.55170
y:	0	0	0	0	0.5	0.5	0.5	0.25043	0.25172	0	0	0.5	0.5	0.5	0	0.5	0
z:	0.45986	0.30124	0.06715	0.81883	0.82067	0.05701	0.30282	0.39471	0.73229	0.69393	0.03496	0.66393	0.43305	0.09177	0.06546	0.05866	0.37034
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.09684	0.74749	0.57810	0.22144	0.38575	0.53780	0.18517	0.47613	0.59290	-0.05984	0.65203	0.29937	0.15005	0.72577	0.80755	-0.02712	0.40119
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.19552	0.18159	0.18203	0.31799	0.31880	0.31886
z:	0.57930	0.22496	0.73813	0.54994	-0.09795	0.67289	0.59432	-0.05473	0.47140	0.53371	0.18402	0.39744	0.80793	-0.02142	0.72107	0.31973	0.14729
	job0105	CC	-305.827	9.33107	6.86625	9.36046	120.1740	a									
Site occ.:	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	P	F	F	O
x:	0.42987	0.04931	0.31197	0.82724	0.06867	0.81430	0.29978	0.73314	0.39573	0.09318	0.66954	0.69367	0.03236	0.45850	0.06702	0.05810	0.55125
y:	0	0	0	0	0.5	0.5	0.5	0.25035	0.25164	0	0	0.5	0.5	0.5	0	0.5	0
z:	0.45968	0.30133	0.06648	0.81860	0.82147	0.05727	0.30306	0.39447	0.73231	0.69424	0.03429	0.66381	0.43371	0.09164	0.06559	0.05924	0.36921
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.09719	0.74655	0.57900	0.22178	0.38591	0.53861	0.18518	0.47694	0.59196	-0.06006	0.65124	0.29963	0.15075	0.72737	0.80752	-0.02756	0.39996
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.19562	0.18168	0.18212	0.31790	0.31871	0.31877
z:	0.57920	0.22419	0.73915	0.55049	-0.09758	0.67277	0.59423	-0.05579	0.47132	0.53348	0.18427	0.39791	0.80813	-0.02083	0.72017	0.31951	0.14674
	job0092	CC	-305.8238	9.35212	6.86603	9.33008	120.1034	b									
Site occ.:	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	P	F	F	O
x:	0.09120	0.05316	0.31449	0.81727	0.06413	0.81453	0.30371	0.72313	0.39823	0.42688	0.66391	0.69424	0.03159	0.46265	0.06118	0.06198	0.53894
y:	0	0	0	0	0.5	0.5	0.5	0.25038	0.25157	0	0	0.5	0.5	0.5	0	0.5	0
z:	0.69457	0.29752	0.07522	0.81367	0.82520	0.05774	0.31084	0.39263	0.72932	0.45566	0.03255	0.66651	0.43152	0.09314	0.05812	0.06687	0.37754
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.12057	0.73804	0.57854	0.22176	0.38977	0.53040	0.19598	0.47067	0.59337	-0.05947	0.65533	0.31386	0.15963	0.72006	0.80819	-0.02493	0.40806
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.1821154	0.19557	0.18165	0.31874	0.31795	0.31871
z:	0.57401	0.22258	0.74022	0.54694	-0.09651	0.64821	0.58620	-0.06103	0.47398	0.53348	0.18625	0.39859	0.82494	-0.02476	0.72443	0.31870	0.15256
	job0093	CC	-305.8269	9.32820	6.86708	9.36209	120.1849	d									
Site occ.:	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	P	F	F	O
x:	0.69503	0.05566	0.31037	0.82539	0.07547	0.81264	0.29744	0.72887	0.39155	0.43109	0.09236	0.66609	0.03152	0.45476	0.06655	0.05754	0.54578
y:	0.5	0	0	0	0.5	0.5	0.5	0.24848	0.24959	0	0	0	0.5	0.5	0	0.5	0
z:	0.66565	0.30395	0.06790	0.82229	0.82440	0.05876	0.30685	0.39292	0.73063	0.46122	0.69202	0.03357	0.43153	0.09069	0.06646	0.06017	0.38582
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.09733	0.73853	0.57368	0.22180	0.37747	0.53261	0.18443	0.47347	0.58584	-0.06075	0.64760	0.31717	0.15248	0.72505	0.82540	-0.02620	0.39733
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.18212	0.18120	0.18123	0.30429	0.31831	0.31793
z:	0.57536	0.22285	0.75629	0.54666	-0.09918	0.65373	0.59173	-0.05930	0.45252	0.53125	0.18048	0.40477	0.80624	-0.02133	0.72711	0.31737	0.14628
	job0094	CC	-305.8227	9.32175	6.86598	9.33919	119.8492	c									
	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	P	F	F	O
Site occ.:	0.6645	0.0590	0.3065	0.8253	0.0705	0.8207	0.3038	0.7306	0.3943	0.4316	0.0923	0.6924	0.0347	0.4603	0.0602	0.0654	0.5460
x:	0	0	0	0	0.5	0.5	0.5	0.25042	0.25146	0	0	0.5	0.5	0.5	0	0.5	0
y:	0.03098	0.30787	0.06982	0.80976	0.82229	0.05837	0.31019	0.40018	0.72600	0.46110	0.69849	0.66085	0.43123	0.09175	0.06416	0.06274	0.38516
z:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Site occ.:	-0.0995	0.7542	0.5768	0.2243	0.3887	0.5323	0.1808	0.4540	0.5914	-0.0582	0.6530	0.3175	0.1486	0.7300	0.8065	-0.0228	0.4034
x:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.18172	0.18200	0.19556	0.31873	0.31879	0.31794
y:	0.58392	0.24284	0.73477	0.54703	-0.09664	0.65318	0.59452	-0.07303	0.46854	0.52932	0.18347	0.40522	0.81168	-0.03544	0.71440	0.31436	0.14863
z:																	
	job0095	CC	-305.8233	9.35073	6.86681	9.32951	120.0948	e									
Site occ.:	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	P	F	F	O
x:	0.03241	0.05912	0.31061	0.82067	0.07024	0.81059	0.30649	0.72572	0.40099	0.42965	0.09202	0.66232	0.69713	0.46117	0.06252	0.06315	0.54565
y:	0.5	0	0	0	0.5	0.5	0.5	0.24828	0.24945	0	0	0	0.5	0.5	0	0.5	0
z:	0.43035	0.29996	0.06864	0.81518	0.82739	0.05114	0.31210	0.39660	0.73329	0.45910	0.69371	0.03324	0.67017	0.09392	0.05887	0.06719	0.38552
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.09782	0.73426	0.58574	0.24474	0.38607	0.53061	0.18340	0.46880	0.59318	-0.07217	0.65347	0.31574	0.14903	0.71617	0.81032	-0.03549	0.40417
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.18123	0.18206	0.18132	0.31786	0.30433	0.31828
z:	0.57938	0.22243	0.74893	0.55231	-0.09650	0.65170	0.59266	-0.06038	0.47768	0.53939	0.18690	0.40120	0.80761	-0.02654	0.72692	0.30084	0.15091
	job0096	CC	-305.8223	9.31973	6.86583	9.33837	119.8370	f									
Site occ.:	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	P	F	F	O
x:	0.45847	0.05697	0.30275	-0.17725	0.06889	-0.18327	0.30117	0.73229	0.39581	0.43385	0.09327	-0.33708	-0.30516	0.03561	0.05919	0.06449	0.54974
y:	0.5	0	0	0	0.5	0.5	0.5	0.24838	0.24934	0	0	0.5	0.5	0.5	0	0.5	0
z:	0.09127	0.30450	0.06398	-0.18658	-0.18084	0.05239	0.31399	0.39778	0.72342	0.46247	-0.30419	0.03035	-0.33774	0.42831	0.06265	0.06141	0.38869
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.09794	-0.26260	0.58074	0.22591	0.37169	0.53487	0.18451	0.47332	0.59390	-0.05439	-0.32801	0.31972	0.14932	0.72309	0.80884	-0.02241	0.39602
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.18131	0.18125	0.18207	0.31829	0.31796	0.30427
z:	0.57709	0.22026	-0.26142	0.53996	-0.11912	-0.34519	0.59457	-0.05991	0.47031	0.52930	0.19633	0.40895	0.80970	-0.02486	0.71795	0.31209	0.15910
	job0097	CC	-308.7272	9.36844	6.88240	9.42597	120.3618	a, d									
Site occ.:	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	F	F	O
x:	0.43022	-0.30601	0.05057	0.31208	-0.17016	0.07326	-0.18693	0.29472	0.73300	0.39083	0.09249	-0.32929	0.03111	0.45438	0.07131	0.05327	0.55100
y:	0	0.5	0	0	0	0.5	0.5	0.5	0.24897	0.25055	0	0	0.5	0.5	0	0.5	0
z:	0.46082	-0.33526	0.30318	0.06564	-0.17217	-0.17778	0.06065	0.29802	0.39178	0.73381	-0.30858	0.03586	0.43425	0.09009	0.07031	0.05546	0.37067
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.09619	-0.25334	0.57279	0.22002	0.37726	0.53817	0.18508	0.47772	0.58568	-0.06150	-0.35346	0.30072	0.15244	0.72893	0.82382	-0.02823	0.39564
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.19605	0.18088	0.18126	0.30400	0.31911	0.31878
z:	0.57579	0.22468	-0.24529	0.55096	-0.09910	-0.32672	0.59291	-0.05468	0.45199	0.53314	0.17987	0.39856	0.80529	-0.01792	0.72677	0.32106	0.14387
	job0104	CC	-309.026	9.35576	6.88433	9.38151	119.4121	a, d									
Site occ.:	V	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	F	F	O
x:	0.16502	-0.03882	0.89170	0.23472	0.32263	-0.19642	0.56274	0.56362	-0.20235	0.32866	-0.06420	0.19047	0.58923	0.53724	0.55559	0.57056	0.25621
y:	0.5	0	0.24915	0.25083	0.5	0.5	0.5	0	0.5	0.5	0.5	0	0.5	0.5	0.5	0.5	0
z:	0.53278	0.59116	0.21998	-0.09593	0.31046	-0.18653	-0.18888	0.31288	0.56474	0.55935	-0.03546	0.15927	0.19734	-0.07328	0.56468	0.55918	-0.25645
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.13010	0.05307	0.07418	0.40094	-0.27632	-0.04804	0.17424	0.03305	0.09412	-0.31965	0.44430	0.90004	0.22609	0.82190	0.30436	0.48424	0.64217
y:	0	0.5	0	0.5	0	0.5	0	0.5	0	0.5	0	0.196238	0.303739	0.319255	0.180779	0.181149	0.318860
z:	0.38037	-0.10608	0.23181	0.08401	0.03905	0.42808	-0.30421	0.15632	-0.03064	0.09614	0.02703	0.65942	0.46450	-0.08942	0.21318	0.81423	0.30983
	job0098	CC	-308.720	9.40642	6.87966	9.35525	120.1058	b, e									
Site occ.:	V	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	F	F	O
x:	0.09094	0.03155	0.05864	0.31494	-0.18436	0.06353	-0.18938	0.30763	0.72008	0.40316	0.42674	-0.33877	-0.30347	0.46439	0.06104	0.06311	0.53921
y:	0	0.5	0	0	0	0.5	0.5	0.5	0.24898	0.25068	0	0	0.5	0.5	0	0.5	0
z:	-0.30643	0.43108	0.29457	0.07407	-0.18592	-0.17001	0.05337	0.31249	0.39341	0.73319	0.45472	0.03311	-0.30833	0.09456	0.05378	0.07153	0.37800
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.11933	-0.26695	0.58486	0.24286	0.39077	0.52960	0.19577	0.46764	0.59341	-0.07276	-0.34400	0.31391	0.15821	0.71390	0.80941	-0.03459	0.40978
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.18150	0.19580	0.18090	0.31892	0.30422	0.31899
z:	0.57464	0.22189	-0.25097	0.55237	-0.09497	-0.35312	0.58583	-0.06166	0.47964	0.54030	0.18832	0.39628	0.82331	-0.02696	0.72977	0.30328	0.15375
	job0099	CC	-308.7188	9.34749	6.88150	9.37597	119.6666	c, f									
Site occ.:	V	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	P	F	F	O
x:	-0.33711	0.45932	0.06082	0.29769	-0.17545	0.06925	-0.17531	0.30318	0.73371	0.39399	0.43502	0.09265	-0.30747	0.03767	0.05574	0.06900	0.55019
y:	0	0.5	0	0	0	0.5	0.5	0.5	0.24927	0.25051	0	0	0.5	0.5	0	0.5	0
z:	0.02916	0.09075	0.30930	0.06365	-0.19157	-0.18137	0.05658	0.31410	0.40201	0.72049	0.46349	-0.30097	-0.34150	0.42894	0.06383	0.06167	0.38949
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.09911	-0.24718	0.57760	0.22681	0.37444	0.53502	0.18081	0.45516	0.59261	-0.05307	-0.32772	0.32097	0.14746	0.73058	0.80643	-0.01987	0.39676
y:	0	0	0.5	0.5	0.5	0.5	0.5	0	0.5	0.5	0.5	0.18111	0.18125	0.19591	0.31911	0.31873	0.30405
z:	0.58244	0.24025	-0.26756	0.54028	-0.11777	-0.34502	0.59539	-0.07303	0.46728	0.52737	0.19540	0.41019	0.81170	-0.03543	0.71170	0.31107	0.15781
	job0100	CC	-311.525	9.41273	6.89983	9.42001	120.0479	a, b, c									
Site occ.:	V	V	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	F	F	O
x:	0.42782	0.09232	0.66730	0.05253	0.31139	0.82426	0.06044	0.82291	0.30348	0.72888	0.39598	0.69060	0.03309	0.46312	0.06298	0.06183	0.54500
y:	0	0	0	0	0	0	0.5	0.5	0.5	0.25235	0.25390	0.5	0.5	0.5	0	0.5	0
z:	0.45757	0.69708	0.03247	0.30117	0.07202	0.81385	0.82190	0.06532	0.30165	0.39594	0.72915	0.66126	0.43509	0.09191	0.06260	0.06283	0.36447
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.11857	0.75925	0.57435	0.22077	0.39354	0.53800	0.19461	0.45542	0.59124	-0.05993	0.65471	0.29982	0.15600	0.73326	0.80383	-0.02478	0.40713
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.19608	0.19601	0.19584	0.31915	0.31925	0.31931
z:	0.57895	0.24272	0.73260	0.55196	-0.09517	0.66976	0.58722	-0.07068	0.46986	0.53307	0.18505	0.39333	0.82513	-0.03006	0.71650	0.32122	0.14913
	job0101	CC	-311.563	9.40023	6.90263	9.45464	120.3002	a, b, d									
Site occ.:	V	V	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	F	F	O
x:	0.42659	0.09153	0.69554	0.04871	0.31471	0.82543	0.07150	0.81427	0.29665	0.72595	0.39491	0.66984	0.03061	0.45664	0.06908	0.05470	0.54341
y:	0	0	0.5	0	0	0	0.5	0.5	0.5	0.25054	0.25182	0	0.5	0.5	0	0.5	0
z:	0.45673	0.69016	0.66665	0.29760	0.06893	0.82565	0.82552	0.06251	0.29776	0.38630	0.73458	0.03526	0.43563	0.08977	0.06530	0.05933	0.36314
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.11873	0.74493	0.57457	0.21908	0.38198	0.53893	0.19805	0.47793	0.58654	-0.06257	0.64847	0.29846	0.16253	0.72874	0.82505	-0.02852	0.40056
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.19642	0.19434	0.18102	0.30514	0.31916	0.31929
z:	0.56745	0.22316	0.75610	0.55211	-0.09772	0.66910	0.58527	-0.05571	0.45464	0.53355	0.17985	0.39220	0.81982	-0.01797	0.73091	0.32232	0.14603
	job0102	CC	-311.564	9.42207	6.90233	9.41986	120.2091	a, b, e									
Site occ.:	V	V	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	F	F	O
x:	0.42337	0.09229	0.03298	0.04911	0.31497	0.81853	0.06405	0.81139	0.30602	0.72457	0.40455	0.66567	0.69677	0.46451	0.06318	0.06007	0.54363
y:	0	0	0.5	0	0	0	0.5	0.5	0.5	0.25019	0.25147	0	0.5	0.5	0	0.5	0
z:	0.45315	0.69209	0.43475	0.29033	0.07049	0.81681	0.82850	0.05506	0.30379	0.39145	0.73836	0.03468	0.67171	0.09452	0.05553	0.06644	0.36351
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.11830	0.74066	0.58620	0.24337	0.39387	0.53544	0.19696	0.47285	0.59324	-0.07229	0.65595	0.29489	0.15968	0.71929	0.80905	-0.03643	0.40837
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.19489	0.19579	0.18083	0.31862	0.30512	0.31979
z:	0.57367	0.22267	0.74974	0.55818	-0.09316	0.66587	0.58523	-0.05656	0.48031	0.54202	0.18821	0.38524	0.82106	-0.02375	0.72917	0.30676	0.15163
	job0103	CC		9.39609	6.90066	9.42036	120.009	a, b, f									
Site occ.:	V	V	V	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	P	P	P	F	F	O
x:	0.42910	0.09277	0.45974	0.05017	0.30911	0.82244	0.06202	0.81751	0.29912	0.73122	0.39849	0.66794	0.69391	0.03326	0.06454	0.05963	0.54937
y:	0	0	0.5	0	0	0	0.5	0.5	0.5	0.25072	0.25137	0	0.5	0.5	0	0.5	0
z:	0.45901	0.69274	0.08949	0.29842	0.06730	0.81781	0.81955	0.05599	0.30579	0.39291	0.72756	0.03332	0.66271	0.43332	0.06316	0.05983	0.36936
Site occ.:	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
x:	-0.11792	0.74575	0.58007	0.22100	0.37777	0.53973	0.19926	0.47820	0.59380	-0.05855	0.67210	0.30120	0.15975	0.72682	0.80742	-0.02566	0.39635
y:	0	0	0.5	0.5	0.5	0	0	0	0.5	0.5	0.5	0.19606	0.19415	0.18189	0.31864	0.31804	0.30699
z:	0.56901	0.22192	0.73732	0.54682	-0.11810	0.67150	0.58742	-0.05456	0.47163	0.53244	0.19609	0.39693	0.82213	-0.02130	0.71990	0.31941	0.15634

*CC = cell-and-coordinate optimization.

Table 3. Continued.

(b) $P\,112_1/m$ models.

Simulation label	*Ab initio* simulation type*	E_{total} (eV per unit cell)	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	Ca in A^{I}-type			Ca in A^{II}-type			Ca in A^{II}-type			Ca in A^{II}-type		
							x	y	z	**x**	**y**	**z**	**x**	**y**	**z**	**x**	**y**	**z**
job 0002	CO	-321.987	9.73700	9.73580	7.00572	120.0020	0.33209	0.66748	0.00147	0.24318	1.00496	0.25	0.99777	0.23767	0.25	0.76072	0.75594	0.25
job 0080	CO	-309.227	9.47240	9.47240	6.92230	120.0000	0.32859	0.67152	0.00101	0.24253	0.99097	0.25	1.00039	0.24762	0.25	0.76480	0.76475	0.25
job 0081	CC	-309.295	9.44727	9.39944	6.89209	120.3243	0.32527	0.67126	0.00072	0.23720	0.98829	0.25	1.00134	0.24759	0.25	0.76305	0.76758	0.25
job 0082	CO	-309.230	9.47240	9.47240	6.92230	120.0000	0.32826	0.65746	0.00119	0.23603	1.00006	0.25	1.00994	0.25112	0.25	0.75166	0.75191	0.25
job 0083	CC	-309.302	9.38634	9.45359	6.89122	120.1136	0.32941	0.65788	0.00101	0.23447	0.99868	0.25	1.01218	0.25187	0.25	0.75196	0.75191	0.25
job 0084	CO	-309.233	9.47240	9.47240	6.92230	120.0000	0.34154	0.67091	0.00121	0.24847	0.99961	0.25	1.00112	0.23418	0.25	0.74782	0.75658	0.25
job 0085	CC	-309.306	9.39913	9.38452	6.88617	119.5118	0.34345	0.67146	0.00086	0.24743	0.99783	0.25	1.00347	0.23447	0.25	0.74875	0.75563	0.25
job 0086	CO	-315.581	9.59910	9.59910	6.96890	120.0000	0.32213	0.66146	0.00106	0.23680	0.99587	0.25	1.00357	0.25016	0.25	0.76497	0.75737	0.25
job 0087	CC	-315.678	9.55071	9.51611	6.93428	120.1872	0.32055	0.66127	0.00069	0.23236	0.99258	0.25	1.00416	0.25029	0.25	0.76415	0.76048	0.25
job 0088	CO	-315.582	9.59910	9.59910	6.96890	120.0000	0.33801	0.67798	0.00147	0.24791	0.99738	0.25	0.99267	0.23350	0.25	0.75813	0.76309	0.25
job 0089	CC	-315.680	9.51524	9.50509	6.92915	119.6738	0.33877	0.67784	0.00101	0.24993	0.99676	0.25	0.99402	0.23123	0.25	0.75819	0.76394	0.25
job 0090	CO	-315.587	9.59910	9.59910	6.96890	120.0000	0.33799	0.66088	0.00145	0.24345	1.00766	0.25	1.00613	0.24020	0.25	0.74909	0.75200	0.25
job 0091	CO	-315.686	9.49955	9.55833	6.92815	120.0570	0.33917	0.66144	0.00109	0.24160	1.00549	0.25	1.00924	0.24137	0.25	0.74934	0.75209	0.25

	Location of V as per Fig. 1	*B*-type site				*B*-type site				*B*-type site			
		x	y	z	Site occ.	x	y	z	Site occ.	x	y	z	Site occ.
job 0002	a,d, b,e,c,f	0.40055	0.37092	0.25	V	0.63188	0.02827	0.25	V	0.97062	0.60028	0.25	V
job 0080	a, d	0.39758	0.36871	0.25	V	0.62862	0.03168	0.25	P	0.97396	0.60843	0.25	P
job 0081	a, d	0.39746	0.36973	0.25	V	0.63090	0.03409	0.25	P	0.97269	0.61079	0.25	P
job 0082	b, e	0.39163	0.36526	0.25	P	0.63228	0.02990	0.25	V	0.96839	0.59667	0.25	P
job 0083	b, e	0.39276	0.36547	0.25	P	0.63246	0.02934	0.25	V	0.96937	0.59646	0.25	P
job 0084	c, f	0.40307	0.37160	0.25	P	0.63541	0.02642	0.25	P	0.97021	0.60106	0.25	V
job 0085	c, f	0.40373	0.37095	0.25	P	0.63421	0.02403	0.25	P	0.97050	0.59784	0.25	V
job 0086	a, d, b, e	0.39307	0.36500	0.25	V	0.62782	0.03041	0.25	V	0.97226	0.60188	0.25	P
job 0087	a, d, b, e	0.39294	0.36545	0.25	V	0.62924	0.03223	0.25	V	0.97180	0.60449	0.25	P
job 0088	a, d, c, f	0.40369	0.37304	0.25	V	0.63064	0.02791	0.25	P	0.97203	0.60700	0.25	V
job 0089	a, d, c, f	0.40416	0.37260	0.25	V	0.63039	0.02615	0.25	P	0.97180	0.60508	0.25	V
job 0090	b, e, c, f	0.39775	0.36971	0.25	P	0.63649	0.02881	0.25	V	0.96961	0.59640	0.25	V
job 0091	b, e, c, f	0.39768	0.36912	0.25	P	0.63658	0.02842	0.25	V	0.96999	0.59528	0.25	V

	O in O1-type			O in O1-type			O in O1-type			O in O2-type			O in O2-type			O in O2-type		
	x	y	z	x	y	z	x	y	z	x	y	z	x	y	z	x	y	z
job 0002	0.32066	0.49361	0.25	0.50966	0.82577	0.25	0.17363	0.68341	0.25	0.60759	0.47243	0.25	0.52837	0.13227	0.25	0.86946	0.39326	0.25
job 0080	0.31027	0.49105	0.25	0.51214	0.84559	0.25	0.16207	0.68556	0.25	0.60852	0.47417	0.25	0.53166	0.12530	0.25	0.88630	0.41848	0.25
job 0081	0.30867	0.49139	0.25	0.50967	0.84353	0.25	0.15854	0.68410	0.25	0.60936	0.47655	0.25	0.53185	0.12593	0.25	0.88559	0.41937	0.25
job 0082	0.31605	0.47748	0.25	0.50920	0.82041	0.25	0.15497	0.66777	0.25	0.58178	0.46629	0.25	0.52680	0.13569	0.25	0.87608	0.40604	0.25
job 0083	0.31732	0.47824	0.25	0.51130	0.81984	0.25	0.15845	0.67032	0.25	0.58460	0.46645	0.25	0.52558	0.13419	0.25	0.87740	0.40553	0.25
job 0084	0.33481	0.48931	0.25	0.52276	0.83885	0.25	0.18024	0.69039	0.25	0.59359	0.46759	0.25	0.53452	0.11582	0.25	0.86637	0.39004	0.25
job 0085	0.33477	0.48967	0.25	0.52532	0.83837	0.25	0.18313	0.69248	0.25	0.59455	0.46680	0.25	0.53305	0.11473	0.25	0.86684	0.38613	0.25
job 0086	0.30368	0.48298	0.25	0.50131	0.82484	0.25	0.15633	0.67465	0.25	0.60272	0.47337	0.25	0.52705	0.13870	0.25	0.88318	0.41402	0.25
job 0087	0.30166	0.48255	0.25	0.50045	0.82291	0.25	0.15576	0.67585	0.25	0.60346	0.47579	0.25	0.52647	0.13938	0.25	0.88338	0.41491	0.25
job 0088	0.32513	0.49987	0.25	0.51767	0.84396	0.25	0.17955	0.69796	0.25	0.61245	0.47308	0.25	0.53288	0.11838	0.25	0.87238	0.39783	0.25
job 0089	0.32292	0.49897	0.25	0.52022	0.84256	0.25	0.18163	0.70018	0.25	0.61392	0.47395	0.25	0.53179	0.11740	0.25	0.87259	0.39471	0.25
job 0090	0.32670	0.48279	0.25	0.51750	0.82190	0.25	0.17562	0.67797	0.25	0.58610	0.46743	0.25	0.52834	0.13020	0.25	0.86321	0.38755	0.25
job 0091	0.32566	0.48222	0.25	0.51937	0.82136	0.25	0.17891	0.68139	0.25	0.58758	0.46770	0.25	0.52680	0.12935	0.25	0.86412	0.38578	0.25

	O in O3-type			O in O3-type			O in O3-type			F		
	x	y	z	x	y	z	x	y	z	x	y	z
job 0002	0.33496	0.24539	0.05642	0.75697	0.08951	0.05641	0.90862	0.66306	0.05572	0.00011	-0.00186	0.25
job 0080	0.33508	0.23999	0.05506	0.74216	0.09063	0.06980	0.91966	0.66573	0.06900	0.00540	0.00647	0.25
job 0081	0.33493	0.24031	0.05447	0.74421	0.09380	0.06900	0.91770	0.66751	0.06828	0.00622	0.00662	0.25
job 0082	0.33344	0.25344	0.06922	0.76043	0.09495	0.05484	0.90929	0.65056	0.06961	-0.00637	-0.00230	0.25
job 0083	0.33398	0.25341	0.06835	0.76156	0.09515	0.05439	0.90902	0.64984	0.06912	-0.00626	-0.00159	0.25
job 0084	0.34763	0.25821	0.06984	0.74744	0.07995	0.06936	0.90341	0.66198	0.05435	0.00159	-0.00744	0.25
job 0085	0.34797	0.25717	0.06924	0.74638	0.07707	0.06856	0.90308	0.65940	0.05365	0.00528	-0.00667	0.25
job 0086	0.32619	0.23836	0.05570	0.75552	0.09774	0.05563	0.91622	0.65715	0.07042	-0.00093	0.00372	0.25
job 0087	0.32636	0.23782	0.05493	0.75729	0.10111	0.05517	0.91526	0.65918	0.06942	-0.00028	0.00470	0.25
job 0088	0.34299	0.24518	0.05606	0.74198	0.08342	0.07031	0.91147	0.67239	0.05527	0.00553	0.00001	0.25
job 0089	0.34394	0.24397	0.05570	0.74203	0.08171	0.06960	0.91049	0.67077	0.05442	0.00822	0.00051	0.25
job 0090	0.34172	0.25862	0.07027	0.76280	0.08767	0.05569	0.90136	0.65538	0.05566	-0.00377	-0.00690	0.25
job 0091	0.34136	0.25757	0.06955	0.76394	0.08815	0.05493	0.90051	0.65404	0.05531	-0.00344	-0.00640	0.25

(c) $P\,6_3/m$ models. Site and atom coordinates labelling as per Table 1, as defined in Mercier *et al*. (2005a).

Composition	*Ab initio* simulation type*	E_{total} (eV per unit cell)	*a* (Å)	*c* (Å)	AIz	AIIx	AIIy	Bx	By	O1x	O1y	O2x	O2y	O3x	O3y	O3z
$Ca_{10}(VO_4)_6F_2$	CC	-322.135	9.63590	6.97236	0.00094	0.00004	0.24001	0.39806	0.36899	0.31248	0.48858	0.60684	0.47510	0.33459	0.24280	0.05590
$Ca_{10}(PO_4)_6F_2$	CO	-303.035	9.36700	6.88400	0.00093	0.00603	0.24746	0.39759	0.36780	0.32445	0.48403	0.58976	0.46788	0.34079	0.25436	0.06880
$Ca_{10}(PO_4)_6F_2$	CO	-303.052	9.37500	6.88700	0.00097	0.00582	0.24738	0.39760	0.36784	0.32463	0.48409	0.58968	0.46778	0.34080	0.25446	0.06885
$Ca_{10}(PO_4)_6F_2$	CC	-303.113	9.30074	6.85123	0.00039	0.00760	0.24777	0.39801	0.36829	0.32392	0.48468	0.59109	0.46904	0.34073	0.25398	0.06802

*CC = cell-and-coordinate optimization; CO = coordinate-only optimization.

Table 4. Standard crystallographic Rietveld refinement results. Numbers in parenthesis are standard uncertainty values output by the *TOPAS* program.

V fraction (x) $Ca_{10}(V_xP_{1-x}O_4)_6F_2$	Rwp	GOF	*a* (Å)	*c* (Å)	AIz	AIIx	AIIy	Bx	By	O1x	O1y	O2x	O2y	O3x	O3y	O3z	beqA1	beqA2	beqO	beqB	beqX	Crystallite Size (Å)	Microstrain (%)
unrestrained																							
0.0	6.69	1.64	9.378341(72)	6.888774(67)	0.00217(24)	0.24146(12)	-0.00825(14)	0.39863(17)	0.36890(16)	0.32665(33)	0.48701(33)	0.59060(35)	0.46666(35)	0.34100(27)	0.25632(26)	0.06877(24)	0.810*	0.666*	0.728*	1.296*	2.252*	181.4*	0.1073(15)
0.1	13.54	3.30	9.38012(26)	6.88888(22)	0.00310(54)	0.24254(27)	-0.00754(32)	0.39927(38)	0.36819(35)	0.32791(75)	0.48992(73)	0.59412(78)	0.46781(78)	0.34478(58)	0.26125(55)	0.06484(52)	0.775*	0.441*	0.869*	1.123*	2.281*	n/a	0.4392(32)
0.2	9.58	2.32	9.43792(21)	6.90967(17)	0.00149(37)	0.24176(19)	-0.00672(22)	0.39816(24)	0.36964(22)	0.32472(51)	0.48689(49)	0.59222(52)	0.46969(53)	0.34206(41)	0.25557(39)	0.06884(37)	0.712*	0.573*	0.482*	1.311*	1.992*	n/a	0.5578(22)
0.3	9.99	2.34	9.47331(21)	6.92272(17)	0.00147(35)	0.24145(18)	-0.00593(21)	0.39797(23)	0.36960(20)	0.32361(49)	0.48660(47)	0.59286(51)	0.47073(51)	0.34172(40)	0.25523(38)	0.06874(36)	0.881*	0.749*	0.521*	1.534*	2.166*	n/a	0.5932(21)
0.4	8.97	2.11	9.51034(22)	6.93674(18)	0.00177(35)	0.24134(18)	-0.00534(21)	0.39800(21)	0.36981(19)	0.32154(48)	0.48556(46)	0.59377(50)	0.47085(50)	0.34098(39)	0.25447(37)	0.06870(35)	0.834*	0.771*	0.503*	1.540*	2.421*	n/a	0.6582(21)
0.5	10.02	2.27	9.56534(19)	6.94712(16)	0.00226(33)	0.24346(18)	-0.00431(21)	0.39809(19)	0.37025(17)	0.32179(47)	0.48625(45)	0.59420(48)	0.47091(48)	0.34071(39)	0.25417(36)	0.06604(35)	0.803*	0.858*	0.382*	1.561*	4.197*	n/a	0.5679(20)
0.6	8.55	1.99	9.58204(28)	6.96275(22)	0.00176(36)	0.24135(19)	-0.00353(22)	0.39782(21)	0.37031(18)	0.32012(50)	0.48568(47)	0.59489(52)	0.47202(51)	0.33974(41)	0.25327(38)	0.06870(36)	0.929*	1.023*	0.547*	1.815*	2.782*	n/a	0.8426(24)
0.7	10.67	2.44	9.60292(48)	6.97121(39)	0.00143(50)	0.24023(25)	-0.00337(31)	0.39802(28)	0.37113(24)	0.31885(68)	0.48496(64)	0.59429(69)	0.46968(68)	0.33967(55)	0.25299(52)	0.06865(48)	0.869*	1.055*	0.559*	1.742*	3.419*	n/a	1.0519(43)
0.8	11.14	2.64	9.64536(72)	6.98546(58)	0.00189(64)	0.23982(31)	-0.00328(40)	0.39743(34)	0.37004(29)	0.31655(85)	0.48698(81)	0.59279(86)	0.46988(86)	0.33944(68)	0.25326(65)	0.06730(59)	0.988*	1.051*	0.372*	1.744*	3.251*	n/a	1.4033(60)
0.9	10.90	2.56	9.68193(47)	7.00145(38)	0.00106(60)	0.24035(30)	-0.00339(36)	0.39756(29)	0.36896(27)	0.31877(83)	0.49182(77)	0.59461(82)	0.47037(82)	0.34339(66)	0.25877(60)	0.06722(57)	1.207*	1.052*	0.455*	1.719*	4.421*	n/a	0.9485(40)
restrained																							
0.0	6.73	1.65	9.378340(72)	6.888770(67)	0.00213(24)	0.24151(12)	-0.00825(14)	0.39854(12)	0.36890(11)	0.32736(22)	0.48644(19)	0.58919(21)	0.46581(32)	0.34126(25)	0.25662(21)	0.06919(18)	0.810*	0.666*	0.728*	1.296*	2.252*	181.4*	0.1068(16)
0.1	13.56	3.30	9.38011(26)	6.88888(22)	0.00303(53)	0.24275(27)	-0.00740(32)	0.39920(26)	0.36852(25)	0.32856(48)	0.48889(42)	0.59234(47)	0.46618(69)	0.34420(53)	0.26035(40)	0.06396(38)	0.775*	0.441*	0.869*	1.123*	2.281*	n/a	0.4388(32)
0.2	9.59	2.33	9.43793(21)	6.90968(17)	0.00137(36)	0.24188(19)	-0.00665(22)	0.39819(17)	0.36969(16)	0.32449(30)	0.48701(28)	0.59158(31)	0.46911(47)	0.34155(36)	0.25472(27)	0.06777(26)	0.712*	0.573*	0.482*	1.311*	1.992*	n/a	0.5580(22)
0.3	10.04	2.35	9.47333(21)	6.92276(17)	0.00131(34)	0.24161(18)	-0.00578(21)	0.39803(16)	0.36968(15)	0.32310(29)	0.48697(26)	0.59260(29)	0.47032(45)	0.34079(36)	0.25377(26)	0.06683(25)	0.881*	0.749*	0.521*	1.534*	2.166*	n/a	0.5937(21)
0.4	9.07	2.13	9.51034(22)	6.93677(18)	0.00159(34)	0.24156(18)	-0.00512(21)	0.39809(15)	0.36992(14)	0.32071(28)	0.48612(26)	0.59395(28)	0.47063(44)	0.33966(35)	0.25249(25)	0.06612(25)	0.834*	0.771*	0.503*	1.540*	2.421*	n/a	0.6591(21)
0.5	10.15	2.29	9.56537(20)	6.94713(16)	0.00214(33)	0.24359(17)	-0.00412(20)	0.39818(14)	0.37023(13)	0.32078(27)	0.48739(25)	0.59500(27)	0.47123(43)	0.33952(35)	0.25245(24)	0.06341(24)	0.803*	0.858*	0.382*	1.561*	4.197*	n/a	0.5683(20)
0.6	8.76	2.04	9.58208(28)	6.96281(23)	0.00141(36)	0.24160(18)	-0.00321(22)	0.39772(15)	0.37030(14)	0.31840(28)	0.48701(26)	0.59591(28)	0.47235(45)	0.33844(35)	0.25059(26)	0.06480(26)	0.929*	1.023*	0.547*	1.815*	2.782*	n/a	0.8450(24)
0.7	10.92	2.50	9.60289(50)	6.97133(40)	0.00115(49)	0.24066(24)	-0.00293(31)	0.39801(20)	0.37133(19)	0.31680(37)	0.48697(35)	0.59712(37)	0.47048(61)	0.33847(46)	0.24993(34)	0.06381(34)	0.869*	1.055*	0.559*	1.742*	3.419*	n/a	1.0588(44)
0.8	11.38	2.69	9.64523(73)	6.98553(59)	0.00138(63)	0.24044(30)	-0.00269(39)	0.39720(24)	0.37056(23)	0.31519(46)	0.48852(43)	0.59692(45)	0.47105(72)	0.33923(58)	0.24970(41)	0.06159(41)	0.988*	1.051*	0.372*	1.744*	3.251*	n/a	1.4138(61)
0.9	11.40	2.68	9.68173(49)	7.00142(39)	0.00079(62)	0.24183(30)	-0.00201(37)	0.39648(22)	0.36975(21)	0.31911(45)	0.49284(41)	0.59714(43)	0.46678(70)	0.34122(58)	0.25167(40)	0.05826(40)	1.207*	1.052*	0.455*	1.719*	4.421*	n/a	0.9599(42)

*This parameter was frozen at the given value during the refinement.

Table 5. Crystal-chemical parameters extracted from standard Rietveld refinement results (Table 4) using the equations given in Table 1(b) of Mercier et al. (2005a).

V fraction (x) $Ca_{10}(V_xP_{1-x}O_4)_6F_2$	(AI-O1) (Å)	$(AI\text{-}O1)^{AIz=0}$ (Å)	$\Delta_{AI\text{-}O}^{AIz=0}$ (Å)	$\Delta_{AI\text{-}O}^{AIz=0}$ (Å)	δ_{AI} (°)	α_{AI} (°)	<B-O> (Å)	$<\tau_{O\text{-}B\text{-}O}>$ (°)	ρ_{AII} (Å)	α_{AII} (°)	(AII-O3) (Å)	$\phi_{O3\text{-}AII\text{-}O3}$ (°)	$\psi_{AI\text{-}O1}^{AIz=0}$ (°)
unrestrained													
0	2.3774	2.3883	0.0688	0.0471	18.555	-20.421	1.5532	111.097	3.9920	118.324	2.3356	140.198	43.856
0.1	2.3580	2.3735	0.0818	0.0512	19.123	-20.671	1.5639	110.382	4.0022	118.489	2.3169	138.784	43.480
0.2	2.3865	2.3939	0.0782	0.0635	18.590	-21.030	1.5701	111.533	4.0086	118.644	2.3526	138.890	43.815
0.3	2.3917	2.3992	0.0826	0.0678	18.556	-21.310	1.5792	111.517	4.0119	118.803	2.3594	138.493	43.834
0.4	2.3982	2.4072	0.0815	0.0638	18.360	-21.706	1.5897	111.607	4.0191	118.922	2.3657	138.297	43.912
0.5	2.4006	2.4120	0.0887	0.0660	18.437	-21.709	1.6066	111.652	4.0703	119.131	2.3519	138.038	43.942
0.6	2.4062	2.4152	0.0890	0.0712	18.320	-22.081	1.6084	111.734	4.0358	119.286	2.3788	137.764	43.885
0.7	2.4133	2.4204	0.0725	0.0586	17.970	-22.068	1.6119	112.192	4.0238	119.303	2.3852	137.323	43.941
0.8	2.3986	2.4082	0.1069	0.0880	17.463	-22.298	1.6264	111.757	4.0340	119.322	2.3815	137.091	43.516
0.9	2.3843	2.3899	0.1186	0.1076	17.939	-22.234	1.6282	111.272	4.0602	119.303	2.3921	136.380	42.913
restrained													
0	2.3840	2.3944	0.0634	0.0428	18.471	-20.131	1.5459	111.168	3.9920	118.324	2.3388	140.163	44.006
0.1	2.3672	2.3821	0.0714	0.0418	18.959	-20.298	1.5611	110.587	4.0062	118.511	2.3105	138.855	43.699
0.2	2.3857	2.3927	0.0779	0.0641	18.469	-20.968	1.5745	111.587	4.0102	118.645	2.3451	138.907	43.783
0.3	2.3886	2.3951	0.0838	0.0710	18.429	-21.335	1.5892	111.549	4.0127	118.823	2.3460	138.402	43.731
0.4	2.3932	2.4012	0.0832	0.0674	18.245	-21.809	1.6047	111.617	4.0224	118.964	2.3472	138.194	43.762
0.5	2.3906	2.4012	0.0960	0.0753	18.379	-21.969	1.6247	111.546	4.0703	119.172	2.3334	137.843	43.672
0.6	2.3946	2.4017	0.0960	0.0821	18.174	-22.469	1.6342	111.792	4.0366	119.347	2.3535	137.289	43.549
0.7	2.3951	2.4011	0.0804	0.0684	17.958	-22.733	1.6477	112.369	4.0278	119.406	2.3544	136.602	43.462
0.8	2.3872	2.3944	0.1021	0.0881	17.703	-23.009	1.6662	112.376	4.0389	119.446	2.3499	135.727	43.166
0.9	2.3811	2.3842	0.0831	0.0770	18.036	-22.263	1.6784	112.694	4.0717	119.591	2.3382	134.782	42.764

Table 6. Selected oxygen-metal-oxygen O3-A^{II}-O3 and O-B-O bond angles for individual crystallographic sites of $P1m1$ and $P112_1/m$ *ab initio* optimized structures.

Vanadium fraction (x)	Vanadium location as per Fig. 1	*Ab initio* simulation type	ϕ(O3i-AII-O3i)	$\langle\phi(\text{O3i-AII-O3i})\rangle_{structure}$	τ(Oi-B-Oi)		$\langle\tau(\text{Oi-B-Oi})\rangle_{site}$	$\langle\tau(\text{Oi-B-Oi})\rangle_{structure}$
				$P1m1$ models				
1/6	a	CC	139.186		114.610	111.482	112.525	
			140.089		111.820	110.947	111.238	
			137.899		111.546	110.345	110.745	
			138.420		111.537	110.928	111.131	
			140.354		110.729	112.008	111.582	
			133.899	138.308	111.159	110.853	110.955	111.363
1/6	a	CC	139.092		114.762	111.472	112.568	
			140.473		111.653	111.001	111.218	
			137.725		111.463	110.140	110.581	
			138.150		111.573	110.896	111.122	
			141.032		110.970	112.114	111.733	
			133.931	138.401	110.897	110.914	110.908	111.355
1/6	b	CC	137.594		115.044	111.325	112.565	
			139.462		111.568	110.154	110.625	
			140.147		111.600	111.171	111.314	
			133.671		111.069	110.936	110.980	
			138.361		111.272	110.753	110.926	
			140.876	138.352	111.155	111.997	111.717	111.355
1/6	d	CC	138.238		114.694	111.545	112.595	
			140.993		111.683	110.871	111.142	
			133.808		110.899	112.126	111.717	
			139.061		110.929	110.895	110.907	
			140.615		111.679	111.056	111.264	
			137.932	138.441	111.419	110.240	110.633	111.376
1/6	c	CC	140.102		114.729	111.038	112.268	
			138.162		111.748	111.061	111.290	
			139.032		110.744	110.529	110.601	
			140.607		111.098	112.083	111.755	
			135.118		111.638	111.327	111.431	
			138.338	138.560	110.696	111.316	111.110	111.409
1/6	e	CC	133.918		114.567	111.387	112.447	
			138.628		110.985	110.963	110.970	
			140.697		111.772	110.720	111.070	
			137.705		110.939	112.235	111.803	
			139.177		111.632	110.173	110.659	
			140.246	138.395	111.843	110.914	111.224	111.362
1/6	f	CC	140.793		113.887	111.849	112.529	
			134.264		111.027	112.120	111.755	
			138.193		110.153	111.301	110.918	
			139.969		111.510	110.390	110.763	
			139.298		111.759	111.023	111.268	
			139.159	138.613	112.194	110.622	111.146	111.397
1/3	a, d	CC	138.313		115.192	111.079	112.450	
			141.930		115.036	111.270	112.526	
			132.287		111.363	112.007	111.792	
			138.418		111.163	110.110	110.461	
			141.721		110.979	112.004	111.663	
			132.495	137.527	111.386	109.922	110.410	111.550
1/3	a, d	CC	138.074		115.607	111.167	112.647	
			138.155		115.605	111.148	112.633	
			142.311		111.118	112.388	111.964	
			142.302		111.651	112.125	111.967	
			131.900		111.138	110.078	110.431	
			131.821	137.427	111.573	110.114	110.600	111.707
1/3	b, e	CC	132.515		115.555	110.891	112.445	
			138.690		114.699	110.943	112.195	
			141.741		111.225	110.047	110.440	
			132.377		111.293	112.344	111.994	
			138.095		111.352	110.063	110.493	
			141.929	137.558	111.806	111.792	111.797	111.560
1/3	c, f	CC	141.658		114.948	110.382	111.904	
			132.998		113.675	111.815	112.435	
			138.308		111.310	112.084	111.826	
			141.534		109.897	110.668	110.411	
			134.583		111.311	112.084	111.826	
			138.506	137.931	112.488	110.691	111.290	111.616
1/2	a, b, c	CC	138.326		115.011	109.771	111.518	
			138.842		114.828	109.850	111.509	
			138.353		114.945	109.672	111.429	
			134.260		110.936	111.800	111.512	
			134.883		111.056	111.857	111.590	
			134.406	136.512	110.628	111.912	111.484	111.507
1/2	a, b, d	CC	137.006		114.901	109.493	111.296	
			141.601		114.551	112.647	113.281	
			134.006		114.589	110.703	111.998	
			134.526		111.379	110.024	110.476	
			140.997		111.217	111.992	111.734	
			134.235	137.062	110.992	110.992	110.992	111.629
1/2	a, b, e	CC	134.005		113.522	109.548	110.872	
			138.979		115.651	110.825	112.434	
			140.739		114.079	112.330	112.913	
			131.845		111.349	111.440	111.410	
			139.633		111.717	109.768	110.418	
			137.217	137.070	110.951	111.813	111.526	111.595
1/2	a, b, f	CC	138.602		113.957	110.823	111.868	
			137.241		114.288	111.829	112.649	
			137.259		113.218	112.516	112.750	
			133.523		111.795	109.708	110.404	
			140.078		111.698	110.671	111.013	
			135.925	137.105	111.707	111.506	111.573	111.709

Table 6. Continued.

Vanadium fraction (x)	Vanadium location as per Fig. 1	*Ab initio* simulation type	ϕ(O3i-AII-O3i)	$\langle\phi(\text{O3i-AII-O3i})\rangle_{\text{structure}}$	τ(Oi-B-Oi)		$\langle\tau(\text{Oi-B-Oi})\rangle_{\text{site}}$	$\langle\tau(\text{Oi-B-Oi})\rangle_{\text{structure}}$
				$P112_1/m$ models				
1/3	a, d	CO	137.779		114.495	111.487	112.490	
			140.585		111.148	112.393	111.978	
			132.715	137.026	111.523	109.804	110.377	111.615
1/3	b, e	CO	133.012		111.504	109.867	110.413	
			137.501		114.279	111.308	112.298	
			141.022	137.178	111.137	112.205	111.849	111.520
1/3	c, f	CO	141.421		111.016	112.335	111.895	
			131.616		111.379	109.942	110.421	
			138.318	137.118	114.549	111.323	112.399	111.572
2/3	a, d, b, e	CO	132.484		114.329	109.370	111.023	
			138.938		113.597	113.053	113.234	
			134.369	135.264	111.405	111.025	111.152	111.803
2/3	a, d, c, f	CO	139.278		113.644	113.108	113.286	
			133.596		111.213	111.169	111.184	
			132.723	135.199	114.367	109.331	111.009	111.827
2/3	b, e, c, f	CO	134.805		111.249	111.037	111.107	
			131.911		113.979	109.347	110.891	
			139.405	135.374	113.775	112.935	113.215	111.738
1	a, c, b, e, c, f	CO	133.646		113.697	110.914	111.842	
			132.600		113.252	111.224	111.900	
			133.370	133.205	113.282	110.945	111.724	111.822
1/3	a, d	CC	136.660		115.022	111.263	112.516	
			140.940		109.656	112.730	111.706	
			134.012	137.204	109.753	110.681	110.372	111.531
1/3	b, e	CC	133.264		111.431	109.965	110.454	
			137.778		114.952	110.982	112.305	
			140.732	137.258	111.425	112.076	111.859	111.539
1/3	c, f	CC	143.032		110.891	112.178	111.749	
			131.154		112.181	109.530	110.413	
			137.434	137.207	116.195	110.535	112.422	111.528
2/3	a, d, b, e	CC	131.866		114.601	109.263	111.043	
			139.500		112.977	113.315	113.202	
			135.147	135.504	110.219	111.457	111.045	111.763
2/3	a, d, c, f	CC	140.889		113.797	112.993	113.261	
			132.653		111.921	110.815	111.184	
			132.286	135.276	115.371	108.776	110.974	111.806
2/3	b, e, c, f	CC	135.239		111.164	111.093	111.117	
			132.264		114.608	109.065	110.912	
			139.389	135.631	114.466	112.517	113.166	111.732

Table 7. Crystal-chemical Rietveld refinement results. Numbers in parenthesis are standard uncertainty values output by the *TOPAS* program.

(a) Parameters refined.

V fraction (x) $Ca_{10}(V_xP_{1-x}O_4)_6F_2$	Rwp	GOF	$d_{AI\text{-}O1}$ (Å)	$\Delta_{AI\text{-}O}$ (Å)	δ_{AI} (°)	α_{AI} (°)	$d_{B\text{-}O}$ (Å)	$\tau_{O\text{-}B\text{-}O}$ (°)	ρ_{AII} (Å)	α_{AII} (°)	$d_{AII\text{-}O3}$ (Å)	$\phi_{O3\text{-}AII\text{-}O3}$ (°)	beqA1	beqA2 (isotropic atomic displacement parameters)	beqO	beqB	beqX	Crystallite Size (Å)	Microstrain (%)
0	6.302	1.545	2.3972(17)	0.0362(11)	18.290(27)	-20.344(27)	1.5561(17)	111.2710*	3.9903(49)	118.274(27)	2.3341(15)	139.2638*	0.747(22)	0.599(15)	1.199(31)	0.702(23)	1.972(93)	181.4*	0.03416(78)
0.1	10.232	2.485	2.3972(40)	0.0351(21)	18.478(46)	-20.384(67)	1.5567(32)	111.3421*	3.998(10)	118.305(46)	2.3383(28)	138.7136*	0.497(38)	0.266(25)	0.774(52)	2.0*	1.11(15)	n/a	0.2121(17)
0.2	7.209	1.747	2.3973(25)	0.0437(15)	18.397(31)	-20.259(47)	1.5698(16)	111.4133*	4.0057(59)	118.475(33)	2.3434(14)	138.1575*	0.640(28)	0.411(19)	0.900(37)	2.35(13)	1.27(11)	n/a	0.2649(13)
0.3	7.375	1.724	2.3970(25)	0.0532(13)	18.336(30)	-20.635(43)	1.5865(21)	111.4844*	4.0112(66)	118.648(32)	2.3411(18)	137.6043*	0.813(29)	0.566(19)	1.121(37)	1.619(71)	1.28(11)	n/a	0.2818(12)
0.4	7.787	1.827	2.3963(32)	0.0538(16)	18.373(34)	-20.860(53)	1.6064(26)	111.5556*	4.0216(82)	118.796(38)	2.3366(23)	137.0511*	0.835(35)	0.532(22)	1.123(44)	1.150(56)	1.31(13)	n/a	0.3239(15)
0.5	9.045	2.042	2.3960(32)	0.0690(16)	18.499(34)	-21.174(53)	1.6226(27)	111.6267*	4.0742(84)	119.061(38)	2.3335(23)	136.4979*	0.701(34)	0.611(23)	1.070(45)	0.766(40)	2.81(16)	n/a	0.2524(13)
0.6	9.009	2.095	2.3960(40)	0.0612(19)	18.532(42)	-21.088(67)	1.6334(33)	111.6979*	4.040(10)	119.224(50)	2.3376(29)	135.9448*	0.925(49)	0.614(29)	1.240(58)	0.760(43)	1.31(17)	n/a	0.4609(22)
0.7	11.377	2.599	2.3960(53)	0.0576(25)	18.724(56)	-21.195(88)	1.6438(45)	111.7691*	4.022(14)	119.069(69)	2.3374(39)	135.3916*	1.000(73)	0.351(39)	1.138(80)	0.287(44)	2.0*	n/a	0.7274(39)
0.8	12.997	3.075	2.3960(72)	0.0593(33)	18.686(75)	-21.23(11)	1.6605(63)	111.8402*	4.034(19)	119.235(98)	2.3349(54)	134.8384*	1.06(10)	0.251(47)	1.20(11)	0.2*	1.6*	n/a	0.9106(61)
0.9	11.063	2.603	2.3962(60)	0.0722(28)	18.750(64)	-21.46(10)	1.6704(51)	111.9114*	4.075(16)	119.376(78)	2.3415(45)	134.2853*	1.176(82)	0.486(44)	1.214(92)	0.448(41)	2.0*	n/a	0.5659(36)

(b) Parameters $\psi_{AI\text{-}O1}$ and η (see Table 1 and Fig. 7) derived from Equations in Mercier *et al*. (2005), along with resulting unit-cell parameters and fractional coordinates calculated by *TOPAS*.

V fraction (x) $Ca_{10}(V_xP_{1-x}O_4)_6F_2$	$\psi_{AI\text{-}O1}$ (°)	η (°)	*a* (Å)	*c* (Å)	AIz	AIIx	AIIy	Bx	By	O1x	O1y	O2x	O2y	O3x	O3y	O3z
0	44.082	-3.577	9.377(11)	6.8880(39)	0*	0.00854(13)	0.24984(44)	0.39794(38)	0.36744(23)	0.32597(14)	0.48526(25)	0.58953(18)	0.46552(22)	0.34130(37)	0.25429(34)	0.06768(16)
0.1	44.084	-3.528	9.378(25)	6.8878(73)	0*	0.00841(23)	0.25023(94)	0.39875(82)	0.36789(50)	0.32650(29)	0.48552(56)	0.59040(38)	0.46604(47)	0.34236(80)	0.25461(75)	0.06769(31)
0.2	43.904	-3.997	9.437(15)	6.9090(37)	0*	0.00753(16)	0.24876(55)	0.39777(50)	0.36827(30)	0.32672(20)	0.48729(34)	0.58985(25)	0.46517(30)	0.34065(49)	0.25464(45)	0.06682(15)
0.3	43.783	-3.827	9.472(16)	6.9223(49)	0*	0.00666(16)	0.24775(59)	0.39740(52)	0.36836(31)	0.32522(19)	0.48765(35)	0.59079(24)	0.46632(30)	0.34036(51)	0.25385(47)	0.06531(20)
0.4	43.643	-3.965	9.510(20)	6.9365(59)	0*	0.00593(19)	0.24706(74)	0.39710(65)	0.36797(39)	0.32462(22)	0.48856(44)	0.59215(29)	0.46626(37)	0.33951(63)	0.25237(59)	0.06346(25)
0.5	43.541	-3.804	9.565(20)	6.9473(61)	0*	0.00465(19)	0.24821(74)	0.39744(64)	0.36907(38)	0.32403(22)	0.48964(43)	0.59331(29)	0.46814(37)	0.34008(62)	0.25288(59)	0.06197(25)
0.6	43.409	-4.217	9.582(26)	6.9626(76)	0*	0.00381(24)	0.24528(92)	0.39705(82)	0.36840(48)	0.32449(27)	0.49058(54)	0.59388(36)	0.46662(46)	0.33887(79)	0.25154(74)	0.06123(32)
0.7	43.351	-4.293	9.599(34)	6.969(10)	0*	0.00454(34)	0.2442(12)	0.3976(11)	0.36836(64)	0.32480(36)	0.49121(72)	0.59531(47)	0.46670(61)	0.3392(11)	0.25085(99)	0.06030(43)
0.8	43.244	-4.582	9.646(47)	6.981(14)	0*	0.00372(48)	0.2433(17)	0.3969(15)	0.36812(86)	0.32460(47)	0.49230(98)	0.59569(62)	0.46599(82)	0.3379(14)	0.2499(13)	0.05880(59)
0.9	43.090	-4.473	9.680(39)	6.999(12)	0*	0.00305(38)	0.2446(14)	0.3971(12)	0.36905(72)	0.32411(42)	0.49314(81)	0.59634(54)	0.46739(70)	0.3383(12)	0.2504(11)	0.05825(48)

*This parameter was fixed at the given value during the refinement.

Table 8. Results of bond valence summation (BVS) for the A^{I}, A^{II} and B sites.

V fraction (x) $Ca_{10}(V_xP_{1-x}O_4)_6F_2$	(AI-O1) [x3] (Å)	(AI-O2) [x3] (Å)	(AI-O3) [x3] (Å)	$<M\text{-}A>_{AI}$ (Å)	BVS at A^{I} (v.u.)	(B-O1) (Å)	(B-O2) (Å)	(B-O3) [x2] (Å)	$<M\text{-}A>_{B}$ (Å)	BVS at B* (v.u.)	(AII-O3) [x2] (Å)	(AII-O3') [x2] (Å)	(AII-O2) [x1] (Å)	(AII-O1) [x1] (Å)	(AII-F) [x1] (Å)	$<M\text{-}A>_{AII}$ (Å)	BVS at A^{II} (v.u.)
unrestrained standard crystallographic refinement																	
0	2.3774	2.4462	2.8076	2.5438	2.120	1.5583	1.5595	1.5475	1.5532	4.754	2.3356	2.5042	2.3734	2.6875	2.3048	2.4351	1.969
0.1	2.3580	2.4398	2.7840	2.5273	2.208	1.5863	1.5826	1.5434	1.5639	4.863	2.3169	2.5468	2.3556	2.7080	2.3107	2.4431	1.961
0.2	2.3865	2.4647	2.8125	2.5546	2.052	1.5731	1.5859	1.5607	1.5701	5.022	2.3526	2.4997	2.3623	2.7050	2.3143	2.4409	1.938
0.3	2.3917	2.4744	2.8253	2.5638	2.008	1.5832	1.5994	1.5672	1.5792	5.154	2.3594	2.4993	2.3659	2.7153	2.3163	2.4450	1.917
0.4	2.3982	2.4798	2.8411	2.5730	1.968	1.5939	1.6129	1.5759	1.5897	5.270	2.3657	2.4985	2.3751	2.7153	2.3204	2.4485	1.895
0.5	2.4006	2.4892	2.8566	2.5821	1.932	1.6034	1.6246	1.5991	1.6066	5.292	2.3519	2.5123	2.3703	2.7382	2.3500	2.4553	1.879
0.6	2.4062	2.4952	2.8709	2.5907	1.896	1.6125	1.6359	1.5925	1.6084	5.542	2.3788	2.4936	2.3838	2.7436	2.3300	2.4575	1.853
0.7	2.4133	2.4858	2.8758	2.5917	1.893	1.6137	1.6325	1.6007	1.6119	5.770	2.3852	2.4940	2.4181	2.7440	2.3231	2.4634	1.818
0.8	2.3986	2.5055	2.8909	2.5983	1.881	1.6615	1.6323	1.6060	1.6264	5.841	2.3815	2.5099	2.4318	2.7490	2.3290	2.4704	1.787
0.9	2.3843	2.5030	2.8787	2.5887	1.931	1.7038	1.6521	1.5786	1.6282	6.162	2.3921	2.5584	2.4305	2.7854	2.3442	2.4944	1.691
restrained standard crystallographic refinement																	
0	2.38401	2.44739	2.8061	2.5458	2.102	1.5472	1.5489	1.5438	1.5459	4.848	2.3388	2.5048	2.3812	2.6905	2.3048	2.4377	1.954
0.1	2.36721	2.43863	2.7859	2.5306	2.184	1.5691	1.5687	1.5534	1.5611	4.893	2.3105	2.5431	2.3666	2.7101	2.3130	2.4424	1.966
0.2	2.38570	2.46356	2.8142	2.5545	2.055	1.5746	1.5810	1.5711	1.5745	4.962	2.3451	2.4972	2.3665	2.7037	2.3153	2.4386	1.952
0.3	2.38863	2.47242	2.8273	2.5628	2.019	1.5896	1.5968	1.5851	1.5892	5.015	2.3460	2.4957	2.3684	2.7138	2.3167	2.4403	1.945
0.4	2.39322	2.47641	2.8444	2.5713	1.985	1.6044	1.6129	1.6007	1.6047	5.057	2.3472	2.4928	2.3749	2.7134	2.3223	2.4415	1.937
0.5	2.39063	2.48667	2.8596	2.5790	1.960	1.6232	1.6305	1.6226	1.6247	5.037	2.3334	2.5082	2.3659	2.7365	2.3500	2.4479	1.925
0.6	2.39461	2.49062	2.8708	2.5853	1.934	1.6363	1.6450	1.6277	1.6342	5.164	2.3535	2.4863	2.3785	2.7384	2.3305	2.4467	1.915
0.7	2.39507	2.47546	2.8729	2.5811	1.962	1.6458	1.6558	1.6445	1.6477	5.235	2.3544	2.4860	2.4060	2.7393	2.3255	2.4502	1.894
0.8	2.38723	2.48932	2.8762	2.5843	1.952	1.6787	1.6681	1.6590	1.6662	5.236	2.3499	2.4994	2.4146	2.7483	2.3318	2.4562	1.870
0.9	2.38110	2.46417	2.8694	2.5716	2.024	1.6947	1.6823	1.6683	1.6784	5.329	2.3382	2.5292	2.4467	2.7993	2.3508	2.4759	1.803
crystal-chemical refinement									$d_{B\text{-}O}$								
0	2.3972	2.4334	2.7954	2.5420	2.108	(B-O1) = (B-O2) = (B-O3) = $d_{B\text{-}O}$			1.5561	4.716	2.3341	2.4940	2.3846	2.6763	2.3038	2.4315	1.980
0.1	2.3972	2.4323	2.7870	2.5388	2.118	"			1.5567	4.951	2.3383	2.4949	2.3759	2.6806	2.3083	2.4330	1.973
0.2	2.3973	2.4410	2.8187	2.5523	2.071	"			1.5698	5.026	2.3434	2.5063	2.4034	2.7128	2.3127	2.4469	1.910
0.3	2.3970	2.4502	2.8280	2.5584	2.044	"			1.5865	5.051	2.3411	2.5075	2.4045	2.7225	2.3159	2.4486	1.906
0.4	2.3963	2.4501	2.8409	2.5625	2.036	"			1.6064	5.033	2.3366	2.5070	2.4137	2.7385	2.3219	2.4516	1.898
0.5	2.3960	2.4650	2.8517	2.5709	1.996	"			1.6226	5.066	2.3335	2.5204	2.3921	2.7588	2.3522	2.4587	1.877
0.6	2.3960	2.4573	2.8635	2.5723	2.004	"			1.6334	5.174	2.3376	2.5102	2.4264	2.7828	2.3323	2.4625	1.860
0.7	2.3960	2.4537	2.8630	2.5709	2.012	"			1.6438	5.289	2.3374	2.5156	2.4449	2.7900	2.3222	2.4662	1.845
0.8	2.3960	2.4553	2.8846	2.5786	1.994	"			1.6605	5.317	2.3349	2.5191	2.4636	2.8135	2.3288	2.4734	1.821
0.9	2.3962	2.4684	2.8918	2.5854	1.961	"			1.6704	5.443	2.3415	2.5300	2.4439	2.8232	2.3527	2.4804	1.790

*The bond valence summation at the B site were computed assuming a Brown bond-valence parameter $r_o = 1.803 \cdot x + 1.617 \cdot (1 - x)$.