

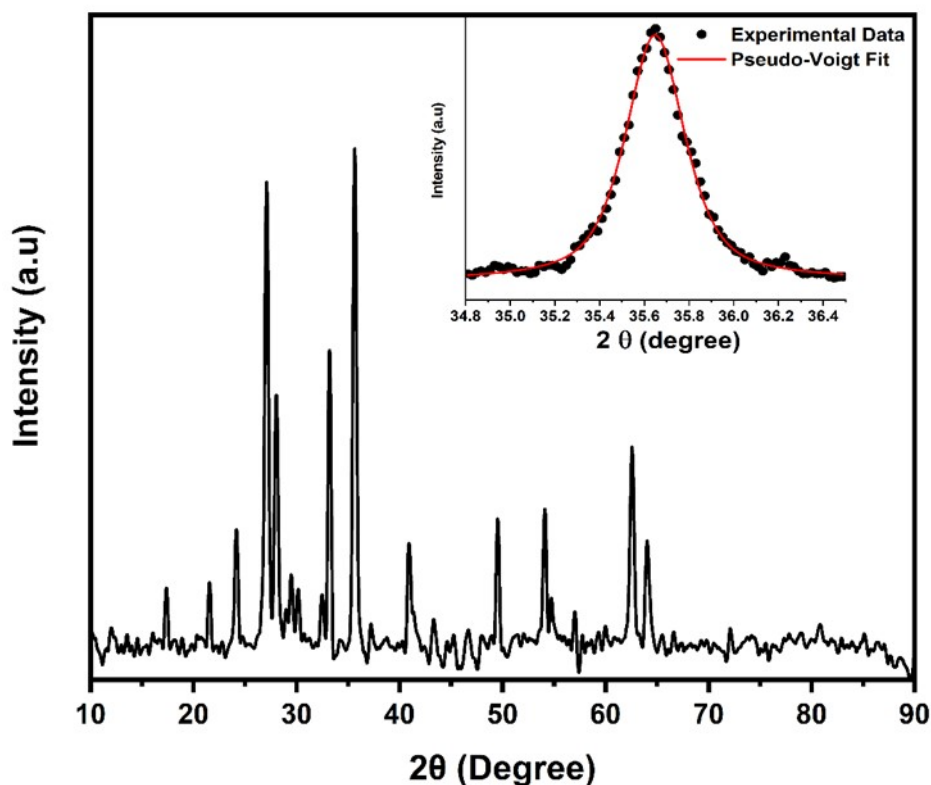
### Table S1, Figure S1 and Table S2— Supplementary Materials

**Table S1.** Complete XRD peak indexing for all 25 peaks identified in the 10–90° 2 $\theta$  range, from geometric indexing. DP = double perovskite-related structure Ia- $\bar{3}d$  (Phase A: a = 10.098 Å refined, 10.128 Å geometric; Phase B: a = 10.402 Å refined, 10.311 Å geometric); d<sub>calc</sub> values in this table use geometric parameters as the indexing basis; refined parameters are reported in Table 2 of the main text; MP = Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> secondary phase (ICDD 00-029-0877); O = ordering reflection (forbidden in Pm- $\bar{3}m$ ); F = fundamental; sec = secondary phase; ★ = among strongest peaks; † = error at or exceeding  $\pm 2.5\%$  tolerance boundary; Peak 5 at  $\Delta = +2.77\%$  and Peak 6 at  $\Delta = -2.42\%$  are assigned on the basis of intensity magnitude and the complete absence of alternative candidate phases at these positions, rather than d-spacing agreement alone; fund. = fundamental (permitted in Pm- $\bar{3}m$ ).  $\Delta\% = 100 \times (d_{\text{obs}} - d_{\text{calc}})/d_{\text{calc}}$ . Deviations within  $\pm 2.5\%$  are consistent with the precision of geometric indexing for laboratory XRD data.

No.	2 $\theta_{\text{obs}}$ (°)	d <sub>obs</sub> (Å)	I (%)	Phase	hkl	d <sub>calc</sub> (Å)	$\Delta$ (%)	Type	Note
1	17.349	5.1075	15.13	MP	( $\bar{1}\bar{1}0$ )	5.1260	-0.36	sec	Mg <sub>2</sub> V <sub>2</sub> O <sub>7</sub>
2	21.525	4.1249	16.07	DP-A	(211)	4.1346	-0.23	O	
3	22.728	3.9093	7.21	MP	(101)	3.8963	+0.33	sec	Mg <sub>2</sub> V <sub>2</sub> O <sub>7</sub>
4	24.156	3.6814	24.18	MP	( $\bar{3}11$ )	3.6940	-0.34	sec	Mg <sub>2</sub> V <sub>2</sub> O <sub>7</sub>
5	27.070	3.2913	94.70	DP-A	(310)	3.2026	+2.77	O	★ †
6	28.023	3.1815	50.73	DP-B	(310)	3.2606	-2.42	O	★ †
7	29.485	3.0270	15.43	DP-B	(222)	2.9765	+1.70	F	fund.
8	30.157	2.9611	12.46	DP-A	(222)	2.9236	+1.28	F	fund.
9	32.447	2.7571	11.64	DP-B	(321)	2.7557	+0.05	O	
10	33.190	2.6971	67.60	DP-A	(321)	2.7067	-0.36	O	★
11	35.622	2.5183	100.00	DP-A	(400)	2.5319	-0.54	F	fund.
12	40.905	2.2045	25.46	DP-A	(332)	2.1592	+2.10	O	†
13	43.248	2.0903	7.89	DP-A	(422)	2.0673	+1.11	F	fund.
14	44.859	2.0189	1.55	DP-B	(431)	2.0221	-0.16	O	
15	46.528	1.9503	4.58	DP-A	(431)	1.9862	-1.81	O	
16	47.882	1.8983	5.91	DP-B	(521)	1.8825	+0.84	O	
17	49.483	1.8405	24.21	DP-A	(521)	1.8490	-0.46	O	
18	54.053	1.6952	25.56	DP-A	(442)	1.6879	+0.43	F	fund.
19	57.582	1.5994	5.22	DP-A	(620)	1.6013	-0.12	F	fund.
20	62.544	1.4839	31.50	DP-A	(631)	1.4932	-0.62	O	
21	64.006	1.4535	19.32	DP-A	(444)	1.4618	-0.57	F	fund.
22	65.412	1.4256	3.33	DP-A	(543)	1.4323	-0.46	O	
23	71.982	1.3108	6.60	DP-A	(730)	1.3298	-1.43	O	
24	75.458	1.2588	4.76	DP-A	(800)	1.2659	-0.56	F	fund.

No.	$2\theta_{\text{obs}}$ (°)	$d_{\text{obs}}$ (Å)	I (%)	Phase	hkl	$d_{\text{calc}}$ (Å)	$\Delta$ (%)	Type	Note
25	84.956	1.1407	4.06	DP-A	(752)	1.1467	-0.53	O	

Summary statistics: total peaks: 25 | indexed to  $\text{Mg}_2\text{FeVO}_6$ : 22/25 (88%) | indexed to  $\text{Mg}_2\text{V}_2\text{O}_7$ : 3/25 (12%) | within  $\pm 2.0\%$ : 19/22 (86%) | at  $\pm 2.0$ – $2.5\%$ : 3/22 (14%, Peaks 5, 6, 12) | ordering reflections: 14 total by geometric analysis (10 Phase A, 4 Phase B); 12 resolved by Le Bail profile fitting (10 Phase A, 2 Phase B) — see Table 2 and main text for reconciliation | fundamental reflections: 8 total.



**Figure S1.** Observed XRD pattern of the magnesium iron vanadate ceramic sintered at 900°C, inset: pseudo-Voigt profile fitting of the isolated (400) fundamental reflection of Phase A at  $2\theta = 35.622^\circ$  ( $R^2 = 0.995$ ), used for crystallite size determination via the Scherrer equation yielding  $D = 26.1$  nm.

**Table S2.** Complete peak assignment from Le Bail profile fitting, Peak 7 ( $29.485^\circ$ , DP-B 222,  $I = 15.43\%$  in geometric indexing) is not resolved in the Le Bail profile refinement due to overlap with  $\text{Mg}_2\text{V}_2\text{O}_7$  contributions at  $\sim 29.0$ – $30.2^\circ$  (Peaks 6, 7, 8 in S1). The 20-peak Le Bail range (17– $90^\circ$ ) excludes this region from reliable profile fitting.

No.	$2\theta_{\text{obs}}$ (°)	$2\theta_{\text{calc}}$ (°)	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$\Delta$ (%)	$I/I_0$ (%)	hkl	Phase / Assignment
1	17.362	17.499	5.104	5.064	0.78	13.7	(200)	A (fund.) + $\text{Mg}_2\text{V}_2\text{O}_7$
2	21.541	21.538	4.122	4.123	-0.01	15.3	(211)	A (fund.)
3	24.172	24.176	3.679	3.679	0.00	23.4	(220)	B (fund.)
4	27.094	27.096	3.289	3.288	0.01	93.8	(310)	B (fund.) — 2nd strongest peak
5	28.043	28.054	3.179	3.178	0.04	42.5	(310)	A (fund.)

6	28.990	~29.0	3.078	—	—	3.9	—	Mg <sub>2</sub> V <sub>2</sub> O <sub>7</sub>
7	29.492	~29.5	3.026	—	—	9.8	—	Mg <sub>2</sub> V <sub>2</sub> O <sub>7</sub>
8	30.167	~30.2	2.960	—	—	8.2	—	Mg <sub>2</sub> V <sub>2</sub> O <sub>7</sub>
9	32.491	—	2.754	—	—	3.5	—	Mg <sub>2</sub> V <sub>2</sub> O <sub>7</sub> / Phase B
10	33.210	33.279	2.695	2.690	-0.22	65.2	(321)*	A (ORD) — 3rd strongest
11	35.649	35.649	2.517	2.525	-0.32	100.0	(400)	A (fund.) — strongest peak
12	40.924	41.119	2.203	2.190	0.62	22.7	(332)	A (fund.)
13	43.285	~43.3	2.089	—	—	8.9	—	Mg <sub>2</sub> V <sub>2</sub> O <sub>7</sub>
14	49.538	49.541	1.839	1.839	0.01	26.4	(521)	A (fund.)
15	54.101	54.051	1.694	1.695	-0.09	23.4	(600)*	A (ORD)
16	54.712	—	1.676	—	—	1.8	—	A (600)* weak
17	57.110	—	1.612	—	—	7.5	—	Overlap region
18	57.726	57.669	1.596	1.597	-0.09	4.5	(620)	A (fund.)
19	62.572	62.502	1.483	1.485	-0.09	33.4	(631)*	A (ORD)
20	64.068	64.092	1.452	1.452	0.03	18.0	(444)	A (fund.)