Supporting Information

A Gd-based Borate-Carbonate Framework, Exhibiting a Large Magnetocaloric Effect at Low Magnetic Field

Bo-Liang Liu, Qiao-Fei Xu, La-Sheng Long,* and Lan-Sun Zheng

Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China.

Experimental Section

Materials and Physical Measurements.

All materials and reagents were commercially available and used without further purification.

Single crystal data of **1** were collected using an Agilent Technologies Super Nova four-circle diffractometer with monochromatic Cu Kα radiation (λ = 1.54184 Å). Data reduction and absorption correction were applied by using the multi-scan program. The structures were determined and refined using full-matrix least-squares based on F^2 with SHELXS-97 and SHELXL-97[1] within Olex2.[2] CCDC number is 2073758 for compound **1**. Crystal data and refinement details are presented in Table S3. Selected bond distances and bond angles are listed in Table S4. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Powder X-ray diffraction data (PXRD) was collected on a Rigaku Ultima IV powder X-ray diffractometer (Cu Kα, λ = 1.54184 Å) in the 2θ range of 10-70° at 300 K. Thermogravimetric analysis (TGA) curve was conducted on an SDT_Q600 thermal analyzer at a rate of 10 °C per minute up to 800 °C under a constant nitrogen gas. Infrared spectra were recorded on a Nicolet iS50 FT-IR spectrophotometer with pressed KBr pellets. Magnetic measurement was carried out using a Quantum Design MPMS superconducting quantum interference device (SQUID).

Synthesis of GdB(OH)$_4$CO$_3$ (1)

Single crystal of **1** was synthesized by a mixture of Gd(NO$_3$)$_3$·6H$_2$O (0.451 g, 1.0 mmol), boric acid (0.247 g, 4 mmol) and ammonium carbonate (0.144 g, 1.5 mmol) dissolved in 10 mL deionized water. The resulting solution was stirred for 30 min before transferred into a Teflon-lined autoclave 200 °C for 3 days and cooled down to room temperature at a rate of 3 °C h^{-1}. Colorless crystals were obtained in 50% yield based on Gd^{3+}.
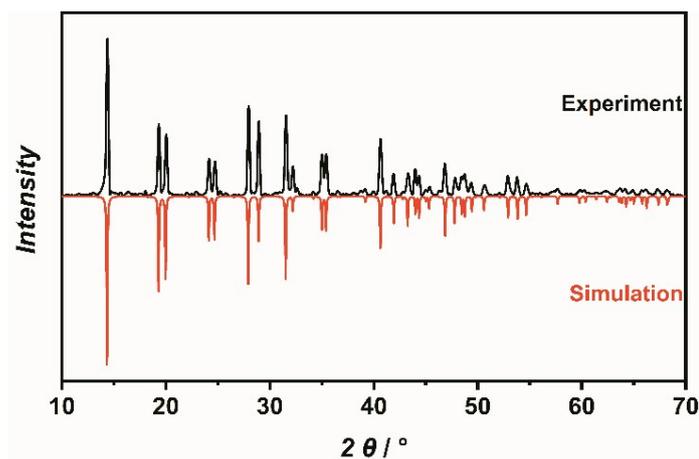
Fig. S1. PXRD curve for **1**.

The PXRD patterns are consistent with the simulated ones based on the single-crystal structure determinations, suggesting the phase purity of **1**.
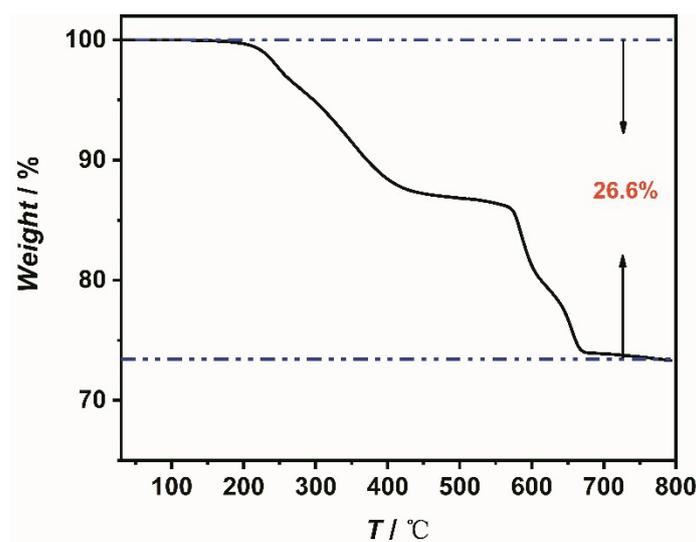

Fig. S2. TGA curve of **1**.

The TGA curve of **1** was carried out under N_2 atmosphere. With temperature rising, two obvious endothermic steps are observed. The first step is attributed to the loss of two H_2O from tetrahydroxyborates, and the second is ascribed to the departure of CO_2 from carbonates. By the end of 800 °C, the weight loss is up to 26.6 %, which matches the theoretical value 27.0 % calculated for the weight loss of two H_2O and one CO_2, indicating that the residue is $GdBO_3$ at 800 °C.
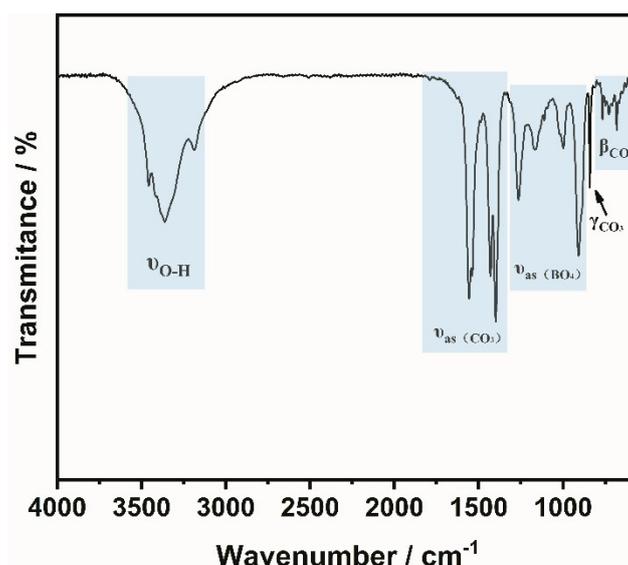
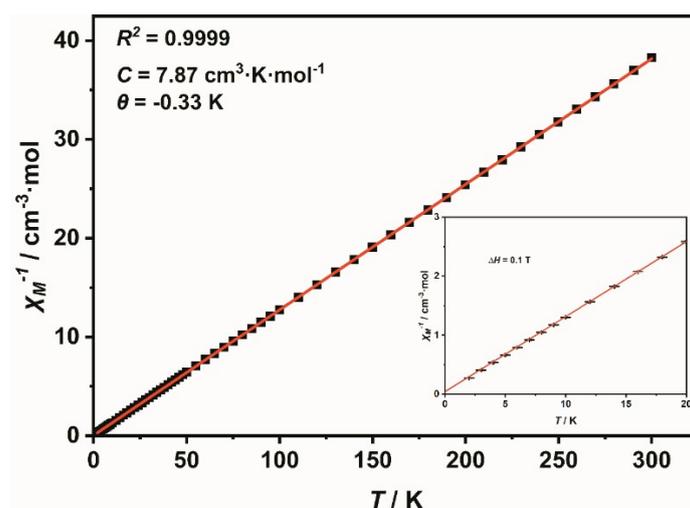**Fig. S3.** IR spectra in 4000-530 cm^{-1} for **1**

Fig. S4. The χ_m^{-1} *vs.* *T* plot of **1** in the temperature range of 2–300 K. The red solid line is the best-fit according to the Curie-Weiss law. Inserted: enlarged figure in the temperature range from 2 K to 20 K with error bar. The positive intercept of y axial suggests the antiferromagnetic coupling interaction in **1**.

Table S1. BVS calculations for oxygen atoms in tetrahydroxyborate.

Atom	bond	R_{ij}	R_0	S_{ij}
O1	Gd–O	2.500	2.031	0.282
	B–O	1.476	1.371	0.753
	Total			**1.035**
	Assignment			**OH⁻**
O2	Gd–O	2.487	2.031	0.292
	B–O	1.478	1.371	0.749
	Total			**1.041**
	Assignment			**OH⁻**

The bond valence sum (BVS)[3] analysis was used to determine the oxidation states of oxygen atoms in compound **1**. The calculation formula is $S_{ij} = \exp[(R_0 - R_{ij})/b]$, in which S_{ij} is the valence of the individual bond, R_{ij} is the observed bond length, R_0 is a constant depended upon the bonded elements, and b is a constant of 0.37. As shown in **Table S1**, the total BVS values of O atoms are very close to the state of +1, for which we identify the states of both O atoms are assigned to hydroxyl groups.

Table S2. The Continuous Shape Measurements (CShM)[4] of **1**.

	Gd
DP-10 (D_{8h})	33.433
EPY-10 (C_{9v})	24.528
OBPY-10 (D_{8h})	15.660
PPR-10 (D_{5h})	12.731
PAPR-10 (D_{5d})	13.562
JBCCU-10 (D_{4h})	10.557
JBCSAPR-10 (D_{4d})	5.142
JMBIC-10 (C_{2v})	9.328
JATDI-10 (C_{3v})	17.680
JSPC-10 (C_{2v})	**2.539**
SDD-10 (D_2)	4.835
TD-10 (C_{2v})	3.941
HD-10 (D_{4h})	9.320

DP-10 = Decagon; EPY-10 = Enneagonal pyramid; OBPY-10 = Octagonal bipyramid; PPR-10 = Pentagonal prism; PAPR-10 = Pentagonal antiprism; JBCCU-10 = Bicapped cube; JBCSAPR-10 = Bicapped square antiprism; JMBIC-10 = Metabidiminished icosahedron; JATDI-10 = Augmented tridiminished icosahedron; JSPC-10 = Sphenocorona; SDD-10 = Staggered Dodecahedron; TD-10 = Tetradecahedron; HD-10 = Hexadecahedron.

Table S3. Crystal data for **1**.

Compound	**1**
Formula	CH_4BGdO_7
Formula weight	296.1
Temperature/K	100
Crystal system	orthorhombic
Space group	*Pbcm*
a/Å	6.1685 (4)
b/Å	8.8840 (6)
c/Å	9.1876 (7)
V/Å^3	503.49 (6)
Z	4
D_c/g cm^{-3}	3.906
μ/mm^{-1}	85.22
θ/º	7.7780-72.7490
Observed reflections	1745
$F(000)$	540
GOOF	1.154
$R_1[I > 2\sigma(I)]^a$	0.0467
wR_2(All data)^b	0.1426

[a] $R_1 = \sum ||Fo| - |Fc|| / \sum |Fo|$ [b] $wR_2 = \{\sum[w(Fo^2 - Fc^2)^2] / \sum[w(Fo^2)^2]\}^{1/2}$

Table S4. Selected bond distances (Å) and bond angles (°) of **1**.

Gd1—O2[i]	2.487 (4)	Gd1—O3[v]	2.851 (6)
Gd1—O2[ii]	2.487 (4)	Gd1—O4[iv]	2.418 (2)
Gd1—O1	2.500 (4)	Gd1—O4[v]	2.418 (2)
Gd1—O1[iii]	2.500 (4)	O2—B1	1.478 (6)
Gd1—O3	2.341 (5)	O1—B1	1.476 (6)
Gd1—O3[iv]	2.851 (6)	O3—C1	1.259 (7)
Gd1—O3[iii]	2.341 (5)	O4—C1	1.287 (11)
Gd1–O3–Gd1[iv]	117.3(2)	Gd1[iv]–O4–Gd1[vi]	143.5(3)

Symmetry codes: (i) x+1, y, z; (ii) x+1, −y+1/2, −z−1; (iii) x, −y+1/2, −z−1; (iv) −x−2, −y+1, −z−1; (v) −x−2, y−1/2, z; (vi) −x−2, −y+1, z−1/2

Reference

(1) G. M. Sheldrick, *Acta Cryst.*, 2015, **71**, 3–8.

(2) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

(3) I. D. Brown and D. Altermatt, *Acta Cryst. B*, 1985, **41**, 244–247.

(4) S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell and D. Avnir, *Coord. Chem. Rev.*, 2005, **249**, 1693–1708.