

Magnetic and thermodynamic properties of α , β , γ and δ - MnO_2

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Table S-I the Experimental molar heat capacities $C_{p,m}$ at constant pressure ($p = 1.2$ mPa) for all MnO_2 samples from $T = (1.9 \text{ to } 300)$ K.

$\alpha\text{-MnO}_2 \cdot 0.16\text{H}_2\text{O}$ (89.82 g/mol)		$\beta\text{-MnO}_2 \cdot 0.01\text{H}_2\text{O}$ (87.12 g/mol)		$\delta\text{-MnNa}_{0.66}\text{O}_3 \cdot 0.17\text{H}_2\text{O}$ (111.18 g/mol)		$\gamma\text{-MnO}_2 \cdot 0.20\text{H}_2\text{O}$ (90.54 g/mol)	
T/K	$C_{m,p}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{m,p}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{m,p}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{m,p}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
1.92	0.0434	1.93	0.0017	1.92	0.0680	1.92	0.0569
2.14	0.0526	2.14	0.0017	2.13	0.0883	2.12	0.0631
2.37	0.0671	2.38	0.0017	2.36	0.1149	2.35	0.0725
2.63	0.0843	2.64	0.0018	2.61	0.1460	2.60	0.0845
2.93	0.1073	2.93	0.0020	2.91	0.1932	2.88	0.1018
3.25	0.1325	3.25	0.0022	3.22	0.2528	3.20	0.1204
3.60	0.1658	3.61	0.0026	3.57	0.3291	3.54	0.1421
4.00	0.2050	4.00	0.0031	3.96	0.4263	3.93	0.1687
4.44	0.2513	4.44	0.0037	4.40	0.5495	4.36	0.2028
4.93	0.3082	4.93	0.0047	4.88	0.7020	4.84	0.2466
5.32	0.3524	5.47	0.0063	5.08	0.7693	5.37	0.2965
5.47	0.3718	6.06	0.0080	5.29	0.8430	5.95	0.3574
5.52	0.3796	6.72	0.0105	5.42	0.8859	6.61	0.4303
5.72	0.4009	7.46	0.0141	5.49	0.9170	7.33	0.5191
5.92	0.4266	8.27	0.0188	5.69	0.9913	8.14	0.6295
6.06	0.4450	9.18	0.0255	5.90	1.0647	9.03	0.7567
6.13	0.4550	10.20	0.0345	6.01	1.1066	10.11	0.9195
6.33	0.4767	11.29	0.0468	6.09	1.1431	11.21	1.1031
6.53	0.5024	12.52	0.0646	6.30	1.2250	12.44	1.3237
6.73	0.5276	13.90	0.0901	6.49	1.3039	13.81	1.5763
6.73	0.5319	15.43	0.1271	6.67	1.3696	15.33	1.8674
6.93	0.5554	17.12	0.1818	6.70	1.3914	17.02	2.2004
7.13	0.5814	19.00	0.2631	6.90	1.4773	18.90	2.5641
7.33	0.6136	21.09	0.3808	7.10	1.5651	20.99	2.9881
7.47	0.6307	23.39	0.5539	7.31	1.6536	23.32	3.4547
7.53	0.6408	25.98	0.7956	7.40	1.6895	25.89	3.9742
7.74	0.6677	28.86	1.1355	7.51	1.7454	28.71	4.6022
7.94	0.6935	32.04	1.6010	7.71	1.8393	31.88	5.3480
8.14	0.7230	35.57	2.2250	7.91	1.9334	35.41	6.2574
8.28	0.7435	39.46	3.0354	8.11	2.0285	39.31	7.3072
8.34	0.7527	43.79	4.0628	8.22	2.0714	43.65	8.5285
8.55	0.7809	48.59	5.3416	8.32	2.1290	48.42	9.6472
8.75	0.8067	53.92	6.9469	8.52	2.2238	53.75	11.1327
8.95	0.8340	59.84	8.9485	8.72	2.3300	59.67	12.8927
9.15	0.8642	60.63	9.2793	8.92	2.4308	66.23	14.8911
9.19	0.8717	61.61	9.6254	9.12	2.5264	73.53	16.9232
9.35	0.8927	62.61	9.9539	9.12	2.5384	81.61	19.6486
9.55	0.9255	63.61	10.3801	9.32	2.6441	90.60	22.2173
9.76	0.9528	64.61	10.7744	9.52	2.7561	100.54	24.5515
9.96	0.9822	65.62	11.1463	9.73	2.8670	110.74	28.0342
10.16	1.0062	66.40	11.4506	9.93	2.9726	120.69	31.2339
10.21	1.0168	66.63	11.5640	10.12	3.0741	130.74	34.0841
10.33	1.0318	67.64	11.9704	10.16	3.0850	140.88	36.9842
10.53	1.0609	68.65	12.3789	10.31	3.1816	151.03	39.6840
10.73	1.0910	69.66	12.8118	10.51	3.2993	161.13	42.1187
10.94	1.1234	70.66	13.2540	10.71	3.4134	171.21	44.7172
11.15	1.1550	71.67	13.7169	10.92	3.5446	181.30	47.4553
11.31	1.1832	72.69	14.1687	11.12	3.6594	191.42	49.5512
11.34	1.1866	73.69	14.6264	11.26	3.7396	201.53	51.4109
11.54	1.2176	73.70	14.6523	11.32	3.7775	211.70	53.8690
11.74	1.2476	74.70	15.1293	11.52	3.8983	221.80	57.0846
11.95	1.2829	75.71	15.6351	11.73	4.0116	231.89	59.2894
12.15	1.3136	76.72	16.1807	11.93	4.1244	241.90	60.9117
12.35	1.3433	77.73	16.7048	12.13	4.2410	251.98	63.0272
12.54	1.3771	78.71	17.3310	12.33	4.3457	262.09	64.5836
12.56	1.3747	79.73	17.9191	12.50	4.4325	272.17	66.0644
12.76	1.4040	80.75	18.6085	12.53	4.4445	282.15	68.3668
12.96	1.4334	81.23	18.9202	12.73	4.5521	292.27	68.6453
13.16	1.4668	81.77	19.2864	12.93	4.6420	302.32	70.5037
13.36	1.4957	81.79	19.2834	13.14	4.7442		
13.57	1.5306	82.27	19.6438	13.34	4.8352		
13.77	1.5634	82.78	20.0410	13.54	4.9389		
13.92	1.5904	83.28	20.4167	13.74	5.0417		

13.97	1.5965	83.79	20.7708	13.87	5.1144
14.17	1.6268	84.29	21.1672	13.94	5.1351
14.37	1.6615	84.79	21.5408	14.14	5.2356
14.57	1.6933	85.29	22.0814	14.35	5.3272
14.78	1.7259	85.80	22.5702	14.55	5.4305
14.98	1.7580	86.30	23.1773	14.75	5.5186
15.18	1.7989	86.80	23.6669	14.95	5.6056
15.38	1.8241	87.29	24.2098	15.15	5.7079
15.45	1.8391	87.79	24.9443	15.35	5.7894
15.59	1.8559	88.30	25.7293	15.39	5.7738
15.79	1.8888	88.82	26.6570	15.55	5.8349
15.99	1.9234	89.32	27.6775	15.75	5.9268
16.19	1.9533	89.83	28.9911	15.96	6.0034
16.39	1.9851	90.33	30.7014	16.16	6.0610
16.59	2.0199	90.67	31.9206	16.36	6.1184
16.79	2.0547	90.83	33.0666	16.56	6.1688
17.00	2.0888	91.33	36.5869	16.76	6.2251
17.14	2.1165	91.82	42.1437	16.96	6.2735
17.20	2.1228	92.31	43.7657	17.10	6.2379
17.40	2.1577	92.82	40.6291	17.16	6.3092
17.60	2.1909	93.34	36.6611	17.37	6.3432
17.80	2.2238	93.86	33.8672	17.57	6.3788
18.00	2.2579	94.38	32.0051	17.77	6.4099
18.21	2.2923	94.88	30.8756	17.97	6.4463
18.41	2.3299	95.38	30.0507	18.17	6.4811
18.61	2.3701	95.89	29.5079	18.37	6.5101
18.81	2.4010	96.38	29.1544	18.58	6.5438
19.01	2.4354	96.89	28.9330	18.78	6.5590
19.02	2.4357	97.39	28.6869	18.98	6.5349
19.22	2.4705	97.87	27.7303	18.98	6.5984
19.42	2.5050	98.38	26.3824	19.18	6.6342
19.62	2.5328	98.88	25.2975	19.38	6.6635
19.82	2.5680	99.39	24.3742	19.58	6.6998
20.02	2.6057	99.92	23.8927	19.78	6.7345
20.23	2.6435	100.42	23.6615	19.99	6.7658
20.43	2.6729	100.92	23.4459	20.19	6.7935
20.63	2.7112	101.36	23.3935	20.39	6.8293
20.83	2.7404	102.44	22.9697	20.59	6.8728
21.03	2.7746	103.45	22.4163	20.79	6.9096
21.11	2.7927	104.46	22.2556	20.99	6.9411
21.25	2.8144	105.47	22.1659	21.06	6.8673
21.44	2.8415	106.48	22.2578	21.20	6.9794
21.64	2.8753	107.49	22.2962	21.40	7.0107
21.85	2.9142	108.47	22.4940	21.60	7.0487
22.05	2.9525	109.48	22.5710	21.80	7.0913
22.25	2.9879	110.49	22.7251	22.00	7.1287
22.45	3.0168	110.91	22.7985	22.20	7.1554
22.65	3.0649	111.53	22.8153	22.41	7.1946
22.86	3.1009	112.54	23.0183	22.61	7.2522
23.06	3.1401	113.54	23.1622	22.81	7.2919
23.26	3.1728	114.56	23.3014	23.01	7.3404
23.43	3.1954	115.54	23.4747	23.21	7.3791
23.46	3.2160	116.54	23.7077	23.38	7.3274
23.66	3.2412	117.58	23.9105	23.42	7.4117
23.86	3.2748	118.59	24.1035	23.61	7.4653
26.01	3.6859	119.59	24.2807	23.82	7.5155
28.86	4.2663	120.60	24.4961	24.02	7.5624
32.03	4.9877	120.96	24.5584	24.22	7.6087
35.60	5.7741	121.58	24.7125	24.42	7.6594
39.50	6.7438	131.00	26.6541	24.62	7.6970
43.84	7.8685	141.15	28.7795	24.83	7.7483
48.65	8.9969	151.27	30.8969	25.03	7.7909

53.98	10.3096	161.35	33.0017	25.23	7.8389
59.91	11.7494	171.44	35.0524	25.95	7.8961
66.48	13.6227	181.50	37.0897	28.82	8.3410
73.79	15.6086	191.60	38.9970	32.01	8.8741
80.73	17.9898	201.73	40.7561	35.51	9.7585
81.76	18.3073	211.85	42.4697	39.38	10.9618
81.89	18.2831	221.94	44.2784	43.72	12.3972
82.77	18.5083	232.07	45.7905	48.52	14.0956
83.78	18.9843	242.09	47.2455	53.86	16.0660
84.78	19.2864	252.19	48.6784	59.77	18.4232
85.79	19.5756	257.49	49.4689	66.36	21.1025
86.77	20.0121	262.31	50.0352	73.66	24.0405
87.77	20.2980	272.41	51.3890	81.74	27.4377
88.82	20.4325	282.42	52.5542	90.73	31.0372
89.81	20.8931	292.55	53.7075	100.68	34.8590
90.82	21.1905	302.58	54.7368	110.82	39.1480
90.88	21.1497			120.87	43.0825
91.81	21.5827			130.92	47.1935
92.81	21.9195			141.02	51.0962
93.84	22.1341			151.13	54.9034
94.85	22.3409			161.22	58.6261
95.85	22.6421			171.28	62.2629
96.87	22.7970			181.38	65.8737
97.84	23.0447			191.46	69.2789
98.86	23.2244			201.56	72.5181
99.88	23.4540			211.70	75.8731
100.88	23.6612			221.80	79.6023
100.90	23.6034			231.93	82.9390
101.90	23.7726			241.93	86.1845
102.89	24.0103			252.00	89.2600
103.89	24.3947			262.12	92.2077
104.91	24.7978			272.16	94.8753
105.94	25.0813			282.11	96.8336
106.95	25.2695			292.16	98.8265
107.96	25.4761			302.05	100.3209
108.94	25.7270				
109.96	25.8342				
110.95	26.2153				
110.96	26.1856				
121.00	28.4258				
131.03	30.9502				
141.11	33.3770				
151.19	35.8681				
161.27	38.1717				
171.32	40.5477				
181.41	42.7815				
191.51	44.8471				
201.60	46.6377				
211.70	48.5891				
221.84	50.8089				
231.92	52.1809				
241.95	54.1100				
252.08	55.4470				
262.15	56.9595				
272.16	58.7346				
282.22	60.3611				
292.33	61.4009				
302.36	63.1422				

Table S-II Fitting parameters in the fitting models for the experimental molar heat capacity of all MnO₂ samples measured by PPMS

	α -MnO ₂	β -MnO ₂	δ -MnO ₂	γ -MnO ₂
Low T fits				
A_{nh}		4.23000E-03		
γ		2.32000E-04	9.73507E-03	2.43550E-02
B_3	7.30698E-04	2.95000E-05	7.31200E-03	1.12800E-03
B_5	-2.86000E-06		-6.94350E-05	-5.20000E-06
B_{fsw}	1.41394E-02			
n_{sch}	0.028178263			
θ	18.4483			
% RMS	0.683	1.950	0.514	1.982
Range/(K)	1.9-8.14	1.9-7.14	1.9-5.89	1.9-5.72
Middle T fits				
A_0	-3.31044E-01	4.35336E-03	-4.10989E-01	2.11483E-01
A_1	1.45747E-01	-1.83129E-03	2.60310E-01	-9.12705E-02
A_2	-7.97477E-03	2.91334E-04	-6.17286E-02	2.59651E-02
A_3	1.20939E-03	3.55500E-05	7.53381E-03	-1.31959E-03
A_4	-7.70860E-05	-5.06619E-06	-3.05631E-04	3.95754E-05
A_5	2.64153E-06	4.42504E-07	6.44893E-06	-6.61487E-07
A_6	-4.90340E-08	-1.35128E-08	-7.57000E-08	5.73902E-09
A_7	4.62750E-11	1.78249E-10	4.66788E-10	-2.02000E-12
A_8	-1.74000E-12	-8.72527E-13	-1.17000E-12	
%RMS	0.617	0.577	0.376	0.616
Range/(K)	8.14-53.75	7.14-60.63	7.36-66.1	5.72-63.75
High T fits				
n_D	0.98675	0.45021	1.98311	0.767942
θ_D	396.8	280.35	307.161	200.04
n_{E1}	1.14887	1.7699	2.63145	1.939332
θ_{E1}	888.68	831.97	812.18	933.4325
n_{E2}		0.844874		1.367568
θ_{E2}		280.29		430.2225
a	0.11717		-0.148616	
b	-0.0001068		0.0001691	
%RMS	0.992	0.691		0.770
Range/(K)	53.75-310	115.54-310	39.38-310	63.75-310

Table S-III Standard thermodynamic functions of all MnO₂ samples as a function of temperature T at the standard pressure of 0.1 MPa.

T / K	$\alpha\text{-MnO}_2$			$\gamma\text{-MnO}_2$		
	$C_{p,m}^0 / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_0^T S_m^0 / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_0^T H_m^0 / \text{kJ}\cdot\text{mol}^{-1}$	$C_{p,m}^0 / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_0^T S_m^0 / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_0^T H_m^0 / \text{kJ}\cdot\text{mol}^{-1}$
0.0	0	0	0	0	0	0
1	0.014868	0.009739	0.000006	0.026533	0.025755	1.2975E-5
2	0.047712	0.028897	0.000035	0.05995	0.053826	5.5368E-5
3	0.111335	0.059055	0.000112	0.106478	0.086398	1.3726E-4
4	0.20547	0.103422	0.000268	0.171033	0.125395	2.74355E-4
5	0.316307	0.160962	0.000528	0.256566	0.172346	4.86348E-4
6	0.436857	0.229156	0.000904	0.361002	0.228197	7.94276E-4
7	0.565917	0.306082	0.001400	0.477698	0.292402	0.00121
8	0.702863	0.390512	0.002040	0.6093	0.364628	0.00175
9	0.842372	0.481297	0.002810	0.753587	0.444609	0.00244
10	0.98667	0.57748	0.003720	0.908617	0.531945	0.00327
11	1.135187	0.678453	0.004790	1.072703	0.626175	0.00426
12	1.287508	0.783732	0.006000	1.24439	0.726823	0.00541
13	1.443159	0.892913	0.007360	1.422443	0.833419	0.00675
14	1.601679	1.005647	0.008880	1.605823	0.945515	0.00826
15	1.762662	1.121628	0.010570	1.793668	1.062687	0.00996
16	1.925795	1.240584	0.012410	1.985283	1.184546	0.01185
17	2.090879	1.362279	0.014420	2.180115	1.310734	0.01393
18	2.257839	1.486507	0.016590	2.377745	1.440927	0.01621
19	2.426725	1.613098	0.018930	2.577868	1.574836	0.01869
20	2.597706	1.741911	0.021450	2.78028	1.712201	0.02137
25	3.495885	2.416502	0.036650	3.824965	2.443805	0.03786
30	4.503849	3.14097	0.056590	4.932625	3.237987	0.05972
35	5.646475	3.919409	0.081910	6.122691	4.086556	0.08732
40	6.885013	4.753601	0.113220	7.4061	4.986877	0.1211
45	8.136782	5.637082	0.150780	8.773134	5.937416	0.16152
50	9.342532	6.557237	0.194500	10.1921	6.934927	0.20892
55	10.501	7.501707	0.244090	11.61887	7.973363	0.26346
60	11.98343	8.478747	0.300290	13.01726	9.044565	0.32506
65	13.48527	9.49718	0.363960	14.45438	10.14175	0.39365
70	14.98655	10.55154	0.435140	15.9353	11.26702	0.46961
75	16.47256	11.6363	0.513800	17.43218	12.41741	0.55303
80	17.93354	12.74621	0.599830	18.93997	13.59055	0.64395
85	19.36399	13.8765	0.693090	20.45253	14.78415	0.74243
90	20.76172	15.02304	0.793410	21.96406	15.99599	0.84848
95	22.12689	16.18229	0.900650	23.46978	17.2239	0.96207
100	23.46119	17.3513	1.014630	24.96619	18.46584	1.08316
110	26.0476	19.7095	1.262260	27.92286	20.98444	1.34765
120	28.54318	22.08352	1.535280	30.8257	23.53891	1.64144
130	30.96689	24.46433	1.832880	33.67355	26.1191	1.96398
140	33.33111	26.84609	2.154420	36.46642	28.71713	2.31472
150	35.64175	29.22479	2.499330	39.20254	31.32669	2.69312
160	37.89979	31.59742	2.867080	41.87774	33.9425	3.09857
170	40.10314	33.96148	3.257140	44.48611	36.55995	3.53045
180	42.24814	36.31472	3.668950	47.02087	39.17482	3.98805
190	44.33073	38.65504	4.101900	49.47542	41.78324	4.4706
200	46.34712	40.98047	4.555340	51.84393	44.3816	4.97727
210	48.29422	43.28916	5.028610	54.12177	46.96657	5.50718
220	50.16982	45.57937	5.520990	56.30571	49.53509	6.05939
230	51.97255	47.84955	6.031760	58.39391	52.0844	6.63297
240	53.7019	50.09828	6.560190	60.38583	54.61205	7.22695
250	55.35805	52.32432	7.105560	62.28204	57.11588	7.84037
260	56.94176	54.52659	7.667110	64.08408	59.59404	8.47228
270	58.45426	56.70418	8.244150	65.79423	62.04495	9.12174
273.15	58.9162	57.38488	8.429010	66.31433	62.81112	9.32982
280	59.89713	58.85631	8.835970	67.41535	64.46729	9.78787
290	61.2722	60.98236	9.441870	68.95072	66.86001	10.46977
298.15	62.34411	62.69545	9.945640	70.14112	68.78758	11.0366
300	62.58146	63.08183	10.061190	70.40393	69.22227	11.16661

T / K	$\beta\text{-MnO}_2$			$\delta\text{-MnO}_2$		
	$C_{p,m}^0 / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_0^T S_m^0 / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_0^T H_m^0 / \text{kJ}\cdot\text{mol}^{-1}$	$C_{p,m}^0 / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_0^T S_m^0 / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_0^T H_m^0 / \text{kJ}\cdot\text{mol}^{-1}$
0.0	2.32E-24	2.32E-24	0	1.91E-23	1.91E-23	0.000000
1	0.000261	0.000242	1.23000E-07	0.005445	0.003089	1.839000E-06
2	0.0007	0.000542	5.82000E-07	0.031923	0.013208	1.789500E-05
3	0.001493	0.000961	1.64100E-06	0.104305	0.03772	8.073400E-05
4	0.002817	0.001557	3.74400E-06	0.265575	0.08704	2.559830E-04
5	0.00485	0.002389	7.51100E-06	0.570697	0.175927	6.599560E-04

6	0.007769	0.003517	1.37400E-05	1.065669	0.320589	0.001460891
7	0.011751	0.004999	2.34040E-05	1.78384	0.535609	0.002864953
8	0.017116	0.006906	3.77500E-05	2.729151	0.833229	0.005104298
9	0.02391	0.009298	5.81260E-05	3.868481	1.218666	0.008387905
10	0.032495	0.012245	8.61650E-05	5.17949	1.692688	0.01289846
15	0.116267	0.038534	4.24107E-04	13.65256	5.303363	0.05885041
20	0.315088	0.095644	0.00144019	24.01895	10.62221	0.1525354
25	0.694261	0.202833	0.00387699	35.1052	17.16674	0.3002098
30	1.29572	0.379065	0.00875555	46.28149	24.55661	0.5037193
35	2.123537	0.638177	0.0172132	57.25149	32.51843	0.7626717
40	3.153133	0.986878	0.0303273	67.88972	40.86187	1.075678
45	4.358769	1.426205	0.0490363	78.12657	49.45343	1.440901
50	5.740212	1.955317	0.0742064	88.24419	58.20008	1.856423
55	7.31566	2.57475	0.106765	96.95654	67.02272	2.319608
60	9.034333	3.284584	0.147617	105.2483	75.81746	2.825287
65	10.91901	4.080637	0.197406	113.1585	84.55658	3.371454
70	12.96116	4.962818	0.256990	120.7286	93.22155	3.956306
75	15.27492	5.934481	0.327473	127.9978	101.8005	4.578239
80	18.09462	7.006799	0.410625	135.0022	110.2862	5.235843
85	21.76128	8.209156	0.509881	141.7735	118.6749	5.927873
90	29.56304	9.629553	0.634304	148.3393	126.9652	6.653235
95	30.6556	11.57712	0.814394	154.7233	135.1573	7.410963
100	23.8478	12.99349	0.952308	160.946	143.2525	8.200200
110	22.63672	15.15145	1.17863	172.9739	159.1605	9.870230
120	24.38105	17.18855	1.41287	184.5329	174.7098	11.65812
130	26.51966	19.22476	1.66741	195.703	189.9238	13.55959
140	28.62834	21.26741	1.94317	206.5425	204.8255	15.57108
150	30.70983	23.31371	2.23988	217.0946	219.4369	17.68949
160	32.75888	25.36128	2.55726	227.3918	233.7778	19.91212
170	34.76646	27.40775	2.89492	237.4582	247.8665	22.23655
180	36.72257	29.45059	3.25242	247.3128	261.7192	24.66058
190	38.61795	31.48714	3.62917	256.9698	275.3503	27.18215
200	40.44495	33.51475	4.02455	266.4405	288.7727	29.79935
210	42.19791	35.53079	4.43782	275.7339	301.998	32.51037
220	43.8731	37.5328	4.86824	284.8571	315.0363	35.31346
230	45.46856	39.51854	5.31502	293.8157	327.897	38.20696
240	46.98383	41.48596	5.77735	302.6144	340.5881	41.18925
250	48.41968	43.43331	6.25443	311.2569	353.1172	44.25873
260	49.7778	45.35907	6.74548	319.7465	365.4908	47.41387
270	51.06059	47.26199	7.24974	328.0855	377.7149	50.65316
273.15	51.44951	47.85651	7.41119	330.6815	381.5355	51.69072
280	52.27092	49.14103	7.76645	336.2763	389.7951	53.97509
290	53.41201	50.99539	8.29492	344.3205	401.7362	57.37820
298.15	54.29314	52.488	8.73385	350.7692	411.3685	60.21075
300	54.48726	52.82445	8.83447	352.2197	413.5428	60.86102

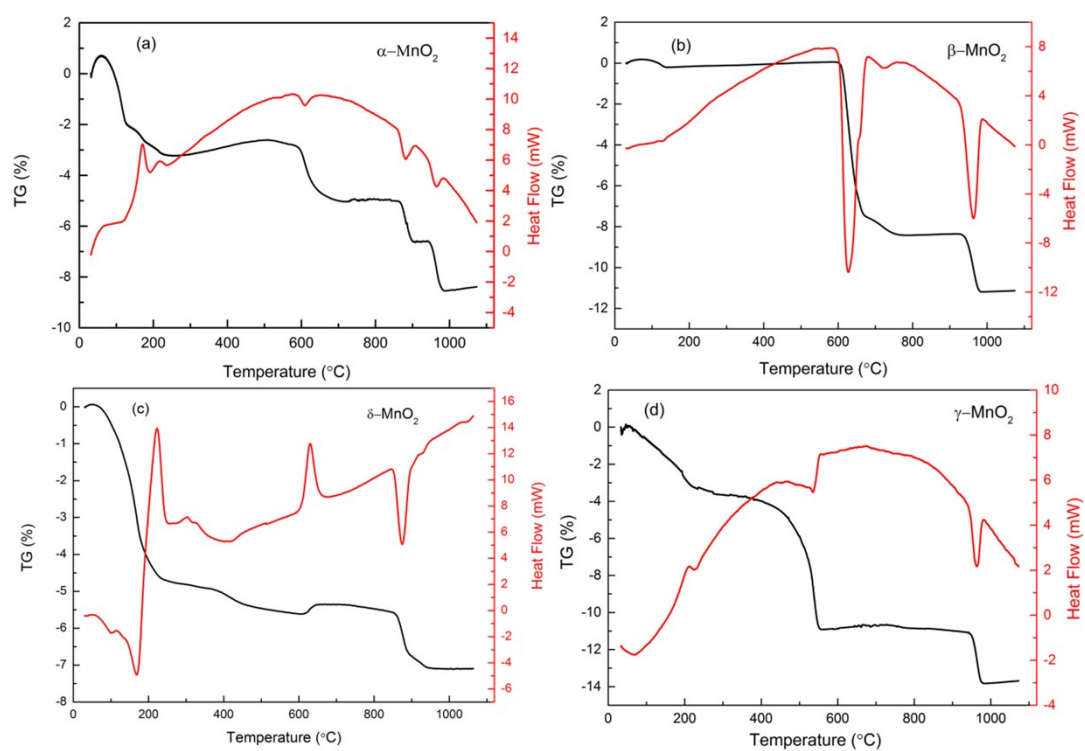


Figure S1. The TGA and DTA curves of (a) $\alpha\text{-MnO}_2$, (b) $\beta\text{-MnO}_2$, (c) $\delta\text{-MnO}_2$, (d) $\gamma\text{-MnO}_2$.

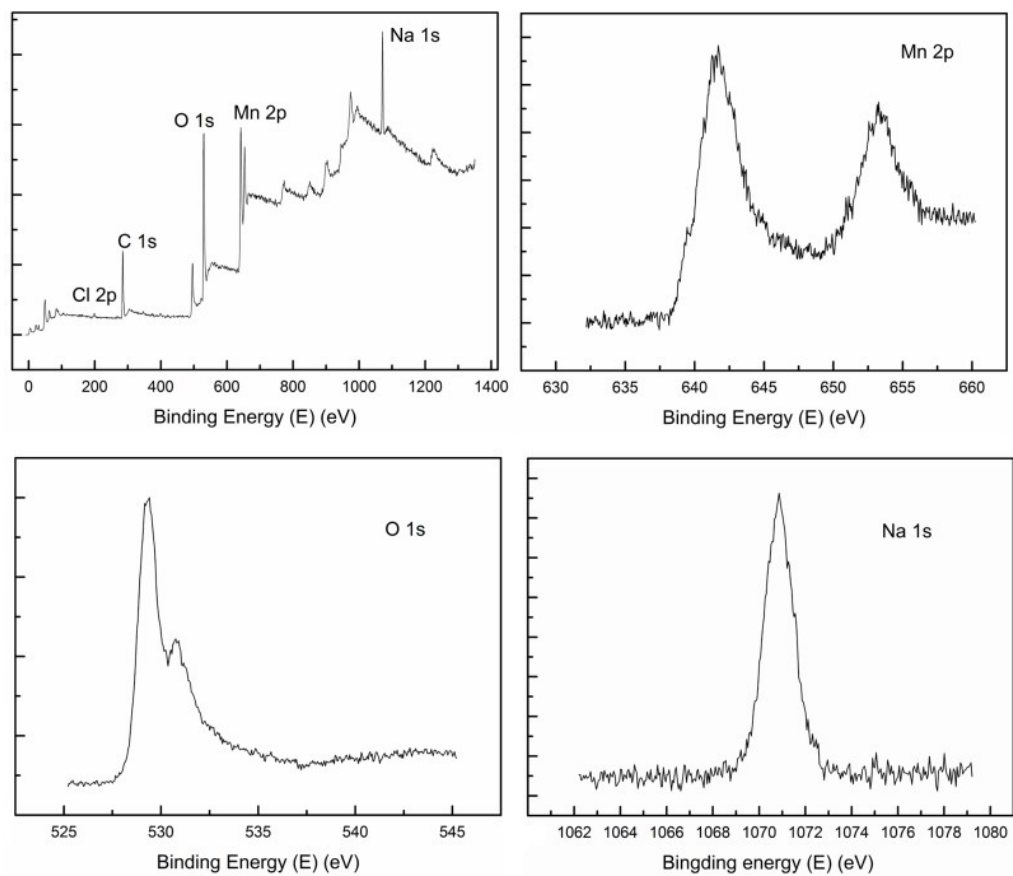


Figure S2. The XPS results of δ -MnO₂