Electronic Supplementary Information (ESI)

Large Magnetocaloric Effect in Gadolinium Borotungstate Gd_3BWO_9

Ziyu Yang,[a] Huihui Zhang,[a] Mingjun Bai,[b] Wei Li,[c] Shaolong Huang,[a] Shuangchen Ruan[a] and Yu-Jia Zeng*[a]

1 Experimental Section

Structural Analysis. High-resolution powder X-ray diffraction patterns for quantitative analysis were collected on a PANalytical X'Pert3 Powder X-ray diffractometer equipped with Cu-*Kα* radiation at 40 kV and 40 mA. Long scans with an angular range 10º ≤ 2*θ* ≤ 70º (step scanning mode, 0.13º steps in a measuring time of 0.8 s per step) were measured. The refinement with Rietveld analysis was performed using the GSAS package with *EXPGUI* interface.[1-3] The first kind Chebyshev polynomial and pseudo-Voigt function were used for fitting backgrounds and modeling peak shape.

Physical Measurements. Magnetic susceptibility data were collected in the Physical Property Measurement System (PPMS®DynaCool™, Quantum Design) with an applied field of 10 mT in the 2-300 K temperature range. Isothermal magnetization curves were collected in the field range $0 \leq \mu_0 H \leq 7$ T and temperature range of 2-11 K with a step of 1 K after cooling in zero fields.

Heat capacity measurements were conducted using the relaxation method on powder samples in a commercial setup Physical Property Measurement System (PPMS-9, Quantum Design) with Helium-3 refrigerator option, under a temperature range of 300 mK-30 K and constant external fields of 0, 1, 3 and 9 T, respectively.

[a] College of Physics and Optoelectronic Engineering, Shenzhen University, 518060, Shenzhen, China.

[b] School of Materials Science and Engineering, Central South University, 410083, Changsha, China.

[c] Beijing Key Laboratory for Magnetoelectric Materials and Device (BKLMMD), Department of Materials Science and Engineering, College of Engineering, Peking University, 100871, Beijing, China.

Correspondence: yjzeng@szu.edu.cn

2 Supplementary Figures

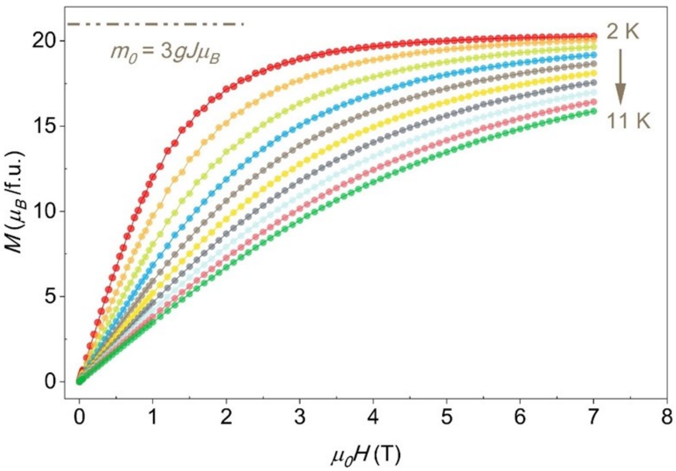

Fig. S1 Isothermal magnetization curves recorded at a field range of 0≤ μ_0H ≤7 T and temperature range of 2-11 K with a step of 1 K after cooling in zero field.

Fig. S2 Collinear spin configurations containing 6 Gd ions with differing nearest-neighbor FM and AFM spin alignments. See text for type-II.

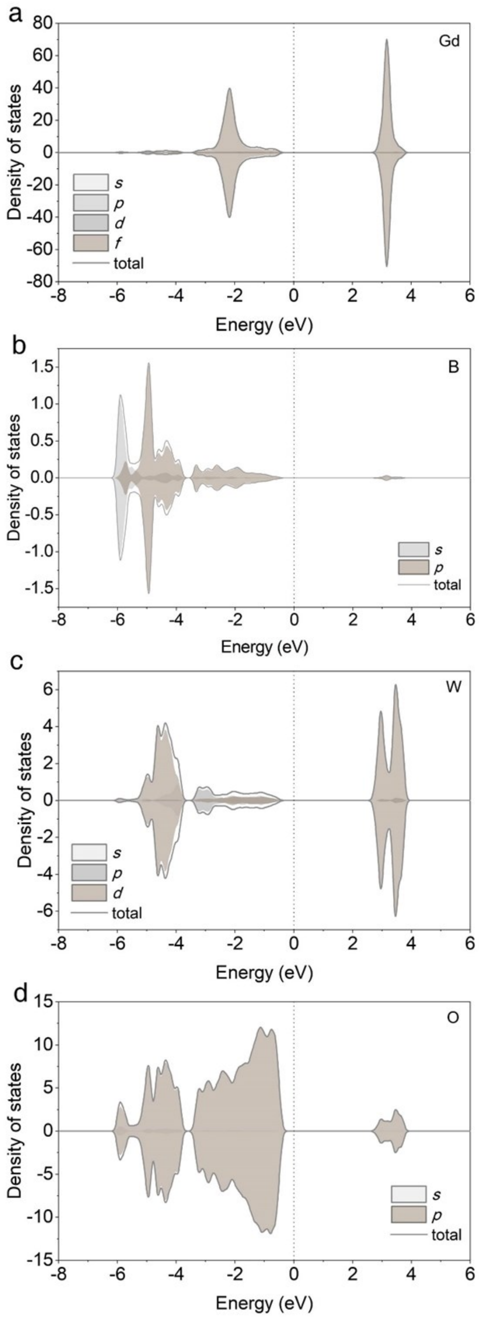

Fig. S3 Spin polarized partial density of states of Gd_3BWO_9. The dashed line is Fermi energy.

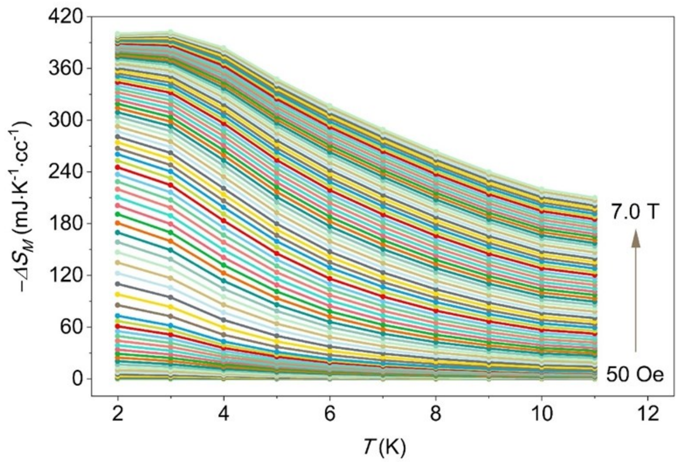

Fig. S4 Magnetic entropy change $-\Delta S_M$ as a function of temperature under applied field $\mu_0 H$ ranging from 50 Oe to 7 T.

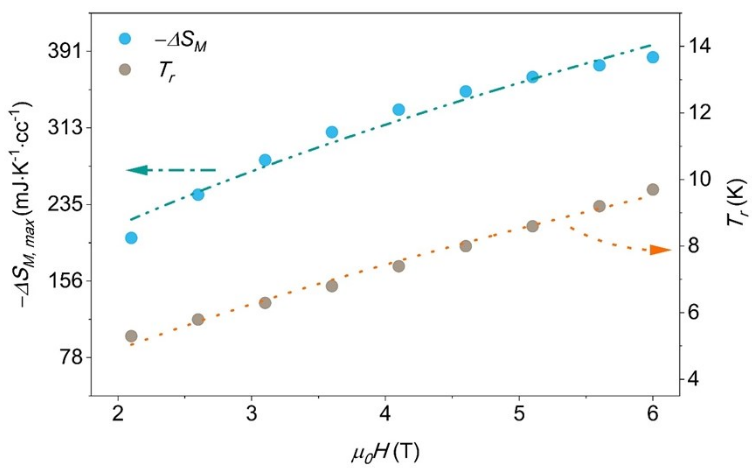

Fig. S5 Field dependence of maximum magnetic entropy change $-\Delta S_{M,\,max}$ and scaling law governing the field variance of the reference temperature T_r. See text for details.

Table S1 Selected bond length values of Gd_3BWO_9.

Vector	Length	Optr Cell	Neighbor atom coordinates
Gd1_Gd1	3.8815(15)	2 0 0-1	0.27581 0.35813 -0.28804
Gd1_Gd1	3.8815(15)	2 0 0 0	0.27581 0.35813 0.71196
Gd1_Gd1	3.8815(15)	6 0 0-1	0.08232 -0.27581 -0.28804
Gd1_Gd1	3.8815(15)	6 0 0 0	0.08232 -0.27581 0.71196
Gd1_W1	3.4666(15)	1 0-1 0	0.33333 -0.33333 0.24008
Gd1_W1	3.528(4)	2 1 0-1	0.66666 0.33333 -0.25992
Gd1_B1	2.841(8)	2 0 0-1	0.00000 0.00000 0.31434
Gd1_O1	2.640(23)	1 0 0-1	0.16683 0.06543 -0.18027
Gd1_O1	2.703(20)	2 0 0-1	0.10141 0.16683 0.31973
Gd1_O1	2.273(20)	6 0 0-1	0.06543 -0.10141 0.31973
Gd1_O2	2.31(4)	5 0 0 0	0.24478 -0.20356 0.04939
Gd1_O2	2.188(28)	6 0 0 0	0.44834 0.24478 0.54939
Gd1_O3	2.447(20)	2 1 0-1	0.63265 0.15489 -0.01620
Gd1_O3	2.542(20)	5 0 0 0	0.36735 -0.15489 0.48380
Gd1_O3	2.457(13)	6 0 0-1	0.52223 0.36735 -0.01620
W1_Gd1	3.4666(15)	1 0 1 0	0.35813 1.08232 0.21196
W1_Gd1	3.528(4)	2 0 0 0	0.27581 0.35813 0.71196
W1_Gd1	3.4667(15)	3 0 0 0	-0.08232 0.27581 0.21196
W1_Gd1	3.528(4)	4 1 1 0	0.64187 0.91768 0.71196
W1_Gd1	3.4667(15)	5 1 1 0	0.72419 0.64187 0.21196
W1_Gd1	3.528(4)	6 0 1 0	0.08232 0.72419 0.71196
W1_O2	1.929(33)	1 0 0 0	0.20356 0.44834 0.04939
W1_O2	1.929(33)	3 1 1 0	0.55166 0.75522 0.04939
W1_O2	1.929(33)	5 0 1 0	0.24478 0.79644 0.04939
W1_O3	1.928(22)	1 0 0 0	0.15489 0.52223 0.48380
W1_O3	1.928(22)	3 1 1 0	0.47777 0.63265 0.48380

W1_O3	1.928(22)	5 0 1 0	0.36735	0.84511	0.48380
B1_Gd1	2.841(8)	2 0 0 0	0.27581	0.35813	0.71196
B1_Gd1	2.841(8)	4 0 0 0	-0.35813	-0.08232	0.71196
B1_Gd1	2.841(8)	6 0 0 0	0.08232	-0.27581	0.71196
B1_O1	1.249(14)	1 0 0 0	0.16683	0.06543	0.81973
B1_O1	1.249(14)	3 0 0 0	-0.06543	0.10141	0.81973
B1_O1	1.249(14)	5 0 0 0	-0.10141	-0.16683	0.81973
B1_Gd1	2.841(8)	2 0 0 0	0.27581	0.35813	0.71196
B1_Gd1	2.841(8)	4 0 0 0	-0.35813	-0.08232	0.71196
B1_Gd1	2.841(8)	6 0 0 0	0.08232	-0.27581	0.71196
B1_O1	1.249(14)	1 0 0 0	0.16683	0.06543	0.81973
B1_O1	1.249(14)	3 0 0 0	-0.06543	0.10141	0.81973
B1_O1	1.249(14)	5 0 0 0	-0.10141	-0.16683	0.81973
O1_Gd1	2.640(23)	1 0 0 1	0.35813	0.08232	1.21196
O1_Gd1	2.273(20)	2 0 0 0	0.27581	0.35813	0.71196
O1_Gd1	2.703(20)	6 0 0 0	0.08232	-0.27581	0.71196
O1_B1	1.249(14)	1 0 0 0	0.00000	0.00000	0.81434
O1_O1	2.163(23)	3 0 0 0	-0.06543	0.10141	0.81973
O1_O1	2.163(23)	5 0 0 0	-0.10141	-0.16683	0.81973
O2_Gd1	2.188(28)	2 0 0-1	0.27581	0.35813	-0.28804
O2_Gd1	2.31(4)	3 0 0 0	-0.08232	0.27581	0.21196
O2_W1	1.929(33)	1 0 0 0	0.33333	0.66667	0.24008
O3_Gd1	2.457(13)	2 0 0 0	0.27581	0.35813	0.71196
O3_Gd1	2.542(20)	3 0 0 0	-0.08232	0.27581	0.21196
O3_Gd1	2.447(20)	6 0 1 0	0.08232	0.72419	0.71196
O3_W1	1.928(22)	1 0 0 0	0.33333	0.66667	0.24008

Table S2 Selected bond angles of Gd_3BWO_9.

Angle	Degrees	atom 1 loc	atom 3 loc
O1_Gd1_O1	74.2(6)	1 0 0-1	6 0 0-1

O1_Gd1_O2	73.5(9)	1 0 0-1	5 0 0 0
O1_Gd1_O2	135.8(13)	1 0 0-1	6 0 0 0
O1_Gd1_O3	95.8(5)	1 0 0-1	2 1 0-1
O1_Gd1_O3	133.4(5)	1 0 0-1	5 0 0 0
O1_Gd1_O3	71.5(6)	1 0 0-1	6 0 0-1
O1_Gd1_O2	68.2(9)	6 0 0-1	5 0 0 0
O1_Gd1_O2	98.3(8)	6 0 0-1	6 0 0 0
O1_Gd1_O3	153.4(6)	6 0 0-1	2 1 0-1
O1_Gd1_O3	76.3(7)	6 0 0-1	5 0 0 0
O1_Gd1_O3	134.7(8)	6 0 0-1	6 0 0-1
O2_Gd1_O2	145.0(18)	5 0 0 0	6 0 0 0
O2_Gd1_O3	85.4(8)	5 0 0 0	2 1 0-1
O2_Gd1_O3	62.3(7)	5 0 0 0	5 0 0 0
O2_Gd1_O3	126.3(13)	5 0 0 0	6 0 0-1
O2_Gd1_O3	105.6(9)	6 0 0 0	2 1 0-1
O2_Gd1_O3	83.4(15)	6 0 0 0	5 0 0 0
O2_Gd1_O3	86.6(9)	6 0 0 0	6 0 0-1
O3_Gd1_O3	94.8(5)	2 1 0-1	5 0 0 0
O3_Gd1_O3	59.6(11)	2 1 0-1	6 0 0-1
O3_Gd1_O3	148.7(6)	5 0 0 0	6 0 0-1
O2_W1_O2	94.1(12)	1 0 0 0	3 1 1 0
O2_W1_O2	94.1(12)	1 0 0 0	5 0 1 0
O2_W1_O3	81.6(10)	1 0 0 0	1 0 0 0
O2_W1_O3	108.7(13)	1 0 0 0	3 1 1 0
O2_W1_O3	157.0(13)	1 0 0 0	5 0 1 0
O2_W1_O2	94.1(12)	3 1 1 0	5 0 1 0
O2_W1_O3	157.0(13)	3 1 1 0	1 0 0 0
O2_W1_O3	81.6(10)	3 1 1 0	3 1 1 0
O2_W1_O3	108.7(13)	3 1 1 0	5 0 1 0
O2_W1_O3	108.7(13)	5 0 1 0	1 0 0 0

O2_W1_O3	157.0(13)	5 0 1 0	3 1 1 0
O2_W1_O3	81.6(10)	5 0 1 0	5 0 1 0
O3_W1_O3	78.4(8)	1 0 0 0	3 1 1 0
O3_W1_O3	78.4(8)	1 0 0 0	5 0 1 0
O3_W1_O3	78.4(8)	3 1 1 0	5 0 1 0
O1_B1_O1	119.95(19)	1 0 0 0	3 0 0 0
O1_B1_O1	119.95(19)	1 0 0 0	5 0 0 0
O1_B1_O1	119.95(19)	3 0 0 0	5 0 0 0
Gd1_O1_Gd1	104.1(8)	1 0 0 1	2 0 0 0
Gd1_O1_B1	125.8(23)	1 0 0 1	1 0 0 0
Gd1_O1_B1	103.7(12)	2 0 0 0	1 0 0 0
Gd1_O2_Gd1	119.2(16)	2 0 0-1	3 0 0 0
Gd1_O2_W1	131.3(19)	2 0 0-1	1 0 0 0
Gd1_O2_W1	109.3(13)	3 0 0 0	1 0 0 0
Gd1_O3_Gd1	101.8(7)	2 0 0 0	3 0 0 0
Gd1_O3_Gd1	118.8(7)	2 0 0 0	6 0 1 0
Gd1_O3_W1	106.5(9)	2 0 0 0	1 0 0 0
Gd1_O3_Gd1	119.9(8)	3 0 0 0	6 0 1 0
Gd1_O3_W1	100.8(7)	3 0 0 0	1 0 0 0
Gd1_O3_W1	106.9(8)	6 0 1 0	1 0 0 0

Table S3 State of the art performances of solid-state cryogenic refrigeration (CR) materials reported in the literature.

Formula	ΔS_M J·K^{-1}·Kg^{-1}	ΔS_M mJ·K^{-1}·cc^{-1}	T K	ΔH T	Ref
$Gd(OH)CO_3$	66.4	355	1.8	7	[4]
$Gd(HCOO)_3$	55.9	215.7	1.8	7	[5]
$\{[Gd_6O(OH)_8(ClO_4)_4(H_2O)_6](OH)_4\}_n$	46.6	215.6	2.5	7	[6]
$[Gd_4(SO_4)_4(\mu_3\text{-}OH)_4(H_2O)]_n$	51.3	198.9	2	7	[7]

$[Gd(HCOO)(bdc)]_n$	47	125	2.3	9	[8]
$[Gd_{48}O_6(OH)_{84}(CAA)_{36}(NO_3)_6(H_2O)_{24}(EtOH)_{12}(NO_3)Cl_2]Cl_3 \cdot 6DMF \cdot 5EtOH \cdot 20H_2O$	43.6	120.7	1.8	7	[9]
$[Gd(C_4O_4)(OH)(H_2O)_4]_n$	47.3	112.7	3	9	[10]
$[Mn^{II}(glc)_2(H_2O)_2]$	60.3	112	1.8	7	[11]
$[Gd(HCOO)(OAc)^2(H^2O)^2]^n$	45.9	110	1.8	7	[12]
$[Gd(OAc)_3(H_2O)_{0.5}]_n$	47.7	106.3	1.8	7	[13]
$\{[Gd_2(IDA)_3] \cdot 2H_2O\}_n$	40.6	100.7	2	7	[14]
$[Gd_{36}O_6(OH)_{49}(NA)_{36}(NO_3)_6(N_3)_3(H_2O)_{20}]_nCl_{2n} \cdot 28nH_2O$	39.66	91.3	2.5	7	[15]
$Gd(OH)_3$	62	346.08	2	7	[16]
$Gd_2Cu(SO_4)_2(OH)_4$	45.52	212.8	4	8	[17]
$Gd(OH)SO_4$	53.5	276	2	7	[18]
$[Gd_3(OH)_8Cl]_n$	61.8	318.9	3	7	[19]
GdF_3	71	506	3	7	[20]
$GdPO_4$	62	375.8	2.1	7	[21]
$GdAlO_3$	40.9	317	2	9	[22]
$GdVO_4$	41.1	227	3	5	[23]
$K_2Gd(BH_4)_5$	54.6	59.8	5	9	[24]
$K_3Li_3Gd_7(BO_3)_9$	56.6	277.2	2	7	[25]
$GdBO_3$	57.8	366.3	2	9	[26]
$Gd_5BSi_2O_{13}$	67	461	3	7	[27]
$GdCrTiO_5$	36		5	7	[28]
$EuTiO_3$	49	331	5	7	[29]
EuSe	37.5	244.8	4.6	5	[30]
Gd_2NiMnO_6	35.5	268	4	7	[31]
$GdCrO_3$	41.24	303	3.8	9	[32]

$EuHo_2O_4$	30	267	2	8	[33]
$EuDy_2O_4$	25	224	2	8	[33]
$GdFeTeO_6$	38.5		5	7	[34]
$GdFeO_3$	44	321	3	7	[35]

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