Supporting Data

Gadolinium Oxyorthogermanate Gd_2GeO_5: an Efficient Solid Refrigerant Material for Magnetic Cryocoolers

Ziyu W. Yang[1], Shijun Qin[2,3], Jie Zhang[2,3], Dabiao Lu[2,3], Haoting Zhao[2,3], Chenxu Kang[1], Hongzhi Cui[1,*], Youwen Long[2,3,4,*], and Yu-Jia Zeng[1,*]

[1] *College of Civil and Transportation Engineering, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen, 518060, China.*

[2] *Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China.*

[3] *School of Physical Sciences, University of Chinese Academy of Sciences, Beijing, 100049, China.*

[4] *Songshan Lake Materials Laboratory, Dongguan, Guangdong, 523808, China.*

[*] **Corresponding author.** E-mail: h.z.cui@szu.edu.cn; ywlong@iphy.ac.cn; yjzeng@szu.edu.cn.

RESULTS AND DISCUSSION

Table S1 shows a collection of some representative magnetocaloric materials in the cryogenic temperature range, with the applied field change $B \geqslant 5$ T.

Table S1. The representative magnetocaloric materials in the cryogenic temperature range at a field change B ≥ 5 T.

Formula	ΔS_M J·K⁻¹·Kg⁻¹	ΔS_M mJ·K⁻¹·cm⁻³	T K	ΔH T	Ref
Gd_3BWO_9	58.1	454	2.4	9	[1]
Gd_2ZnTiO_6	53.5	398.5	3.1	9	[2]
$EuTi_{0.85}Nb_{0.15}O_3$	51.3	346.7	9.5	9	[3]
$GdFe_2Si_2$	30.01	210[a]	8.6	7	[4]
$HoCoC_2$	15.6	172[a]	11	5	[5]
$HoCrO_4$	31	185[a]	20	8	[6]
$GdCrO_4$	29.1	161[a]	22	9	[7]
$Gd(OH)CO_3$	66.4	355	1.8	7	[8]
$Gd(HCOO)_3$	55.9	215.7	1.8	7	[9]
$\{[Gd_6O(OH)_8(ClO_4)_4(H_2O)_6](OH)_4\}_n$	46.6	215.6	2.5	7	[10]
$[Gd_4(SO_4)_4(\mu_3\text{-}OH)_4(H_2O)]_n$	51.3	198.9	2	7	[11]
$[Gd(HCOO)(bdc)]_n$	47	125	2.2	9	[12]
$[Gd(C_4O_4)(OH)(H_2O)_4]_n$	47.3	112.7	3	9	[13]
$[Mn^{II}(glc)_2(H_2O)_2]$	60.3	112	1.8	7	[14]
$[Gd(HCOO)(OAc)_2(H_2O)_2]_n$	45.9	110	1.8	7	[15]
$[Gd(OAc)_3(H_2O)_{0.5}]_n$	47.7	106.3	1.8	7	[16]
$\{[Gd_2(IDA)_3]\cdot 2H_2O\}_n$	40.6	100.7	2	7	[17]
$[Gd_{36}O_6(OH)_{49}(NA)_{36}(NO_3)_6(N_3)_3(H_2O)_{20}]_nCl_{2n}\cdot 28nH_2O$	39.66	91.3	2.5	7	[18]
$Gd(OH)_3$	62	346.08	2	7	[19]
$Gd_2Cu(SO_4)_2(OH)_4$	45.52	212.8	4	8	[20]
$Gd(OH)SO_4$	53.5	276	2	7	[21]
$[Gd_3(OH)_8Cl]_n$	61.8	318.9	3	7	[22]
GdF_3	71	506	3	7	[23]
$GdPO_4$	62	375.8	2.1	7	[24]

$GdAlO_3$	40.9	317	2	9	[25]
$GdVO_4$	41.1	227	3	5	[26]
$K_2Gd(BH_4)_5$	54.6	59.8	5	9	[27]
$K_3Li_3Gd_7(BO_3)_9$	56.6	277.2	2	7	[28]
$GdBO_3$	57.8	366.3	2	9	[29]
$Gd_5BSi_2O_{13}$	67	461	3	7	[30]
$GdCrTiO_5$[b]	36	212.4	5	7	[31]
$EuTiO_3$	49	331	5	7	[32]
EuSe	37.5	244.8	4.6	5	[33]
Gd_2NiMnO_6	35.5	268	4	7	[34]
$GdCrO_3$	41.24	303	3.8	9	[35]
$EuHo_2O_4$	30	267	2	8	[36]
$EuDy_2O_4$	25	224	2	8	[36]
$GdFeTeO_6$[c]	38.5	246.7	5	7	[37]
$GdFeO_3$	44	321	3	7	[38]

[a] The superscript represents density values estimated by proposed crystallographic information.
[b] The density ρ = 5.9 g cm^{-3} was adopted.
[c] The density ρ = 6.4 g cm^{-3} was adopted.

REFERENCES

[1] Z. Yang, H. Zhang, M. Bai, W. Li, S. Huang, S. Ruan and Y.-J. Zeng, Large magnetocaloric effect in gadolinium borotungstate Gd_3BWO_9, *J. Mater. Chem. C* 8 (2020) 11866-11873.

[2] Z. Yang, J.-Y. Ge, S. Ruan, H. Cui and Y.-J. Zeng, Cryogenic magnetocaloric effect in distorted double-perovskite Gd_2ZnTiO_6, *J. Mater. Chem. C* 9 (2021) 6754-6759.

[3] S. Roy, N. Khan and P. Mandal, Giant low-field magnetocaloric effect in single-crystalline $EuTi_{0.85}Nb_{0.15}O_3$, *APL Materials* 4 (2016) 026102.

[4] Y. Zhang, J. Zhu, S. Li, Z. Zhang, J. Wang and Z. Ren, Magnetic properties and promising magnetocaloric performances in the antiferromagnetic $GdFe_2Si_2$ compound, *Science China Materials* 65 (2022) 1345-1352.

[5] L. Meng, Y. Jia and L. Li, Large reversible magnetocaloric effect in the $RECoC_2$ (RE=Ho and Er) compounds, *Intermetallics* 85 (2017) 69-73.

[6] A. Midya, N. Khan, D. Bhoi and P. Mandal, 3d-4f spin interaction induced giant magnetocaloric effect in zircon-type $DyCrO_4$ and $HoCrO_4$ compounds, *Appl. Phys. Lett.* 103 (2013) 092402.

[7] E. Palacios, C. Tomasi, R. Sáez-Puche, A. J. Dos santos-García, F. Fernández-Martínez and R. Burriel, Effect of Gd polarization on the large magnetocaloric effect of $GdCrO_4$ in a broad temperature range, *Phys. Rev. B* 93 (2016) 064420.

[8] Y.-C. Chen, L. Qin, Z.-S. Meng, D.-F. Yang, C. Wu, Z. Fu, Y.-Z. Zheng, J.-L. Liu, R. Tarasenko, M. Orendáč, J. Prokleška, V. Sechovský and M.-L. Tong, Study of a magnetic-cooling material $Gd(OH)CO_3$, *J. Mater. Chem. A* 2 (2014) 9851-9858.

[9] G. Lorusso, J. W. Sharples, E. Palacios, O. Roubeau, E. K. Brechin, R. Sessoli, A. Rossin, F. Tuna, E. J. L. McInnes, D. Collison and M. Evangelisti, A Dense Metal–Organic Framework for Enhanced Magnetic Refrigeration, *Advanced Materials* 25 (2013) 4653-4656.

[10] Y.-L. Hou, G. Xiong, P.-F. Shi, R.-R. Cheng, J.-Z. Cui and B. Zhao, Unique (3,12)-connected coordination polymers displaying high stability, large magnetocaloric effect and slow magnetic relaxation, *Chemical Communications* 49 (2013) 6066-6068.

[11] S.-D. Han, X.-H. Miao, S.-J. Liu and X.-H. Bu, Magnetocaloric effect and slow magnetic relaxation in two dense (3,12)-connected lanthanide complexes, *Inorg. Chem. Front.* 1 (2014) 549-552.

[12] R. Sibille, T. Mazet, B. Malaman and M. François, A Metal–Organic Framework as Attractive Cryogenic Magnetorefrigerant, *Chemistry – A European Journal* 18 (2012) 12970-12973.

[13] S. Biswas, A. Adhikary, S. Goswami and S. Konar, Observation of a large magnetocaloric effect in a 2D Gd(iii)-based coordination polymer, *Dalton Transactions* 42 (2013) 13331-13334.

[14] Y.-C. Chen, F.-S. Guo, J.-L. Liu, J.-D. Leng, P. Vrábel, M. Orendáč, J. Prokleška, V. Sechovský and M.-L. Tong, Switching of the Magnetocaloric Effect of MnII Glycolate by Water Molecules, *Chemistry – A European Journal* 20 (2014) 3029-3035.

[15] G. Lorusso, M. A. Palacios, G. S. Nichol, E. K. Brechin, O. Roubeau and M. Evangelisti, Increasing the dimensionality of cryogenic molecular coolers: Gd-based polymers and metal–organic frameworks, *Chem. Commun.* 48 (2012) 7592-7594.

[16] F.-S. Guo, J.-D. Leng, J.-L. Liu, Z.-S. Meng and M.-L. Tong, Polynuclear and Polymeric Gadolinium Acetate Derivatives with Large Magnetocaloric Effect, *Inorganic Chemistry* 51 (2012) 405-413.

[17] J.-M. Jia, S.-J. Liu, Y. Cui, S.-D. Han, T.-L. Hu and X.-H. Bu, 3D GdIII Complex Containing Gd_{16} Macrocycles Exhibiting Large Magnetocaloric Effect, *Crystal Growth & Design* 13 (2013) 4631-4634.

[18] M. Wu, F. Jiang, X. Kong, D. Yuan, L. Long, S. A. Al-Thabaiti and M. Hong, Two polymeric 36-metal pure lanthanide nanosize clusters, *Chem. Sci.* 4 (2013) 3104-3109.

[19] Y. Yang, Q.-C. Zhang, Y.-Y. Pan, L.-S. Long and L.-S. Zheng, Magnetocaloric effect and thermal conductivity of $Gd(OH)_3$ and $Gd_2O(OH)_4(H_2O)_2$, *Chem. Commun.* 51 (2015) 7317-7320.

[20] Y. Tang, W. Guo, S. Zhang, M. Yang, H. Xiang and Z. He, $Gd_2Cu(SO_4)_2(OH)_4$: a 3d–4f hydroxysulfate with an enhanced cryogenic magnetocaloric effect, *Dalton Transactions* 44 (2015) 17026-17029.

[21] Y. Han, S.-D. Han, J. Pan, Y.-J. Ma and G.-M. Wang, An excellent cryogenic magnetic cooler: magnetic and magnetocaloric study of an inorganic frame material, *Materials Chemistry Frontiers* 2 (2018) 2327-2332.

[22] Y. Wang, L. Qin, G.-J. Zhou, X. Ye, J. He and Y.-Z. Zheng, High-performance low-temperature magnetic refrigerants made of gadolinium-hydroxy-chloride, *Journal of Materials Chemistry C* 4 (2016) 6473-6477.

[23] Y.-C. Chen, J. Prokleška, W.-J. Xu, J.-L. Liu, J. Liu, W.-X. Zhang, J.-H. Jia, V. Sechovský and M.-L. Tong, A brilliant cryogenic magnetic coolant: magnetic and magnetocaloric study of ferromagnetically coupled GdF_3, *Journal of Materials Chemistry C* 3 (2015) 12206-12211.

[24] E. Palacios, J. A. Rodríguez-Velamazán, M. Evangelisti, G. J. McIntyre, G. Lorusso, D. Visser, L. J. de Jongh and L. A. Boatner, Magnetic structure and magnetocalorics of $GdPO_4$, *Phys. Rev. B* 90 (2014) 214423-214423.

[25] S. Mahana, U. Manju and D. Topwal, Giant magnetocaloric effect in $GdAlO_3$ and a comparative study with GdMnO3, *Journal of Physics D: Applied Physics* 50 (2016) 035002.

[26] K. Dey, A. Indra, S. Majumdar and S. Giri, Cryogenic magnetocaloric effect in zircon-type RVO_4 (R = Gd, Ho, Er, and Yb), *Journal of Materials Chemistry C* 5 (2017) 1646-1650.

[27] P. Schouwink, E. Didelot, Y.-S. Lee, T. Mazet and R. Černý, Structural and magnetocaloric properties of novel gadolinium borohydrides, *Journal of Alloys and Compounds* 664 (2016) 378-384.

[28] M. Xia, S. Shen, J. Lu, Y. Sun and R. Li, $K_3Li_3Gd_7(BO_3)_9$: A New Gadolinium-Rich Orthoborate for Cryogenic Magnetic Cooling, *Chemistry – A European Journal* 24 (2018) 3147-3150.

[29] P. Mukherjee, Y. Wu, G. I. Lampronti and S. E. Dutton, Magnetic properties of monoclinic lanthanide orthoborates, $LnBO_3$, Ln=Gd, Tb, Dy, Ho, Er, Yb, *Materials Research Bulletin* 98 (2018) 173-179.

[30] C. Tao and R. Li, High-Performance Magnetic Refrigerant Featuring One-Dimensional Gd-O Chains and O-Gd_3 Triangles, *Chemistry – An Asian Journal* 13 (2018) 2834-2837.

[31] M. Das, S. Roy, N. Khan and P. Mandal, Giant magnetocaloric effect in an exchange-frustrated $GdCrTiO_5$ antiferromagnet, *Phys. Rev. B* 98 (2018) 104420-104420.

[32] A. Midya, P. Mandal, K. Rubi, R. Chen, J.-S. Wang, R. Mahendiran, G. Lorusso and M. Evangelisti, Large adiabatic temperature and magnetic entropy changes in $EuTiO_3$, *Phys. Rev. B* 93 (2016) 094422-094422.

[33] D. X. Li, T. Yamamura, S. Nimori, Y. Homma, F. Honda and D. Aoki, Giant and isotropic low temperature magnetocaloric effect in magnetic semiconductor EuSe, *Applied Physics Letters* 102 (2013) 152409-152409.

[34] J. K. Murthy, K. D. Chandrasekhar, S. Mahana, D. Topwal and A. Venimadhav, Giant magnetocaloric effect in Gd_2NiMnO_6 and Gd_2CoMnO_6 ferromagnetic insulators, *Journal of Physics D: Applied Physics* 48 (2015) 355001.

[35] S. Mahana, U. Manju and D. Topwal, $GdCrO_3$: a potential candidate for low temperature magnetic refrigeration, *Journal of Physics D: Applied Physics* 51 (2018) 305002.

[36] A. Midya, N. Khan, D. Bhoi and P. Mandal, Giant magnetocaloric effect in magnetically frustrated $EuHo_2O_4$ and $EuDy_2O_4$ compounds, *Applied Physics Letters* 101 (2012) 132415-132415.

[37] D. D. Lei, Z. W. Ouyang, X. Y. Yue, L. Yin, Z. X. Wang, J. F. Wang, Z. C. Xia and G. H. Rao, Weak magnetic interaction, large magnetocaloric effect, and underlying spin model in triangular lattice $GdFeTeO_6$, *Journal of Applied Physics* 124 (2018) 233904-233904.

[38]M. Das, S. Roy and P. Mandal, Giant reversible magnetocaloric effect in a multiferroic $GdFeO_3$ single crystal, *Physical Review B* 96 (2017) 174405.