

## Table S1 — Supplementary Material

**Table S1.** Complete XRD peak indexing for all 52 peaks identified in the 10–90° 2 $\theta$  range. DP: cubic Ia-3d perovskite-related phase,  $a = 10.040 \text{ \AA}$ . D1 and D2 denote domain populations with  $a_1 = 10.048 \text{ \AA}$  and  $a_2 = 9.935 \text{ \AA}$  respectively, identified from doublet peak analysis; domain assignments are given only for peaks appearing as resolved doublets with splitting exceeding the expected  $K\alpha_1/K\alpha_2$  separation; single DP peaks without domain assignment represent reflections that could not be resolved into domain components. MP1:  $\text{Sr}_{10}\text{V}_6\text{O}_{25}$  (PDF 00-052-1578, hexagonal P63/m,  $a = 10.063 \text{ \AA}$ ,  $c = 7.415 \text{ \AA}$ ). MP2:  $\text{Sr}_2\text{VO}_4$  (PDF 01-085-2430, orthorhombic Pna21,  $a = 14.088 \text{ \AA}$ ,  $b = 5.809 \text{ \AA}$ ,  $c = 10.110 \text{ \AA}$ ). BG: instrumental background.  $\Delta\% = 100 \times (d_{\text{obs}} - d_{\text{indexed}}) / d_{\text{indexed}}$ . Deviations within  $\pm 2.0\%$  are consistent with the precision of geometric indexing for laboratory XRD data.

No.	2 $\theta_{\text{obs}}$ (°)	$d_{\text{obs}}$ (Å)	I%	Phase	hkl	$d_{\text{indexed}}$ (Å)	$\Delta\%$	Type	Note
1	12.452	7.109	8.69	DP	(110)	7.092	+0.2	ordering	†
2	5.172	17.088	3.09	BG	—	—	—	background	‡
3	19.633	4.522	10.36	MP2	(211)	4.473	+1.1	minor phase	
4	21.636	4.108	34.53	DP	(211)	4.094	+0.3	ordering	†
5	23.693	3.755	12.65	MP1	(002)	3.708	+1.27	minor phase	
6	24.187	3.680	8.21	MP2	(112)	3.681	−0.03	minor phase	
7	24.782	3.593	14.92	MP2	(311)	3.534	+1.7	minor phase	
8	27.421	3.253	8.94	MP1	(210)	3.294	−1.24	minor phase	
9	28.310	3.153	58.08	DP-D2	(310)	3.141	+0.38	ordering	†
10	28.502	3.132	25.84	DP-D2	(310)	3.141	−0.29	ordering	†
11	29.947	2.984	17.97	MP1	(112)	2.985	−0.03	minor phase	
12	30.915	2.893	100.0	DP	(222)	2.895	−0.07	fundamental	allowed in Pm-3m
13	31.587	2.833	8.49	MP1	(202)	2.824	+0.32	minor phase	
14	33.188	2.699	26.35	DP-D1	(321)	2.685	+0.52	ordering	†
15	33.787	2.653	53.94	DP-D2	(321)	2.655	−0.08	ordering	†
16	35.668	2.517	16.28	DP-D1	(400)	2.512	+0.20	fundamental	allowed in Pm-3m
17	36.093	2.489	19.37	DP-D2	(400)	2.484	+0.20	fundamental	allowed in Pm-3m
18	37.385	2.406	5.27	DP-D1	(330)	2.369	+1.56	ordering	† X
19	37.865	2.376	31.17	DP-D1	(330)	2.369	+0.30	ordering	†
20	38.121	2.361	18.83	DP-D1	(330)	2.369	−0.34	ordering	†
21	38.471	2.340	7.28	DP-D2	(330)	2.342	−0.09	ordering	†
22	39.298	2.293	4.63	MP1	(311)	2.298	−0.22	minor phase	
23	39.867	2.261	24.55	DP-D1	(420)	2.247	+0.62	fundamental	allowed in Pm-3m
24	40.959	2.203	4.68	DP-D2	(420)	2.221	−0.81	fundamental	allowed in Pm-3m
25	41.766	2.163	12.35	DP-D1	(332)	2.142	+0.98	ordering	†
26	43.568	2.077	14.09	DP-D1	(422)	2.051	+1.27	fundamental	allowed in Pm-3m
27	43.984	2.059	6.63	DP-D1	(422)	2.051	+0.39	fundamental	allowed in Pm-3m
28	44.691	2.028	3.55	DP-D2	(422)	2.028	0.00	fundamental	allowed in Pm-3m
29	45.714	1.985	5.60	DP-D1	(431)	1.971	+0.71	ordering	†

30	46.326	1.960	6.39	DP-D1	(431)	1.971	-0.56	ordering	†
31	48.435	1.879	15.12	MP1	(402)	1.878	+0.05	minor phase	
32	49.469	1.843	8.62	DP	(521)	1.831	+0.65	ordering	†
33	51.128	1.787	8.77	DP	(440)	1.773	+0.79	fundamental	allowed in Pm-3m
34	53.380	1.716	5.88	DP	(433)	1.720	-0.23	ordering	†
35	54.095	1.695	11.51	DP	(442)	1.672	+1.38	fundamental	allowed in Pm-3m
36	56.136	1.638	10.24	DP-D1	(532)	1.630	+0.49	ordering	†
37	56.752	1.622	10.78	DP-D1	(532)	1.630	-0.49	ordering	†
38	57.619	1.600	2.44	DP-D1	(620)	1.589	+0.69	fundamental	allowed in Pm-3m
39	58.551	1.577	4.33	DP-D2	(620)	1.571	+0.38	fundamental	allowed in Pm-3m
40	59.454	1.555	3.27	DP	(541)	1.548	+0.45	ordering	†
41	61.502	1.508	2.60	DP	(622)	1.512	-0.26	fundamental	allowed in Pm-3m
42	62.558	1.485	5.24	DP	(631)	1.479	+0.41	ordering	†
43	64.492	1.445	15.06	DP	(444)	1.448	-0.21	fundamental	allowed in Pm-3m
44	65.930	1.418	4.14	DP	(543)	1.418	0.00	ordering	†
45	67.576	1.386	2.03	DP	(640)	1.391	-0.36	fundamental	allowed in Pm-3m
46	68.365	1.371	15.37	DP-D1	(552)	1.367	+0.29	ordering	†
47	68.772	1.365	2.69	DP-D1	(552)	1.367	-0.15	ordering	†
48	71.995	1.312	1.76	DP	(730)	1.317	-0.38	ordering	†
49	77.207	1.236	5.92	DP	(554)	1.235	+0.08	ordering	†
50	80.767	1.190	1.54	DP	(660)	1.182	+0.68	fundamental	allowed in Pm-3m
51	85.969	1.131	2.00	DP	(752)	1.136	-0.44	ordering	†
52	88.251	1.106	4.30	DP	(833)	1.108	-0.18	ordering	†

† All peaks classified as ordering type are systematically absent in disordered simple perovskite (Pm-3m) but permitted in Ia-3d, providing evidence for B-site cation ordering; see main text Section 3.1.  $\chi$  = marginally exceeds  $\pm 2.0\%$  tolerance. ‡ Peak at  $2\theta = 5.172^\circ$  ( $d = 17.088 \text{ \AA}$ ,  $I\% = 3.09$ ) does not match any reference phase screened and is attributed to instrumental background scatter at very low angles.