Electronic Supplementary Information

Crystal Growth and Spontaneous Polarization Mechanism of Polar Metal Borate Halides: $Mn_3B_7O_{13}Cl$

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Methods:

Single crystal growth of $Mn_3B_7O_{13}Cl$: Firstly, a certain amount of $MnCl_2·4H_2O$ (Beijing Yili Fine Chemicals Co., Ltd, 99%) and $Na_2B_4O_7·10H_2O$ (Beijing Yili Fine Chemicals Co., Ltd, 99%) raw materials were weighed according to the molar mass ratio, and put into a beaker to dissolve and stir respectively, stirred well and then mixed, adjusted the PH to 6, and continued to stir until the solution was clarified. The mixed solution was dried in a drying oven to obtain the precursor. Then the precursor was uniformly ground and put into a crucible, and then put into a muffle furnace, heated to 793 K at a rate of 5 K/min, and held for 4 h to obtain the solid product. The obtained product was ground, rinsed and dried to obtain $Mn_3B_7O_{13}Cl$ powder crystals. Finally, the $Mn_3B_7O_{13}Cl$ powder crystals were pressed into flakes, packed into quartz tubes under vacuum (RVD-1, KYKY, Ultimate pressure of $5*10^{-2}$Pa), sealed by an oxy-hydrogen flame, and then placed into a muffle furnace, set the temperature increase rate at 5 K per minute to 1363 K, held at this temperature for 10 h, and reduced to 1123 K at a cooling rate of 0.024 K per minute, and then to room temperature within 8 h to obtain the $Mn_3B_7O_{13}Cl$ single crystals.

Pyroelectric measurement: The pyroelectric coefficient of $Mn_3B_7O_{13}Cl$ single crystal was measured by a TF-3000 ferroelectric system. $Mn_3B_7O_{13}Cl$ single crystals were placed on a Lincam platform with the upper and lower surfaces connected to electrodes, the current range was set to 10nA, and the temperature was ramped up from room temperature to 400 K at a rate of 3 k/min. The experiments were repeated more than three times to ensure the correctness of the experimental data.

Structural characterization: The crystal structure was characterized using a single crystal X-ray diffractometer (XtaLAB Synergy, Rigaku, Japan) with a test temperature range of 100～400 K. The single-crystal x-ray analysis was carried out using a Rigaku Diffraction XtaLAB rotating anode micro-focus x-ray source (1200 W, Mo Kα, λ=0.71073 Å) and a HyPix-6000 detector. The analytical conditions were 50 kV and 24 mA. Structural parameters, including atomic coordinates and lattice constants, were obtained by Olex2 refinement using data collected at different temperatures.

THz measurement：THz absorption spectrum measured by CIP-TDS. The THz-TDS system is used in transmission mode. Photodetection of terahertz pulses through a (110) oriented ZnTe detector crystal with a thickness of 2 mm. By controlling the mechanical delay line to propagate in 0.005mm steps, The time delay between the pump pulse and the probe pulse is adjusted by controlling the time delay system. Scanning this time delay gives the time domain waveform of a terahertz pulse. The scanning path is 3 mm and the time range is 20 ps. The effective spectral range obtained is 0 to 3 THz with a spectral resolution of 50 GHz.

Table S1-5

We have uploaded the crystallographic data from this paper to the Cambridge Crystallographic Data Center (CCDC) database, the CCDC number is 2336925-2336931.

Table S1 Atomic coordinates at different temperatures.

Atom occupying	Coordinate (A˚)	Temperature (K)						
		100	150	200	250	300	350	400
Mn1	x	0.26103(7)	0.26088(8)	0.26080(9)	0.26140(5)	0.26112(8)	0.26106(7)	0.26059(9)
	y	0.75205(6)	0.75206(6)	0.75215(7)	0.75223(4)	0.75210(6)	0.75208(5)	0.75208(6)
	z	0.12071(8)	0.12070(9)	0.12023(10)	0.11941(6)	0.11911(8)	0.11887(8)	0.11921(10)
Mn2	x	0.01734(7)	0.01712(8)	0.01685(9)	0.01658(5)	0.01616(7)	0.01582(7)	0.01563(9)
	y	0.53474(7)	0.53470(8)	0.53456(9)	0.53405(5)	0.53371(7)	0.53314(7)	0.53278(9)
	z	0.33808(4)	0.33819(5)	0.33787(6)	0.33747(3)	0.33750(5)	0.33735(4)	0.33802(4)
Mn3	x	0.51881(7)	0.51865(8)	0.51838(9)	0.51807(5)	0.51774(7)	0.51730(7)	0.51688(9)
	y	0.03436(7)	0.03429(8)	0.03424(9)	0.03361(5)	0.03340(7)	0.03273(7)	0.03244(9)
	z	0.34166(4)	0.34174(5)	0.34143(6)	0.34106(3)	0.34103(5)	0.34082(4)	0.34149(4)
B1	x	0.04330(7)	0.0435(8)	0.04290(8)	0.04310(4)	0.04290(7)	0.04370(7)	0.04500(7)
	y	0.25070(5)	0.25090(5)	0.25070(5)	0.25080(4)	0.25070(4)	0.25030(4)	0.25060(4)
	z	0.48970(4)	0.49020(5)	0.48970(5)	0.48930(4)	0.48910(4)	0.48980(4)	0.49050(5)
B2	x	0.24240(5)	0.24270(5)	0.24310(7)	0.24260(4)	0.24250(7)	0.24180(5)	0.24220(7)
	y	0.25280(4)	0.25270(5)	0.25240(5)	0.25320(4)	0.25240(4)	0.25300(4)	0.25290(4)
	z	0.34340(5)	0.34490(5)	0.34470(7)	0.34410(4)	0.34410(5)	0.34440(4)	0.34470(5)
B3	x	0.09550(7)	0.09490(7)	0.09490(7)	0.09540(4)	0.09510(5)	0.09540(5)	0.09520(7)
	y	0.25020(4)	0.25040(5)	0.24990(5)	0.250100(4)	0.25000(4)	0.25000(4)	0.25030(4)
	z	0.02010(4)	0.02020(4)	0.02020(5)	0.01940(4)	0.02020(4)	0.01930(4)	0.01960(4)
B4	x	0.24690(5)	0.24720(7)	0.24690(7)	0.24700(4)	0.24690(5)	0.24700(4)	0.24670(5)
	y	0.09790(5)	0.09830(7)	0.09860(7)	0.09900(4)	0.09910(5)	0.09860(4)	0.09790(5)
	z	0.17130(4)	0.17160(4)	0.17110(5)	0.17060(2)	0.17020(4)	0.17060(4)	0.17090(4)
B5	x	0.24740(5)	0.24740(7)	0.24730(7)	0.24670(4)	0.24660(5)	0.24680(4)	0.24690(5)
	y	0.40300(5)	0.40220(7)	0.40280(7)	0.40210(4)	0.40260(5)	0.40230(4)	0.40310(5)
	z	0.17040(4)	0.17070(4)	0.17020(5)	0.16990(2)	0.17010(4)	0.16970(4)	0.17010(4)
B6	x	0.00310(7)	0.00340(7)	0.00330(7)	0.00230(4)	0.00150(7)	0.00230(7)	0.00220(7)
	y	0.50200(8)	0.50290(9)	0.50330(10)	0.50290(7)	0.50360(10)	0.50170(9)	0.50050(11)
	z	0.08980(4)	0.09040(4)	0.09080(5)	0.08990(4)	0.09060(4)	0.08930(4)	0.08970(5)
B7	x	0.50370(7)	0.50420(7)	0.50390(7)	0.50250(4)	0.50330(7)	0.50240(7)	0.50330(7)
	y	0.00320(9)	0.00350(9)	0.00400(1)	0.00430(7)	0.00510(10)	0.00260(9)	0.00200(11)
	z	0.09060(4)	0.09160(4)	0.09200(5)	0.09110(4)	0.09170(4)	0.09060(4)	0.09030(5)
Cl	x	0.73013(12)	0.73033(14)	0.73065(16)	0.73045(9)	0.73070(13)	0.73161(13)	0.73222(16)
	y	0.24980(1)	0.24991(11)	0.24984(12)	0.24972(6)	0.24970(11)	0.24959(10)	0.24966(11)
	z	0.33190(12)	0.33222(13)	0.33201(16)	0.33133(9)	0.33150(12)	0.33154(12)	0.33235(16)
O1	x	0.03550(4)	0.03590(4)	0.03550(4)	0.03490(2)	0.03500(4)	0.03540(4)	0.03600(4)
	y	0.40830(4)	0.40820(4)	0.40830(4)	0.40830(2)	0.40850(4)	0.40770(4)	0.40790(4)
	z	0.48890(2)	0.48940(4)	0.48930(4)	0.48874(16)	0.48900(2)	0.48910(2)	0.48940(2)
O2	x	0.31790(4)	0.31760(4)	0.31770(4)	0.31713(18)	0.31720(4)	0.31730(4)	0.31730(4)

	y	0.13710(4)	0.13700(4)	0.13710(4)	0.13700(2)	0.13710(4)	0.13700(4)	0.13730(4)
	z	0.27490(4)	0.27510(4)	0.27490(4)	0.27485(16)	0.27430(2)	0.27450(2)	0.27450(2)
O3	x	0.54060(4)	0.54020(4)	0.54030(4)	0.54113(18)	0.54090(4)	0.54080(4)	0.54020(4)
	y	0.16830(4)	0.16830(4)	0.16800(4)	0.16820(2)	0.16870(4)	0.16820(04)	0.16810(4)
	z	0.06450(4)	0.06470(4)	0.06440(4)	0.06401(17)	0.06390(4)	0.06420(2)	0.06450(4)
O4	x	0.40910(4)	0.40890(4)	0.40890(4)	0.40884(18)	0.40880(4)	0.40860(4)	0.40820(4)
	y	0.44280(4)	0.44340(4)	0.44310(4)	0.44270(2)	0.44230(4)	0.44310(4)	0.44340(4)
	z	0.18230(2)	0.18260(4)	0.18230(4)	0.18201(16)	0.18170(2)	0.18180(2)	0.18200(2)
O5	x	0.04840(4)	0.04840(4)	0.04820(4)	0.04820(2)	0.04790(4)	0.04770(4)	0.04760(4)
	y	0.09270(4)	0.09280(4)	0.09300(4)	0.09290(2)	0.09340(4)	0.09300(4)	0.09320(4)
	z	0.00000(2)	0.00000(4)	0.00000(4)	0.00000(16)	0.00000(2)	0.00000(2)	0.00000(4)
O6	x	0.11720(4)	0.11720(4)	0.11740(4)	0.11660(2)	0.11620(4)	0.11740(4)	0.11770(4)
	y	0.17500(4)	0.17510(4)	0.17500(4)	0.17480(2)	0.17530(4)	0.17520(4)	0.17560(4)
	z	0.40650(4)	0.40690(4)	0.40670(4)	0.40590(16)	0.40550(2)	0.40590(2)	0.40650(4)
O7	x	0.17690(4)	0.17670(4)	0.17690(4)	0.17710(2)	0.17710(4)	0.17690(4)	0.17690(4)
	y	0.37450(4)	0.37450(4)	0.37440(4)	0.37510(2)	0.37490(4)	0.37470(4)	0.37440(4)
	z	0.27610(2)	0.27660(4)	0.27670(4)	0.27646(16)	0.27630(2)	0.27610(2)	0.27620(2)
O8	x	0.83900(4)	0.83890(4)	0.83910(4)	0.83870(2)	0.83920(4)	0.83830(4)	0.83880(4)
	y	0.01340(4)	0.01370(4)	0.01350(4)	0.01360(2)	0.01380(4)	0.01350(4)	0.01360(4)
	z	0.11260(4)	0.11290(4)	0.11290(4)	0.11260(16)	0.11290(4)	0.11260(2)	0.11260(4)
O9	x	0.16560(4)	0.16540(4)	0.16490(4)	0.16530(2)	0.16530(4)	0.16540(4)	0.16520(4)
	y	0.52440(4)	0.52470(4)	0.52460(4)	0.52470(2)	0.52480(4)	0.52450(4)	0.52450(4)
	z	0.11470(4)	0.11490(4)	0.11500(4)	0.11486(17)	0.11510(4)	0.11460(2)	0.11470(4)
O10	x	0.09250(4)	0.09260(4)	0.09260(4)	0.09230(2)	0.09240(4)	0.09210(4)	0.09250(4)
	y	0.03740(4)	0.03750(4)	0.03710(4)	0.03680(2)	0.03700(4)	0.03710(4)	0.03700(4)
	z	0.18770(2)	0.18770(4)	0.18770(4)	0.18767(16)	0.18790(2)	0.18740(2)	0.18760(2)
O11	x	0.47090(4)	0.47090(4)	0.47080(4)	0.47046(17)	0.47030(4)	0.47050(4)	0.47050(4)
	y	0.65950(4)	0.65950(4)	0.65950(4)	0.65890(2)	0.65960(4)	0.65950(4)	0.65930(4)
	z	0.06750(4)	0.06770(4)	0.06750(4)	0.06708(17)	0.06680(4)	0.06680(2)	0.06730(4)
O12	x	0.35680(4)	0.35690(4)	0.35720(4)	0.35660(18)	0.35720(4)	0.35720(4)	0.35700(4)
	y	0.32010(4)	0.32050(4)	0.32020(4)	0.32010(2)	0.32020(4)	0.31990(4)	0.31930(4)
	z	0.417700(2)	0.41780(4)	0.41780(4)	0.41758(16)	0.41710(2)	0.41700(2)	0.41720(4)
O13	x	0.23090(4)	0.23040(5)	0.22990(5)	0.23020(4)	0.23010(4)	0.22930(4)	0.22990(5)
	y	0.24990(4)	0.25000(4)	0.24990(4)	0.24998(16)	0.24990(4)	0.25010(2)	0.25000(4)
	z	0.10310(4)	0.10380(4)	0.10360(4)	0.10360(2)	0.10360(4)	0.10270(4)	0.10330(4)

Table S2 Refinement parameters for single crystal analysis at different temperatures.

$Mn_3B_7O_{13}CL$	Reflections collected	Parameter refined	Data range	Peak	Hole	Goodness of fit	R1	wR2
100K	2692	99	2732	2.082	-1.225	1.101	0.0338	0.0953
150K	2908	99	2716	2.480	-1.540	1.111	0.0383	0.1069
200K	2863	98	2716	2.061	-2.235	1.126	0.0436	0.1220
250K	3135	219	2591	0.550	-0.480	1.068	0.0230	0.0598
300K	1574	218	2436	0.544	-0.578	1.000	0.0301	0.0713
350K	6572	219	3274	1.685	-0.820	1.085	0.0314	0.0835
400K	2347	219	2822	1.774	-0.962	1.113	0.0361	0.1051

Table S3 The temperature-dependent lattice parameters a (a), b (b), c (c), and unit volume v (d) for $Mn_3B_7O_{13}Cl$.

Temperature/K	Unit cell parameters			
	a (Å)	b (Å)	c (Å)	V (Å^3)
100	8.6794(3)	8.6833(3)	12.2930(4)	926.47(5)
150	8.6762(3)	8.6812(3)	12.2926(4)	925.88(5)
200	8.6785(3)	8.6826(3)	12.2960(4)	926.53(5)
250	8.6814(2)	8.6910(2)	12.3000(3)	928.04(4)
300	8.6814(5)	8.6912(3)	12.3002(6)	928.07(8)
350	8.6811(2)	8.6934(2)	12.3009(3)	928.33(4)
400	8.6895(3)	8.6891(3)	12.3038(4)	928.99(5)

Table S4 Changes of $MnCl_2O_4$ octahedron 、 BO_4-BO_3 polytope and cell electric dipole moment in $Mn_3B_7O_{13}Cl$ cells at different temperatures.

Temperature (K)	$\|MnCl_2O_4\|$ (10^{-30} C·m)	$\|BO_4\text{-}BO_3\|$ (10^{-30} C·m)	$\|Sum\|$ (10^{-30} C·m)
100	4.6485	0.8816	5.5301
150	4.5688	1.2960	5.8648
200	4.4783	1.2864	5.7647
250	4.4352	0.8310	5.2662
300	4.4019	1.2512	5.6531
350	4.3307	0.9744	5.3051
400	4.3887	1.0320	5.4207

Table S5 Variation of electric dipole moments of $MnCl_2O_4$ octahedra and BO_4-BO_3 polytope in $Mn_3B_7O_{13}Cl$ cells at different temperature intervals.

Temperature (K)	$\|MnCl_2O_4\|$ (10^{-30} C·m)	$\|BO_3\text{-}BO_4\|$ (10^{-30}C·m)	$\|Sum\|$(10^{-30}C·m)
100-150	0.0797	0.4144	0.3347
150-200	0.0905	0.0096	0.1001
200-250	0.0431	0.4554	0.4985
250-300	0.0333	0.4202	0.3869
300-350	0.0712	0.2768	0.3480
350-400	0.0580	0.0576	0.1156

Fig. S1-7

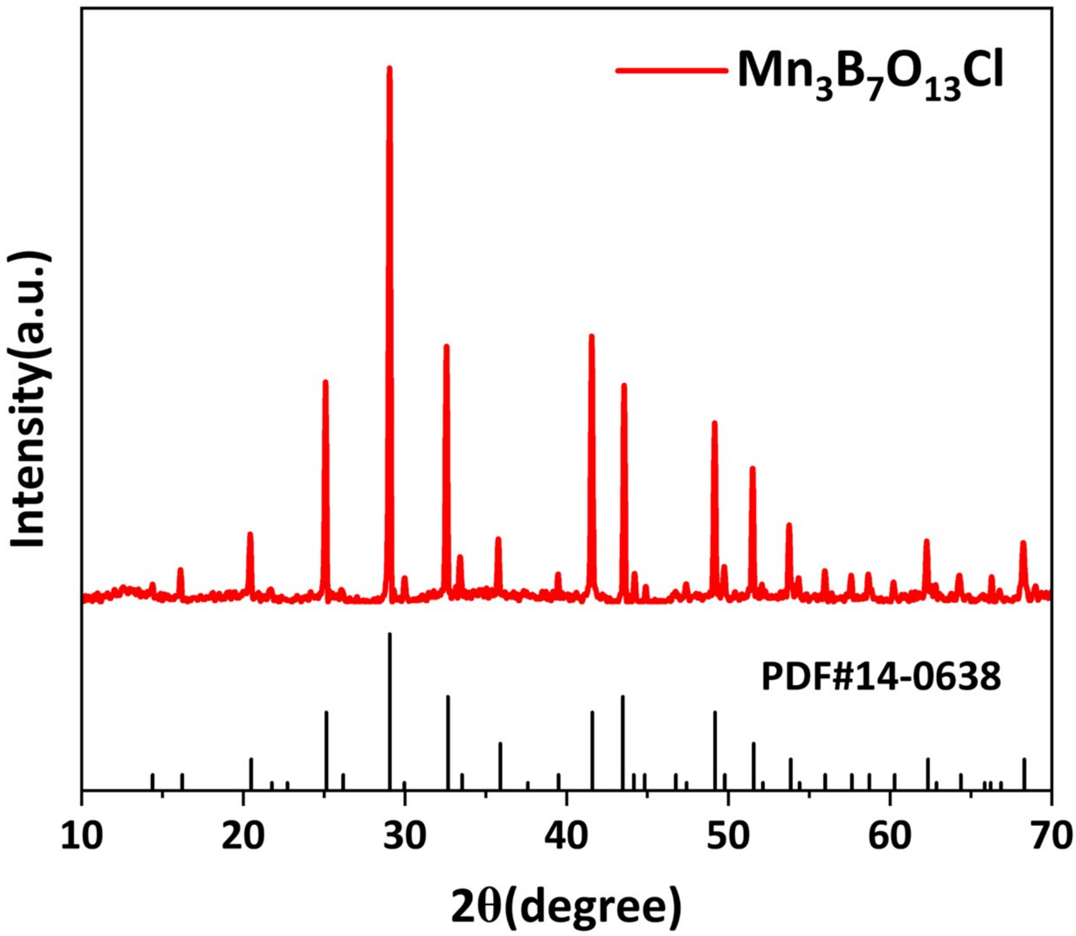

Fig. S1 XRD pattern of $Mn_3B_7O_{13}Cl$ powder crystal.

As shown in the Fig. S1, it can be seen that the positions of the major diffraction peaks and peak intensities of the synthesized $Mn_3B_7O_{13}Cl$ powder crystals are consistent with the standard PDF card and have the same crystallographic orientation, indicating that the $Mn_3B_7O_{13}Cl$ powder crystals have been successfully synthesized. Meanwhile, the diffraction peaks are almost free of heterogeneous peaks, indicating that the synthesized $Mn_3B_7O_{13}Cl$ powder crystals are of high purity.

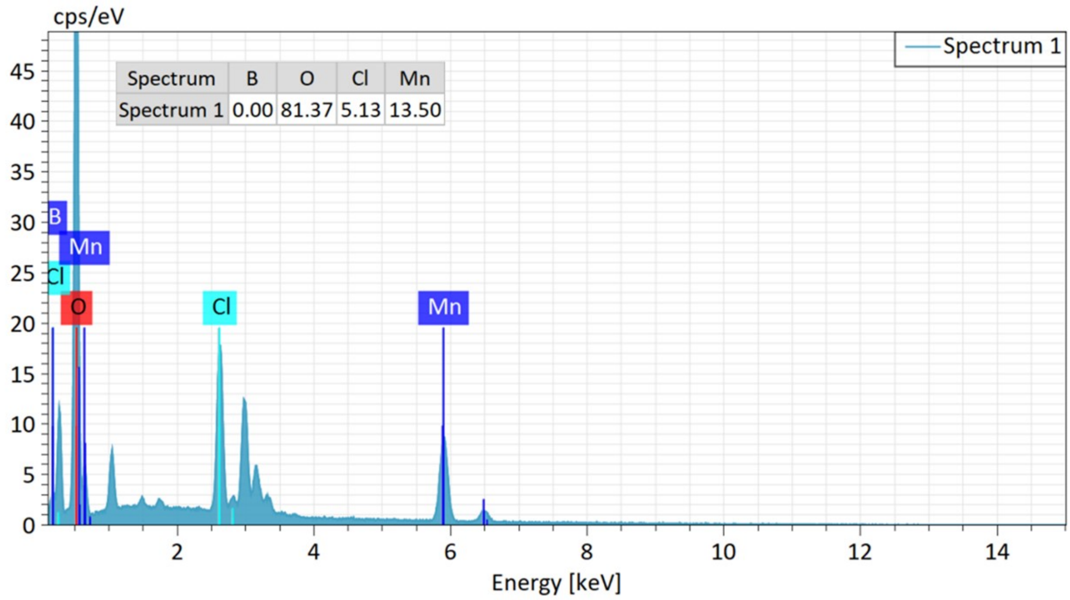

Fig. S2 EDS test results of $Mn_3B_7O_{13}Cl$ single crystals.

As show in Fig. S2, the elements contained in the $Mn_3B_7O_{13}Cl$ single crystal are Mn, O, Cl, Mn: Cl～3:1, and the results are slightly deviation because the B element cannot be measured accurately.

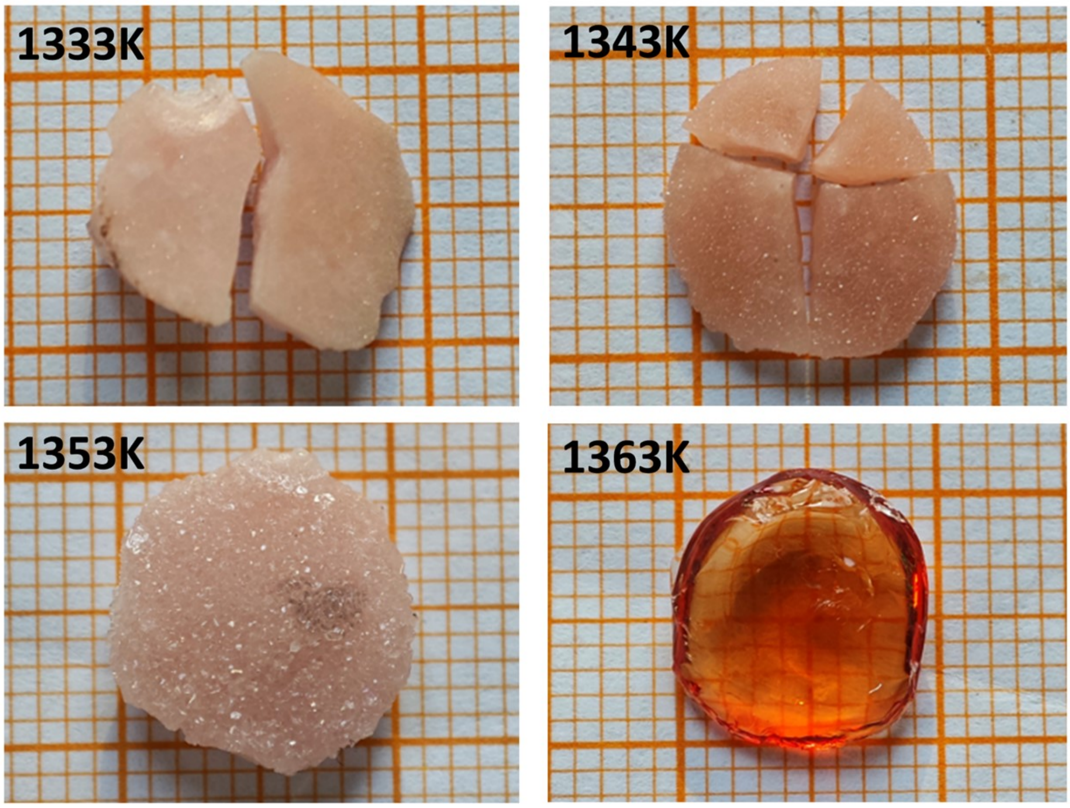

Fig. S3 Relationship between crystal growth temperature range and crystal size of $Mn_3B_7O_{13}Cl$.

In Fig. S3, the crystals used for single crystal refinement are small single crystals taken from the same batch of fired crystals.

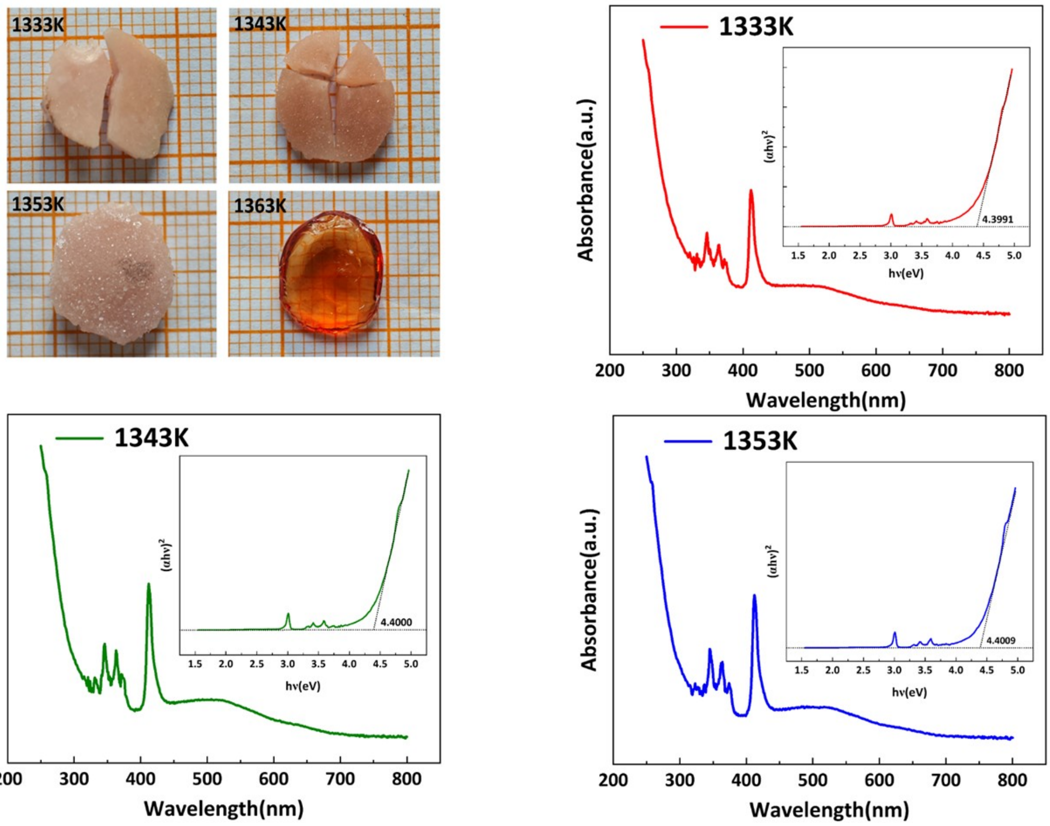

Fig. S4 UV absorption spectra and bandgap of $Mn_3B_7O_{13}Cl$ crystals grown at three temperatures.

We tested the UV absorption spectra (Lambda 750, PerKinElmer) of $Mn_3B_7O_{13}Cl$ crystals grown at three temperatures and calculated their band gaps, the formula used is $(\alpha h\upsilon)^2 = B(h\upsilon - E_g)$, where α is the absorption coefficient, υ is the frequency, h is Planck constant, and B is a constant (Z. J. Wang, H. M. Qiao, R. B. Su, B. Hu, X. M. Yang, C. He and X. F. Long, *Adv. Funct. Mater.*, 2018, 28, 1804089(1)), the results are shown in Fig. S4, which shows that the band gaps of $Mn_3B_7O_{13}Cl$ crystals grown at the three temperatures are basically the same. Therefore, the reason for the slight change in the color of the crystals may be the effect of the crystal size.

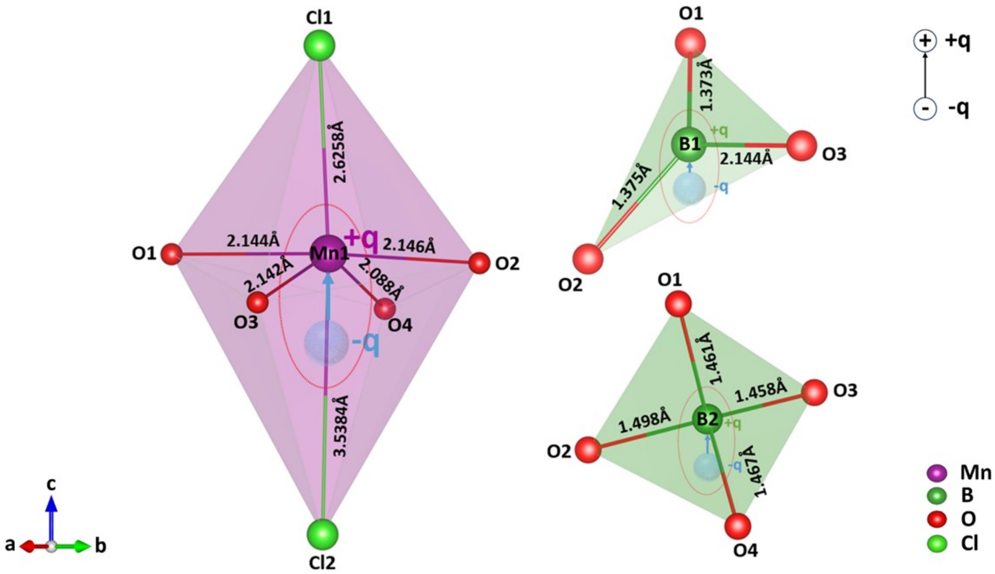

Fig.S5 Polarization diagram of $[MnCl_2O_4]$ and $[BO_4\text{-}BO_3]$ along the c-axis.

$[MnCl_2O_4]$ (deg.)				$[BO_4]$ (deg.)		$[BO_3]$ (deg.)	
Cl1-Mn1-O1	88.76(11)	Cl2-Mn1-O4	70.93(11)	O1-Mn1-O2	107.8(5)	O1-B1-O2	119.9(3)
Cl1-Mn1-O2	94.18(11)	O1-Mn1-O2	174.46(13)	O1-Mn1-O3	110.1(4)	O1-B1-O3	119.5(4)
Cl1-Mn1-O3	103.16(11)	O1-Mn1-O3	86.72(11)	O1-Mn1-O4	109.7(6)	O2-B1-O3	119.9(4)
Cl1-Mn1-O4	113.03(11)	O1-Mn1-O4	88.61(11)	O2-Mn1-O3	111.2(6)		
Cl2-Mn1-O1	88.90(11)	O2-Mn1-O3	88.04(11)	O2-Mn1-O4	108.8(4)		
Cl2-Mn1-O2	87.84(11)	O2-Mn1-O4	94.54(11)	O3-Mn1-O4	109.3(5)		
Cl2-Mn1-O3	72.68(11)	O3-Mn1-O4	143.38(15)				

Fig. S6 Bond angles of $[MnCl_2O_4]$ and $[BO_4\text{-}BO_3]$

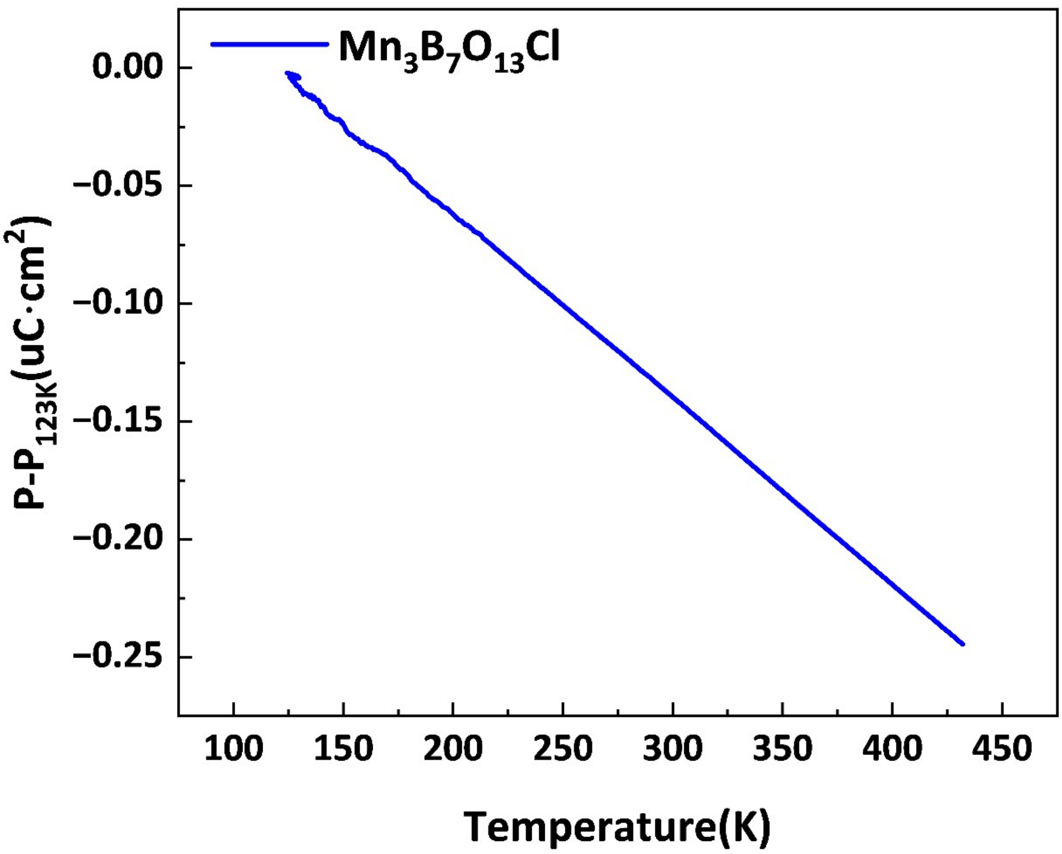

Fig. S7 Variation of polarization intensity with temperature for $Mn_3B_7O_{13}Cl$ along the c-axis.