



# Magnetic properties and giant cryogenic magnetocaloric effect in B-site ordered antiferromagnetic Gd<sub>2</sub>MgTiO<sub>6</sub> double perovskite oxide

Yikun Zhang<sup>a,b,c,\*</sup>, Yun Tian<sup>b</sup>, Zhenqian Zhang<sup>c</sup>, Youshun Jia<sup>c</sup>, Bin Zhang<sup>b</sup>, Minqiang Jiang<sup>d</sup>, Jiang Wang<sup>b</sup>, Zhongming Ren<sup>b</sup>

<sup>a</sup> School of Electronics and Information Engineering, Hangzhou Dianzi University, Hangzhou 310012, China

<sup>b</sup> State Key Laboratory of Advanced Special Steels and Shanghai Key Laboratory of Advanced Ferrometallurgy and School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

<sup>c</sup> Key Laboratory of Novel Materials for Sensor of Zhejiang Province, Hangzhou Dianzi University, Hangzhou 310012, China

<sup>d</sup> State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China



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## ABSTRACT

The magnetic refrigeration (MR) technology by utilizing the magnetocaloric (MC) effects of magnetic solids have been realized to be a promising energy efficiency and environmentally friendly technology. Developing or discovering proper magnetic solids with promising MC performances is one of the most important tasks at present stage since a huge gap still exists between the requirement of practical MR application and the MC performances of the magnetic solids. Herein, we reported a combined theoretical and experimental investigation of the crystal structure together with the magnetic properties, magnetic phase transition (MPT) and MC performances in Gd<sub>2</sub>MgTiO<sub>6</sub> oxide. The Gd<sub>2</sub>MgTiO<sub>6</sub> is confirmed to crystallize in a B-site ordered monoclinic double perovskite (DP) crystal structure. A rather unstable antiferromagnetic (AFM) interaction with large magnetic moment and semi-conductor characteristic with the band gap of 2.977 eV have been confirmed in Gd<sub>2</sub>TiMgO<sub>6</sub> DP oxide at ground state. Giant reversible cryogenic MC effect together with excellent MC performances have been confirmed by a series of the figure of merits including the values of maximum magnetic entropy change ( $-\Delta S_M$ ) and refrigerant capacity (RC), which are evaluated to be 46.21 J/kgK and 300.27 J/kg around 3.3 K with the magnetic change of 0–7 T, these values are much better than most of the recently reported famous cryogenic MC materials and the commercialized magnetic refrigerants gadolinium gallium garnet (GGG) as well. The observed excellent MC performances suggest that Gd<sub>2</sub>TiMgO<sub>6</sub> DP oxide is a promising candidate material for cryogenic MR applications.

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## 1. Introduction

The magnetic solids with both structural and magnetic phase transitions have attracted widespread attentions because of their unique and novel functional performances as well as potential applications in various advanced technologies [1–10]. Among those, the magnetic refrigeration (MR) method by utilizing the magnetocaloric (MC) effect of magnetic solids have been realized to be an attractive alternative technology to our current well-used gas compression/expansion technology [1–5]. The MC effect being an inherent magneto-thermodynamic phenomenon, manifests itself in the production and absorption of heat experienced by a magnet-

ically ordered material under the variation of external magnetic fields [1–3]. For this purpose, lots of studies have been dedicated for developing and discovering new materials exhibiting the appropriate MC effect at different working temperature regions from sub-Kelvin to the room temperature or above [11–22]. However, a huge gap still exists between the requirement of practical MR application and the MC performances of the magnetic solids. Developing and discovering proper magnetic solids with promising MC performances is one of the most important tasks at present stage.

The heavy rare earths (RE) based materials with highly localized 4f orbitals can be taken as good candidates for MC materials because of their large magnetic moments. Consequently, many selected RE based intermetallic compounds, oxides, amorphous alloys and molecular materials have been usually explored as potential magnetic refrigerants [23–33]. Several series RE-based intermetallics are reviewed very recently by Li and Yan in terms of the structure, magnetic phase transition (MPT) and MC perfor-

\* Corresponding author at: State Key Laboratory of Advanced Special Steels and Shanghai Key Laboratory of Advanced Ferrometallurgy and School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China.

E-mail address: [ykzhang@shu.edu.cn](mailto:ykzhang@shu.edu.cn) (Y. Zhang).

manes [25]. Similarly, we have summarized the MPT, magnetic and MC performances in  $RE_2T_2X$  series intermetallic compounds recently [24]. Additionally, the  $RE$ -based oxides have received particular attentions due to the fact of easy to be fabricated as well as good physical and chemical stabilities, especially for the low cost of raw materials. Thus, large numbers of the  $RE$ -based oxides have been fabricated and determined systematically in terms of the MPT and MC effects as well. The  $RE$ -based double perovskite (DP) oxide with the general formula of  $RE_2BB'O_6$  ( $B$  and  $B'$  are two different transition metal elements) is as a sub-class of perovskite oxide have attracted special attentions due to their flexible combination of  $RE$  and  $B$  elementals [33,34]. Outstanding electrical, magnetic, optical, catalytic as well as MC properties have been reported by several research groups independently in  $RE_2BB'O_6$  DP oxides by suitable combination and selection of the  $RE$  and  $B$  atoms in recent years [33–40]. Considerable MC performances have been reported by us recently in  $RE_2CuMnO_6$  [36] and  $RE_2FeAlO_6$  [37] DP oxides. The investigation of magnetic properties and MC performances in  $RE_2ZnMnO_6$  DP oxides with  $B$  site ordered structure [38] have illustrated that  $Gd_2ZnMnO_6$  exhibits excellent MCE performances with  $-\Delta S_M^{\max}$  of 25.2 J/kgK around 6.4 K under  $\Delta H$  of 0–7 T [38]. Very recently, Xu et al. have fabricated  $Sr_2GdNbO_6$  DP oxide and checked its magnetic properties and MC effect [39], pronounced  $-DS_M$  was realized with the peak value of 29.7 J/kgK around  $\sim 2$  K. Very recently, the luminescence properties in the pure and doped  $RE_2MgTiO_6$  DP oxides have been reported [40–42]. Whereas, the investigation on the magnetic and MC properties in  $RE_2MgTiO_6$  DP oxides are still lacking. Herein we have further investigated the crystal structure, magnetic properties, MPT and MC performances of  $Gd_2MgTiO_6$  DP oxide with aim to enlarge and deepen our understanding the fundamental mechanisms behind some of the DP oxides foundational performances and to figure out whether  $Gd_2MgTiO_6$  is suitable for application in cryogenic MR application. Our findings illustrate that the studied  $Gd_2MgTiO_6$  possesses a remarkably cryogenic giant MCE, which could be a promising candidate material for cryogenic MR applications.

## 2. Experimental and simulation details

The polycrystalline  $Gd_2MgTiO_6$  oxide was synthesized by the transitional ceramic sol-gel route. Firstly, stoichiometric weight amount of  $Gd(NO_3)_3$ ,  $Mg(NO_3)_2$  and  $Ti(SO_4)_2$  with the minimum purity better than 99.99% were completely dissolved into the deionized  $H_2O$  at ambient. Then, the citric acid (CA) was adjusted with the molar ratio of 2:1 for (CA):(Gd<sup>3+</sup>+Mg<sup>2+</sup>+Ti<sup>3+</sup>). After that, the solution was evaporated by continuous stirring at 355 K to obtain an organic resin that includes a homogeneous distribution of all the cations, consequently the resin was directly dried at 373 K for 12 h in air. Later on, the resulting dried gel was grounded and fired at 800 K for 5 h to eliminate all the organic residues, sulfates and nitrates. Finally, the well-prepared precursors were ground again and cold-pressed under 30 MPa pressure into small thin pellets and annealed for 28 h at 1423 K followed by furnace cooling. All the samples are stable in the air at least up to several months. The crystal structure of  $Gd_2MgTiO_6$  was identified by X-ray diffraction (XRD) at room temperature which is performed on a Rigaku-SmartLab-9KW diffractometer. XRD patterns have been collected in an angular range of 20–80° with a step of 0.02° on a grounded power sample. The microstructure, elements distribution and chemical compositions of  $Gd_2MgTiO_6$  were analyzed on a JSM-7800F scanning electron microscope (SEM) with the Energy Dispersive X-Ray Spectroscopy (EDS) options using an accelerating voltage of 20 kV. The magnetic and MC properties of  $Gd_2MgTiO_6$  were carried out using a superconducting quantum interference device (SQUID) magnetometer which was an option of magnetic properties measurement system (MPMS-7T, Quantum Design) in the tem-

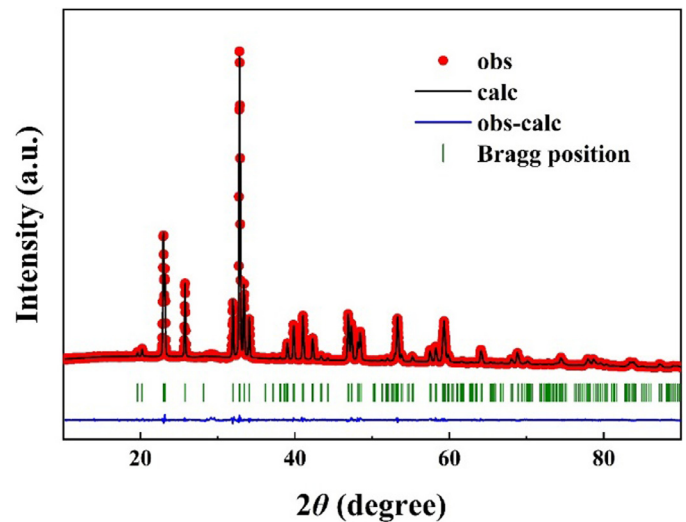


Fig. 1. The room temperature XRD pattern for  $Gd_2MgTiO_6$  DP oxide.

perature range of 1.8–300 K and the magnetic field range of 0–7 T. The results of heat capacity under 0 and 7 T were measured by using the physical property measurement system (PPMS-9T, Quantum Design).

The atomic-level first-principles calculations based on density functional theory (DFT) were performed for unveiling the electronic and magnetic structure of  $Gd_2MgTiO_6$  DP oxide. The standard Vienna *ab initio* Simulation Package (VASP) [43,44] was employed using plane waves to reproduce the one-electron wave functions with an energy of cutoff of 520 eV for constructing the basis set and projected augmented waves (PAW) pseudopotentials for all the species involved. And the valence electrons contributions in pseudopotentials are as  $[5s^2 5p^6 4f^7 5d^1 6s^2]$  for Gd,  $[3s^2]$  for Mg,  $[3d^2 4s^2]$  for Ti and  $[2s^2 2p^4]$  for O. Thus, the  $f$  electrons of Gd atom were firmly considered to accurately describe its magnetism. The electronic exchange and correlation were modeled by the Perdew-Burke-Ernzerhof (PBE) functional within the spin polarized generalized gradient approximation (GGA) [45]. Structural optimizations were performed using a conjugate gradient algorithm until the Hellman-Feynman forces were converged to less than 0.01 eV/Å and each self-consistent electronic loop converged to a tolerance smaller than  $10^{-6}$  eV. And the  $k$ -points grid using Monkhorst-Pack method was set as  $9 \times 9 \times 7$  for structural optimizations and static self-consistent calculations. To accurately compute the electronic properties, the  $k$ -points grid was set as  $13 \times 13 \times 11$ .

## 3. Results and discussion

The experimentally obtained XRD pattern for  $Gd_2MgTiO_6$  powder sample along with the Rietveld refinement by the FULLPROF software [46] are plotted in Fig. 1. Both conventional perovskite-type  $Pbnm$  and  $B$ -site ordered  $P2_1/n$  (No. 14) space group were performed in the refinement. A better fitting result with the  $P2_1/n$  space group is realized, and therefore the  $Gd_2MgTiO_6$  crystallizes with monoclinic DP-type  $P2_1/n$  symmetry. The refinement pattern shows phase-purity and crystallographic information of the oxide without any signature of impurity phases. The reasonable and goodness of fit of  $R_p$ ,  $R_{wp}$  and  $R_f$  are evaluated to be 2.25, 1.67%, 2.18% and 1.45%, respectively. The lattice parameters of  $a$ ,  $b$ ,  $c$  and  $V$  are determined to be 5.3636(9) Å, 5.5997(2) Å, 7.6819(6) Å and 230.72(9) Å<sup>3</sup>, respectively. Moreover, the tolerance factor  $t$ ,  $t = \frac{r_{RE} + r_O}{\sqrt{2}(r_B + r_O)}$  where  $r$  is ionic radius, can be used to evaluate the structural stability of perovskite-type oxides [47], which can only

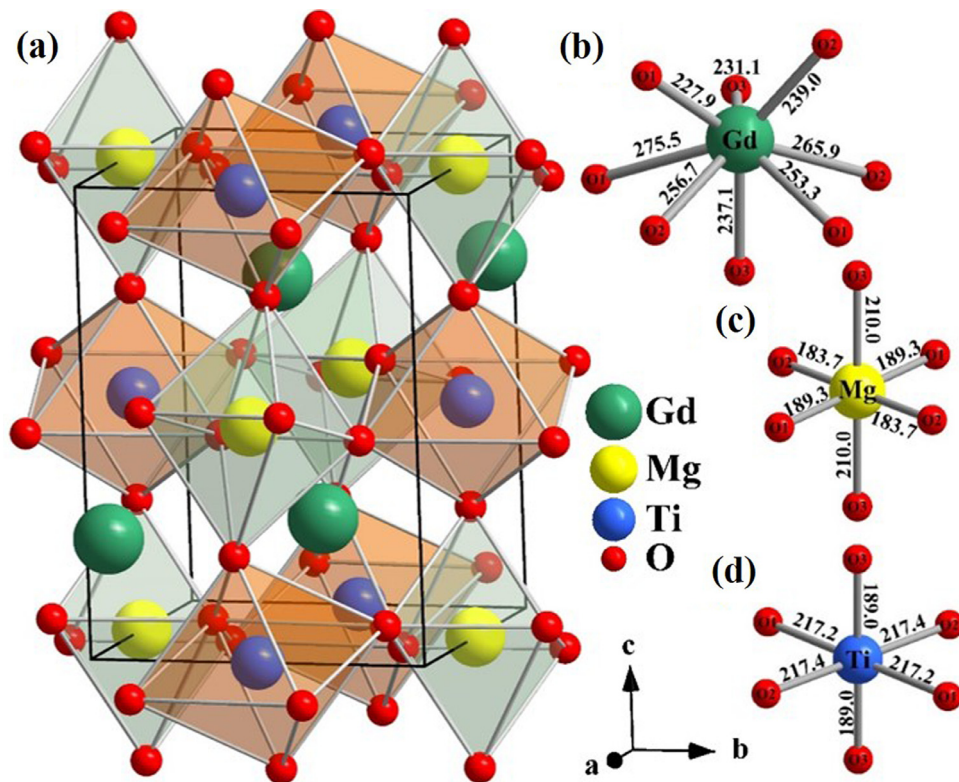


Fig. 2. The crystal structure (a) and atomic environment (b–d) for  $\text{Gd}_2\text{MgTiO}_6$  DP oxide.

be stable with  $t$  ranging from 0.78 to 1.05. The value of  $t$  for  $\text{Gd}_2\text{MgTiO}_6$  is 0.840, which also verifies the stability of DP-type crystal structure. Fig. 2(a–d) illustrate the detailed crystal structure of  $\text{Gd}_2\text{MgTiO}_6$  DP oxide and near-neighbor environments of constituent elements. In a single ordered unit, it has 20 independent atoms including two Mg atoms, two Ti atoms and twelve O atoms. Both Mg and Ti atoms coordinate with six O atoms forming the  $\text{MgO}_6$  and  $\text{TiO}_6$  octahedron, respectively. The bond distance ranges and average bond distance are 1.837–2.100 Å and 1.943 Å, as well as 1.890–2.174 Å and 2.079 Å for  $\text{MgO}_6$  and  $\text{TiO}_6$ , respectively. The O–Mg–O and O–Ti–O bond angles for  $\text{MgO}_6$  and  $\text{TiO}_6$  units range from 86.293° to 92.097° and 88.631° to 92.330°, respectively. Gd atom locates in the gap of  $\text{MgO}_6/\text{TiO}_6$  octahedron forming the 8-coordination polyhedron with the bond distances from 2.279 Å to 2.755 Å. The occupation sites for Gd are 4e Wyckoff position, Mg and Ti ions are independent positions of 2d and 2c, while there exist three different O ions (O1, O2 and O3) and they are assumed three different 4e sites, respectively. Furthermore, the atomic environment information of the constituent elements is summarized in Table 1 for  $\text{Gd}_2\text{MgTiO}_6$  DP oxide. Fig. 3(a–e) illustrate the secondary electron SEM image of the typical microstructure together with the element EDS mapping results of  $\text{Gd}_2\text{MgTiO}_6$  DP oxide. The prominent grain boundaries and high density nature confirm  $\text{Gd}_2\text{MgTiO}_6$  DP oxide possessing pronounced polycrystalline nature. A number of EDS mapping analysis were performed and fractions confirmed the stoichiometric compositions of 19.36 mol%, 10.26 mol%, 11.42 mol% and 58.96 mol% for Gd, Ti, Mg and O atoms [as illustrated in Fig. 3(b–e)], respectively, which are rather close to the nominal atomic ratio 2:1:1:6 of synthesized  $\text{Gd}_2\text{MgTiO}_6$  oxide.

Moreover, the *ab initio* calculations based on DFT can also provide valuable information of the crystal structure, charge transfer, distribution of magnetic moment and electronic structure by GGA method [43–45]. To further check the stability of the crystal structure, the ordered DP structure of monoclinic  $P2_1/n$  space

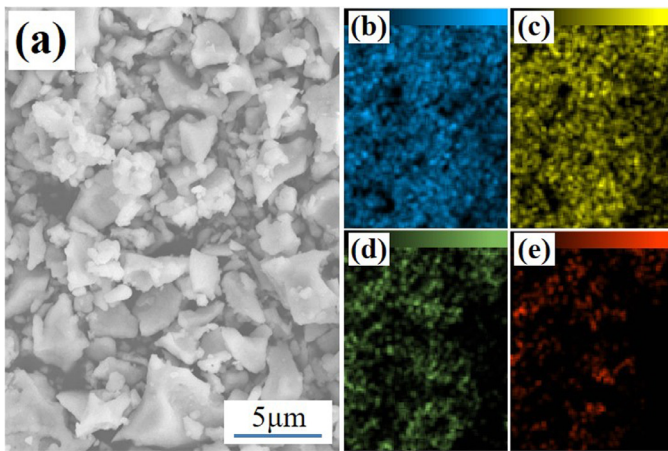
Table 1

The structure parameters for  $\text{Gd}_2\text{MgTiO}_6$  DP oxide.

Parameters	Wyckoff position	$\text{Gd}_2\text{MgTiO}_6$
Space group		$P2_1/n$ (No.14)
$a$ (Å)		5.3636(9)
$b$ (Å)		5.5997(2)
$c$ (Å)		7.6819(6)
$V$ (Å <sup>3</sup> )		230.72(9)
Gd	4e (x, y, z)	
x		0.5152(4)
y		0.5605(5)
z		0.2462(6)
Mg	2d (1/2, 0, 0)	
Ti	2c (0, 1/2, 0)	
O <sub>1</sub>	4e (x, y, z)	
x		0.0988(8)
y		0.4713(3)
z		1/4
O <sub>2</sub>	4e (x, y, z)	
x		0.3207(7)
y		0.7281(4)
z		−0.0477(8)
O <sub>3</sub>	4e (x, y, z)	
x		0.4048(1)
y		0.9698(0)
z		0.2641(9)
$c^2$		3.05
$R_p$ (%)		1.67
$R_{wp}$ (%)		2.18
$R_f$ (%)		1.45

group as detected by the XRD was selected as the initial structure for optimization. The lattice parameters  $a$ ,  $b$ ,  $c$  were determined as 5.34845 Å, 5.64097 Å and 7.71152 Å, respectively. The differences of optimized lattice parameters with the experimental results from XRD is less than 1%, which suggests the crystal structure by optimization is reasonable and available. Therefore, optimal structure was adopted in the following calculations. Fig. 4(a–c) il-



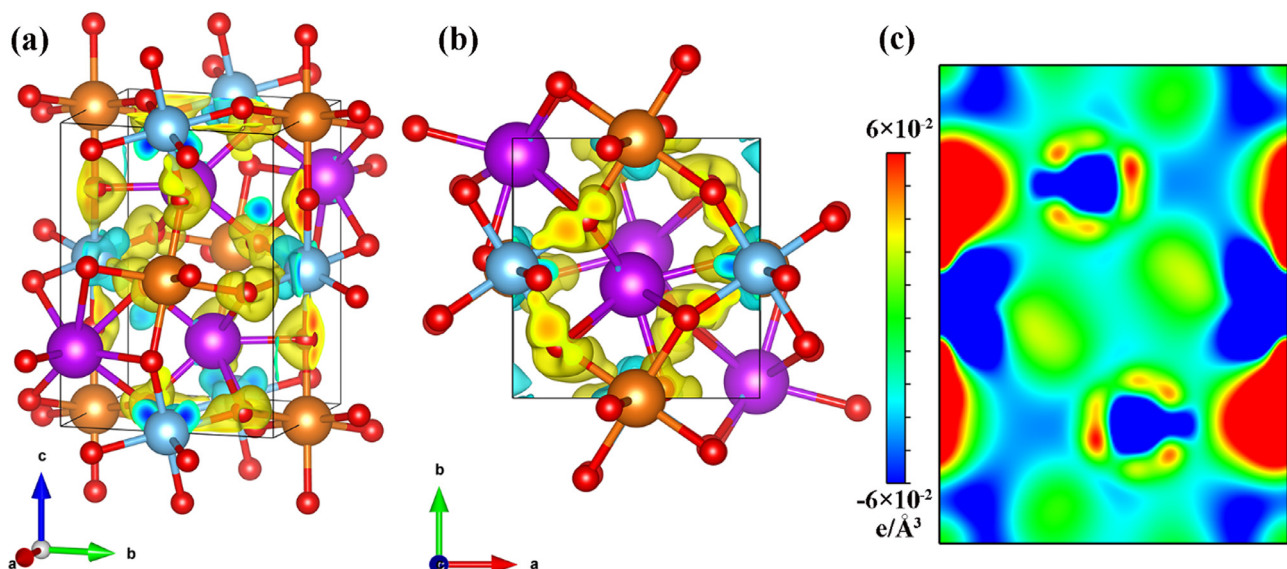


**Fig. 3.** The Scanning electron microscopy (SEM) image (a) and the distributions of Gd, Mg, Ti and O elements (b–e) for  $Gd_2MgTiO_6$  DP oxide.

illustrate the difference charge density, which describe the charge transfer between metal ions and oxygen ions, where Fig. 4(c) illustrates the diagram at (100) cross section. Obviously, the charge is transferred from  $Ti^{4+}$  and  $Mg^{2+}$  to  $O^{2-}$  indicating the formation of ionic bond between  $Ti^{4+}$  ( $Mg^{2+}$ ) and  $O^{2-}$ , whereas, the charge around  $Gd^{3+}$  is well localized, which indicates the  $Gd^{3+}$  probably has large local magnetic moment. Moreover, to determine the magnetic ground state of  $Gd_2MgTiO_6$  DP oxide, the total energy ( $E_{tot}$ ) at various potential magnetic structures were calculated. Due to the single magnetic component in this oxide, parallel magnetic state and three typical anti-parallel magnetic states were set for  $Gd^{3+}$  ions which are defined as FM, C-AFM, A-AFM and G-AFM states and the spin configuration which are given in Fig. 5(a–d), respectively. The values of  $E_{FM}$ ,  $E_{C-AFM}$ ,  $E_{A-AFM}$  and  $E_{G-AFM}$  are  $-99.37188$ ,  $-99.37631$ ,  $-99.37462$  and  $-99.40434$  eV/f.u., respectively. Apparently, the anti-parallel magnetic moment of  $Gd^{3+}$  ions have lower  $E_{tot}$  than parallel magnetic moment, which proves that the type of G-AFM coupling is present in  $Gd_2MgTiO_6$  DP oxide. Moreover, the atomic magnetic moment of  $Gd^{3+}$  is determined as  $7 \mu_B$ . According to the state of anti-parallel magnetic ground state, the total density of states (DOS) of this oxide and partial DOS of each elements indicating the information of the electronic structure were

calculated by ab initio calculations with GGA+PBE method and the results are illustrated in Fig. 5(e). Obviously, a large band gap with the value of 2.977 eV proves the existence of semi-conductor characteristic in  $Gd_2MgTiO_6$  DP oxide. And the 4f orbital of  $Gd^{3+}$  ions have obvious splitting behavior in the range of  $\sim 3.003\text{--}3.854$  eV, which suggests each  $Gd^{3+}$  ion will spontaneously polarize to produce large magnetic moment. However, in the different positions of  $Gd^{3+}$  ions, the spins of electron are opposite, indicating that the magnetic moments generated spontaneously are canceled out, exhibiting the AFM ground state, which probably causes by hybridizing of electrons of  $Ti^{4+}$  and  $Gd^{3+}$  and proves the origin of AFM in  $Gd_2MgTiO_6$  DP oxide. Moreover, the total DOS is mainly controlled by partial DOS of  $Gd^{3+}$  ions from  $\sim 3.003$  to  $\sim 3.854$  eV and by partial DOS of  $Ti^{4+}$  ions from  $\sim 5.403$  to  $7.226$  eV, and hybridize with  $O^{2-}$  ions in the corresponding range. Below the fermi level, the total DOS is mainly contributed by  $O^{2-}$  ions, and  $Mg^{2+}$  and  $Ti^{4+}$  ions hybridize with  $O^{2-}$  ions in the range from  $\sim -4.195$  to  $\sim 0$  eV. Compared with  $Mg^{2+}$  and  $Ti^{4+}$  ions, partial DOS of  $Gd^{3+}$  and  $O^{2-}$  have a lower degree of overlap in the range of  $-2.313\text{--}1.432$  eV.

To further probe the magnetic properties and MPT, the temperature dependent magnetic susceptibility  $\chi (=M/H)$ , the  $\chi(T)$  curves, for  $Gd_2MgTiO_6$  DP oxide was measured in terms of field cooling (FC) and zero-field cooling (ZFC) protocols with an external field  $H$  of 0.01 T, as illustrated in Fig. 6(a). The results suggest that  $c$  increases monotonously with the decrease of temperature, and exhibit a peak at around the Néel temperature  $T_N \sim 3.3$  K, then decreases gradually with further increased of temperature, these behaviors suggesting a long-range MPT from paramagnetic to antiferromagnetic (PM to AFM) transition in  $Gd_2MgTiO_6$  DP oxide. The FC and ZFC  $\chi(T)$  curves are well overlapped in the whole measured temperature regime and thus there exists a negligible thermal hysteresis during their MPT in  $Gd_2MgTiO_6$  DP oxide. The perfect reversibility of MPT is desirable for RE based materials, making the  $Gd_2MgTiO_6$  DP oxide potentially interesting of practical cryogenic MR application. Furthermore, the  $c(T)$  curves under various magnetic fields from 0.2, 1, 2, 3.5 and 5 T for  $Gd_2MgTiO_6$  DP oxide are also illustrated in Fig. 6(a). Generally, the  $\chi(T)$  curves show similar behaviors, except the peak temperature decreases slightly with increasing  $H$ , with  $H$  up to 3 T. Whereas, the  $c$  increases continuously with decreasing temperature under high magnetic fields of 3.5 and 5 T, and only some change in slope (as marked by arrows) at low temperature can be observed. These behaviors are



**Fig. 4.** The charge density difference with the 3D-display (a), along the  $c$  direction (b) and 2D-display in (100) plane (c) for  $Gd_2MgTiO_6$  DP oxide.

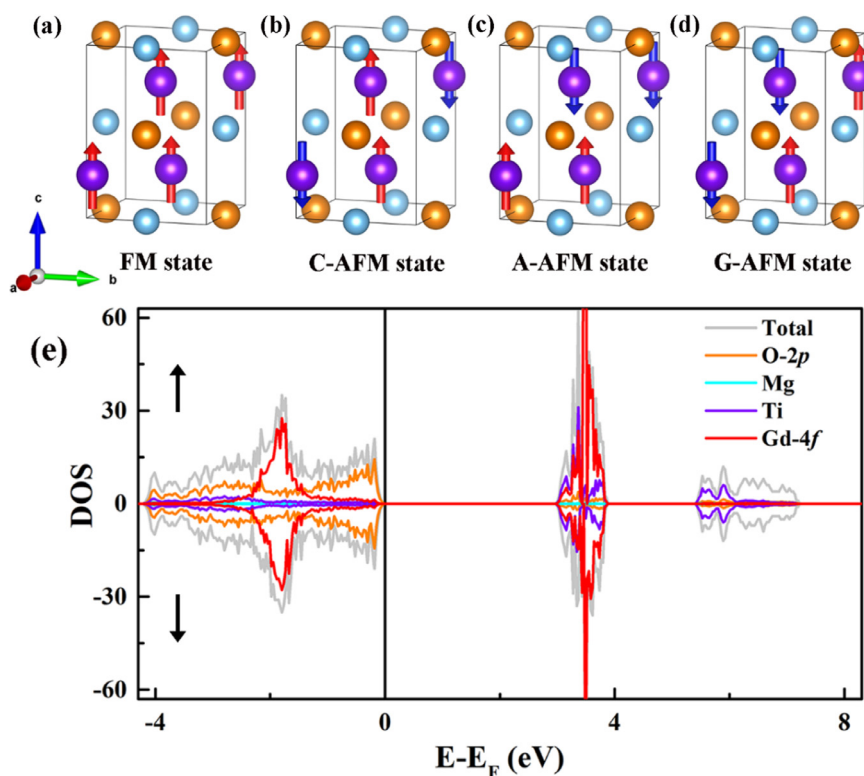


Fig. 5. (a–d): Four potential magnetic structure for  $Gd_2MgTiO_6$  DP oxide. (e): The total DOS and partial DOS of O-2p, Mg, Ti, and Gd-f for  $Gd_2MgTiO_6$  DP oxide.

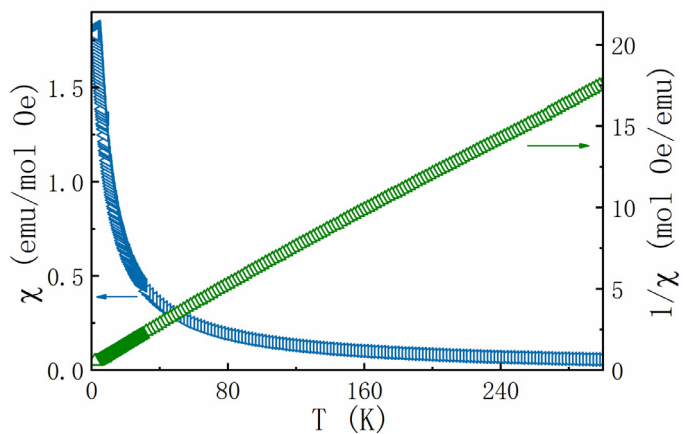
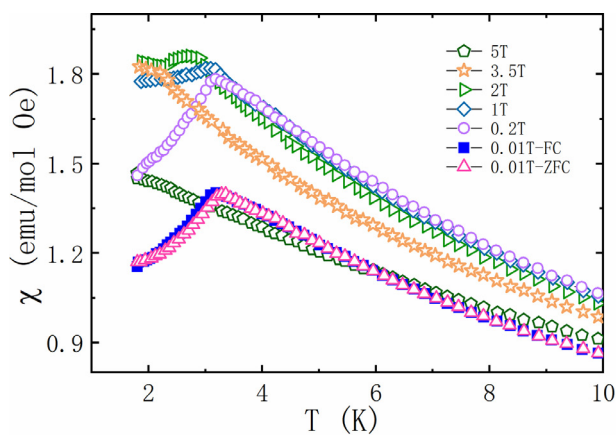


Fig. 6. (a): The  $\chi(T)$  curves under various magnetic fields including  $c(T)$  curves with ZFC and FC modes under 0.01 T for  $Gd_2MgTiO_6$  DP oxide. (b): The  $\chi(T)$  (left axis) and  $1/\chi(T)$  (right axis) curves under  $H$  of 1 T for  $Gd_2MgTiO_6$  DP oxide.

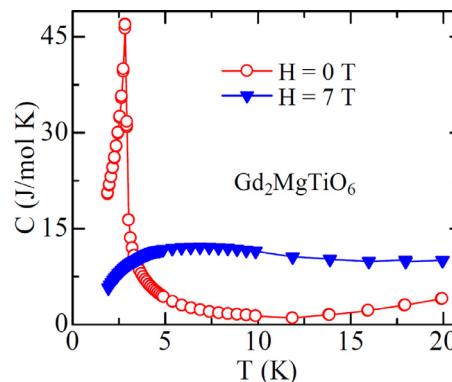
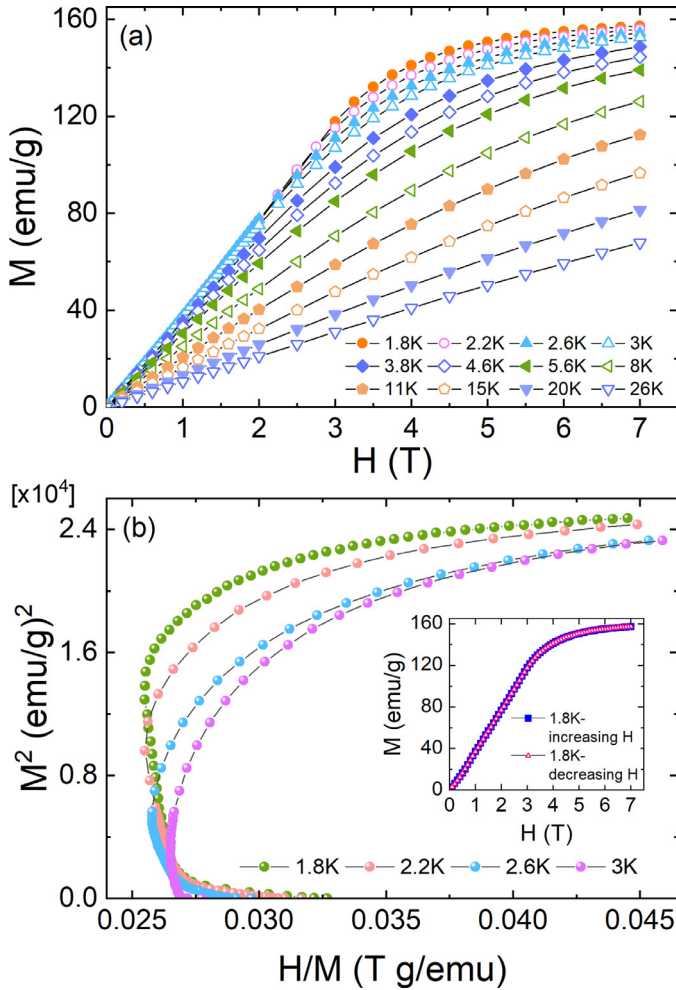


Fig. 7. The  $C(T)$  curves under the magnetic fields of 0 and 7 T for  $Gd_2MgTiO_6$  DP oxide.

fully consistent with the weakly interacting spins (dipolar). The  $\chi(T)$  curve (left scale) and the reciprocal susceptibility  $1/\chi(T)$  under  $H$  of 1 T are illustrated in Fig. 6(b). Clearly, the  $1/\chi(T)$  curve nicely follows the Curie-Weiss law:  $\chi(T) = C/(T - \theta_p)$ , where  $q_p$  denotes PM Curie temperature and  $C$  denotes Curie constant with  $C = N(\mu_B \mu_{eff})^2 / 3k_B$  ( $\mu_{eff}$ : effective magnetic moment). Their linear fits yield negative  $q_p$  value of  $-5.6$  K which is indicating the AFM interaction at the ground state. The  $\mu_{eff}$  value of  $7.98 \mu_B/f.u.$  which is very close to that of the theoretical calculated free  $Gd^{3+}$  ions ( $7.94 \mu_B$ ). These experimental observed magnetic properties for  $Gd_2MgTiO_6$  DP oxide are consistent with those of theoretically predicted results. The temperature dependent heat capacity  $C(T)$  curves for  $Gd_2MgTiO_6$  DP oxide was measured under the magnetic fields of 0 and 7 T, as illustrated in Fig. 7. The observed pronounced peak around 3.0 K in the  $C(T)$  curves under zero magnetic field is corresponding to the MPT which was confirmed by the magnetiza-



**Fig. 8.** The  $M(H)$  curves (a) and the Arrott plots ( $M^2-H/M$ ) curves (b) for  $Gd_2MgTiO_6$  DP oxide. Inset of (b) displays the  $M(H)$  curves with increasing and decreasing magnetic field at 1.8 K.

tion measurement, whereas, only a broad hump can be observed in the  $C(T)$  curves under the magnetic field of 7 T.

To further identify the MPT and MC properties of  $Gd_2MgTiO_6$  DP oxide, series isothermal magnetization  $M(H)$  curves were determined with applied  $H$  up to 7 T in the temperature range of 1.8–30 K, as illustrated in Fig. 8(a). The value of  $M$  at 1.8 K increases linearly with the increasing  $H$  up to 4 T, above which show a saturation behavior with the magnetic moment as high as  $13.73 m_B$  per formula (two  $Gd^{3+}$  ions), which is almost 98% of the theoretical value of  $7.0 \mu_B$  for a non-interacting  $Gd^{3+}$  single ion. Since the  $Ti^{4+}$  and  $Mg^{2+}$  sub-lattices have no contribution on the overall magnetism, thus the  $Gd^{3+}$  sub-lattice should be in charge of the magnetism of  $Gd_2MgTiO_6$  DP oxide. In addition,  $M(H)$  curves at 1.8 K with increasing  $H$  and decreasing are illustrated in the inset of Fig. 8(b). Both curves overlap well with each other during the whole measured magnetic field range, suggesting no magnetic hysteresis in  $Gd_2MgTiO_6$  DP oxide. Accordingly, a giant reversible MC effect would be happened at low temperature in  $Gd_2MgTiO_6$  which is of great importance for practical MR application. It is well accepted that MC effect of the magnetic solids has strong relationship with the MPT, it is therefore crucial to confirm the orders of the corresponding MPT for  $Gd_2MgTiO_6$  DP oxide. The MPT nature is further confirmed by using the Arrott plots based on the Banerjee criterion [48] which were constructed from the already recorded sets of  $M(H)$  curves. In principle, the negative or positive

slopes in  $M^2$  vs.  $H/M$  plots are indicative of a first or second-order phase transition (F/SOPT) for a magnetic solid. The curves at low temperatures of 1.8, 2.2, 2.6 and 3 K show negative slopes [as illustrated in Fig. 8(b)], which probably indicates the occurrence of FOPT in  $Gd_2MgTiO_6$  DP oxide.

Generally, the investigation on the MC effect is based on the analysis of the temperature and magnetic field change ( $\Delta H$ ) dependences of magnetic entropy change ( $-\Delta S_M$ ), which is derived according to the Maxwell thermodynamic relation by Eqs. (1) and (2) [13–16]:

$$\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0) = \int_0^H \left( \frac{\partial M(T, H)}{\partial T} \right) H dH \quad (1)$$

and from the temperature dependence of the heat capacity (as illustrated in Fig. 7) under the zero magnetic field  $C(T, H_0)$  and applied magnetic field  $C(T, H_1)$  by using the equation,

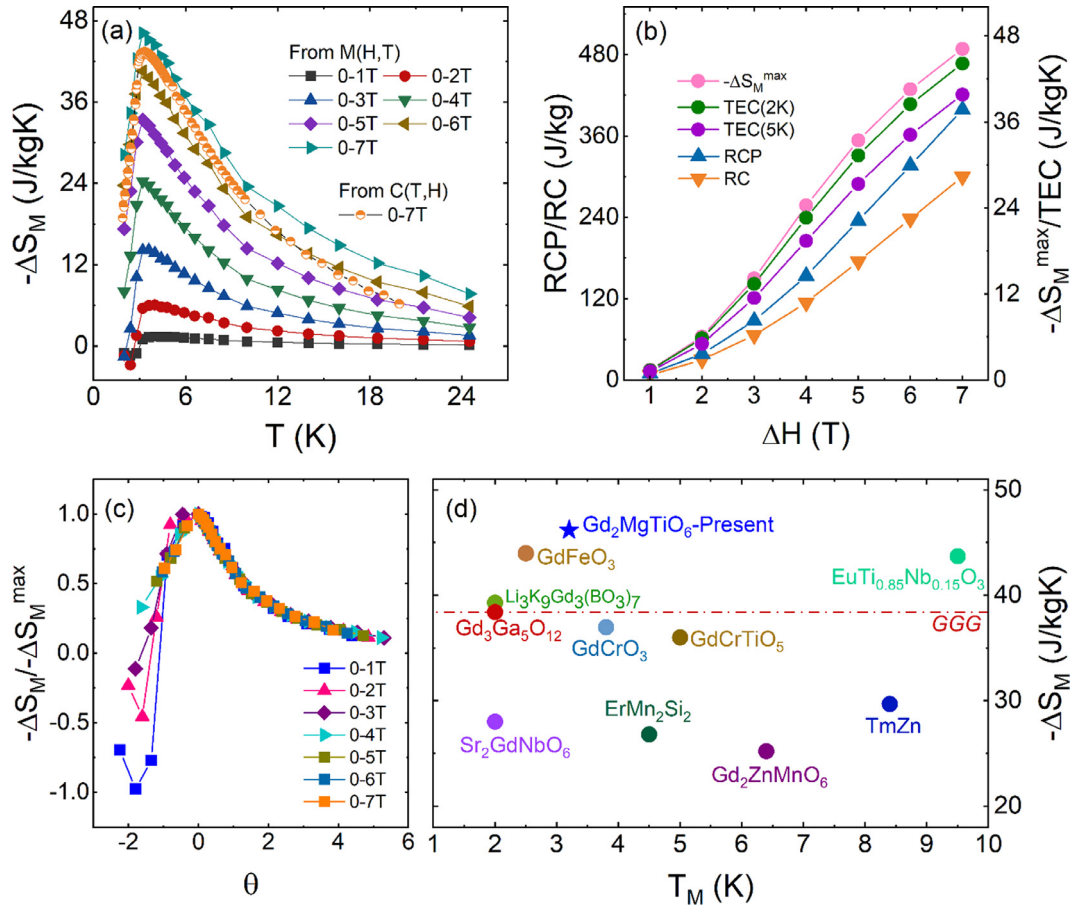
$$\Delta S_M(T, \Delta H) = [S(T)_{H_1} - S(T)_{H_0}]_T = \int_0^T \frac{C(T, H_1) - C(T, H_0)}{T} dT, \quad (2)$$

respectively. The evaluated temperature dependence of  $-\Delta S_M$  calculated from  $M(H, T)$  and  $C(T, H)$  data for  $Gd_2MgTiO_6$  DP oxide are all illustrated in Fig. 9(a) under several typical  $\Delta H$  up to 0–7 T. The results obtained by using both methods are generally in consistent with each other. The  $-\Delta S_M$  values for  $Gd_2MgTiO_6$  DP oxide rise progressively with decreasing temperature above  $T_N$  and increase gradually with increasing  $H$ , which is in accordance with the usual behavior of MC effects. It is well known that the commercial permanent magnet is difficult to generate the magnetic field higher than 2 T, large values of  $-\Delta S_M$  under low magnetic field changes are feasible to design the MR cycle using permanent magnets. The maximum value of positive  $-\Delta S_M$  ( $-\Delta S_M^{\max}$ ) is 6.06 J/kgK with  $\Delta H$  of 0–2 T. The moderate values of  $-\Delta S_M$  under low  $\Delta H$  would limit its practical application by using the permanent magnet. Moreover, we should note that the value  $-\Delta S_M^{\max}$  increases continuously with increasing  $\Delta H$ , as illustrated in Fig. 9(b). The values of  $-\Delta S_M^{\max}$  under  $\Delta H$  of 0–7 T are as high as 46.21 and 43.46 J/kgK calculated from  $M(H, T)$  and  $C(T, H)$  data, respectively. In the below, we use the  $\Delta S_M$  data obtained from the  $M(H, T)$  for comparison with other MC materials which were calculated in the similar way. This value is much larger than that of the commercialized famous gadolinium gallium garnet  $Gd_3Ga_5O_{12}$  (abbreviated as GGG) developed has long been deemed as the benchmark cryogenic MC material with  $-\Delta S_M^{\max}$  of 38.4 J/kgK under  $\Delta H$  of 0–7 T around 2.0 K [13,49]. Moreover, this value at 0–7 T is still far below the theoretical limitation  $-\Delta S_{M\text{-limit}}$  which is usually produced by using the contribution of the uncoupled  $Gd^{3+}$  ions and can be approximately evaluated by the Eq. (3) [17]:

$$-\Delta S_{M\text{-limit}} = R \ln(2S + 1) \quad (3)$$

in which  $R$  presents the gas constant, and  $S$  presents the half-filled  $4f$  orbital of  $Gd^{3+}$  ions with a large spin state of  $S = 7/2$ . The calculated upper limit of  $-\Delta S_{M\text{-limit}}$  is 71.59 J/kgK for  $Gd_2MgTiO_6$  DP oxide. Such differences would be probably related to the additional internal entropy loss from the phonon contribution and the limitation of  $\Delta H$  for present measurements. By considering the fact of that the  $-\Delta S_M^{\max}$  value does not show any saturation trends with  $\Delta H$  up to 0–7 T, thus a much larger  $-\Delta S_M^{\max}$  would be attained for  $Gd_2MgTiO_6$  DP oxide by further increasing  $\Delta H$ . Moreover, the temperature-averaged magnetic entropy change,  $TEC$ , has been recently introduced as an important figure of merit [50] to further examine the performances of the MC materials. The  $TEC$  considers the mean value at the certain temperature span ( $\Delta T_{\text{iff}}$ ) under a





**Fig. 9.** (a): The  $-\Delta S_M(T)$  curves from 0 to 1 to 0–7 T of  $Gd_2MgTiO_6$  DP oxide. (b): The magnetic field change  $\Delta H$  dependence of  $TEC(2/5\text{ K})$  and  $-\Delta S_M^{\max}$  together with the RCP and RC for  $Gd_2MgTiO_6$  DP oxide. (c): The  $(\Delta S_M(T)/\Delta S_M^{\max})$  vs. rescaled temperature ( $\theta$ ) curves of  $Gd_2MgTiO_6$  DP oxide. (d): The comparison of  $-\Delta S_M^{\max}$  for the present  $Gd_2MgTiO_6$  DP oxide and some famous RE-based MC materials with working temperature below 10 K.

fixed  $\Delta H$  and has been described by Eq. (4)

$$TEC(\Delta T_{\text{lifft}}) = \frac{1}{\Delta T_{\text{lifft}}} \max_{T_{\text{mid}}} \left\{ \int_{T_{\text{mid}} - \frac{\Delta T_{\text{lifft}}}{2}}^{T_{\text{mid}} + \frac{\Delta T_{\text{lifft}}}{2}} \Delta S_M(T)_{\Delta H, T} dT \right\} \quad (4)$$

$T_{\text{mid}}$  is the value of the temperature at the center of the average and selected the largest value for a given  $\Delta T_{\text{lifft}}$ . Two different  $\Delta T_{\text{lifft}}$  values of 2 K and 5 K are chosen to evaluate the value of  $TEC$  for the  $Gd_2MgTiO_6$  DP oxide. The resulting values of  $TEC(2\text{ K})$  and (5 K) values at  $\Delta H$  of 0–7 T are 44.15 and 39.84 J/kgK for  $Gd_2MgTiO_6$ , respectively. Similar  $\Delta H$  dependent trend of  $TEC(2\text{ K})$ ,  $TEC(5\text{ K})$  and  $-\Delta S_M^{\max}$  for  $Gd_2MgTiO_6$  DP oxide can be observed, as given in Fig. 9(b). Obviously, the values of  $TEC(2\text{ K})$  are much closer to the calculated  $-\Delta S_M^{\max}$  as compared to the values calculated for  $TEC(5\text{ K})$ . The reason should ascribe to the fact that the peak width is slightly narrow, thus a small  $\Delta T_{\text{lifft}}$  will result in little reduction of the  $TEC$ . Moreover, the relative cooling power (RCP) as expressed by Eq. (5) and refrigerant capacity (RC) as expressed by Eq. (6) are another two well-known correlated factors [24–26] which enable us to evaluate the amounts of energy that can be transferred between the cold end and hot end in an ideal MR cycle.

$$RCP = |\Delta S_M^{\max}| \times \delta TFWHM \quad (5)$$

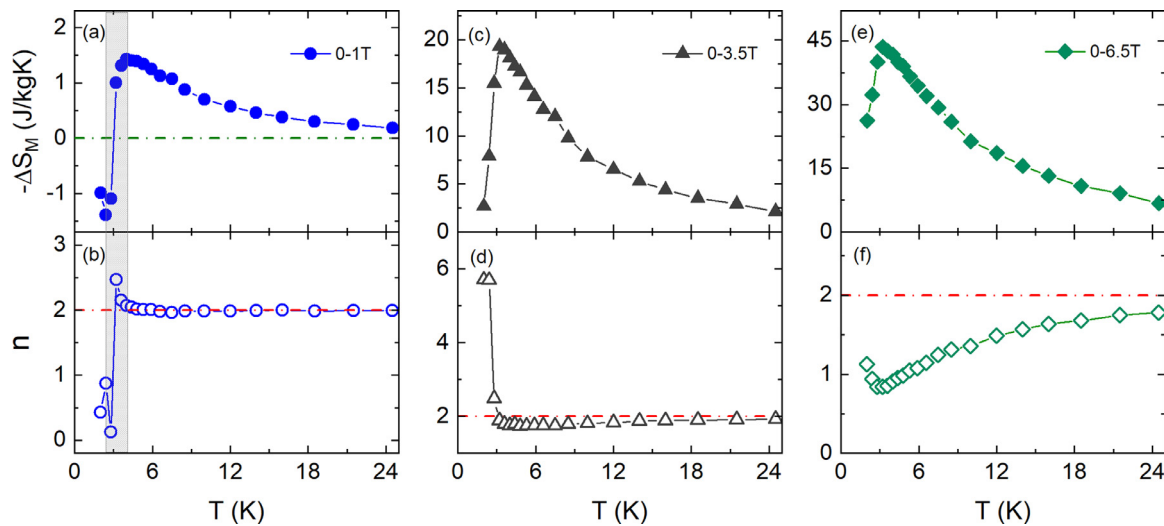
$$RC = \int_{T_{\text{cold}}}^{T_{\text{hot}}} |\Delta S_M(T)| dT, \quad (6)$$

where integration limits ( $T_{\text{cold}}$  and  $T_{\text{hot}}$ ) represent the two sides at  $\frac{1}{2} |\Delta S_M^{\max}|$  value of  $-\Delta S_M(T)$  profile, and  $\delta TFWHM (= T_{\text{hot}} - T_{\text{cold}})$ .

The RC and RCP against  $\Delta H$  are also displayed in the right-hand side axis of Fig. 9(b). Significantly, RC and RCP show similar increasing tendency of continuous increase with  $\Delta H$ . The calculated RCP/RC values are 38.77/30.04 and 399.05/300.03 J/kg for  $Gd_2MgTiO_6$  DP oxide, with  $\Delta H$  of 0–2 and 0–7 T, respectively. For a more direct observation of MC performances, we use the  $\Delta S_M^{\max}$  values for judgement. A comparison of representative of recently reported famous RE-based MC materials [38,39,49,51–57] with the working temperatures below 10 K of their  $-\Delta S_M$  under  $\Delta H$  of 0–7 T have been summarized in Fig. 9(d). As can be seen, the  $-\Delta S_M^{\max}$  is dramatically as high as 46.21 J/kgK for  $Gd_2MgTiO_6$  DP oxide, approximately 20% higher than that of the commercialized magnetic refrigerant GGG (38.4 J/kgK under  $\Delta H$  of 0–7 T) [49], and outperform most of the famous recently reported MC materials at cryogenic temperature region. The present results indicate that  $Gd_2MgTiO_6$  DP oxide is an excellent MC material working at the temperature region for the liquefaction of helium.

Additionally, a phenomenological constructed universal curve [58,59] has been proposed and widely applied by normalizing the  $-\Delta S_M(T)$  curve to its peak  $-\Delta S_M^{\max}$  as  $\Delta S' (= \Delta S_M(T)/\Delta S_M^{\max})$ , and rescaling the temperature axis to  $(T - T_{\text{peak}})/(T_r - T_{\text{peak}})$  as  $\theta$ , in which  $T_{\text{peak}}$  denotes the temperature of  $-\Delta S_M^{\max}$ , and  $T_{r1}$  and  $T_{r2}$  denote the temperatures corresponding to  $0.6 \times \Delta S_M^{\max}$  above and below  $T_c$  for each  $\Delta H$ , respectively, and is expressed by Eq. (7):

$$\theta = \begin{cases} -(T - T_{\text{peak}})/(T_{r1} - T_{\text{peak}}), & T \leq T_{\text{peak}} \\ (T - T_{\text{peak}})/(T_{r2} - T_{\text{peak}}), & T > T_{\text{peak}} \end{cases} \quad (7)$$



**Fig. 10.** The temperature dependence of  $\Delta S_M$  and corresponding exponent  $n$  under different fields of 0–1, 0–3.5 and 0–6.5 T for  $Gd_2MgTiO_6$  DP oxide.

The processed  $\Delta S'$  ( $\theta$ ) curves for  $Gd_2MgTiO_6$  DP oxide are depicted in Fig. 9(c). It can be noticed that all the  $\Delta S'$  ( $\theta$ ) curves show clear branches below MPT, whereas a single master curve behavior can be observed above MPT, which resembles the existing both first-order and second-order MPTs for present  $Gd_2MgTiO_6$  DP oxide at different temperature zones, respectively.

Furthermore, the order of MPT can be checked by novel MC criterion, the field dependence exponent of  $\Delta S_M$  which was computed according to the Eq. (8) [60–62]:

$$n(T, H) = \frac{d \ln |\Delta S_M|}{d \ln H} \quad (8)$$

Fig. 10 illustrates the temperature dependence of  $\Delta S_M$  and exponent  $n$  under three different  $\Delta H$  of 0–1, 0–3.5 and 0–6.5 T for  $Gd_2MgTiO_6$  DP oxide. Previous investigation suggested that, a clear overshoot of  $n$  above 2 should be existed in the  $n(T)$  curves for a FOPT material around its transition temperature [60–62]. For  $\Delta H$  of 0–1.5 T, an obvious characteristic spike can be observed as displayed in the shaded gray zone, suggesting the switching from inverse to conventional MCE. The  $n$  value just shows a small increase but below 2 within the inverse MCE region, which is ascribed to the ultralow MPT of  $Gd_2MgTiO_6$  oxide, as shown in Fig. 10(a) and (b). For  $\Delta H$  of 0–3.5 T, the overshoot feature ( $n$  above 2) can be clearly noted at low temperatures, which indicates the FOPT nature of the MPT, as shown in Fig. 10(c) and (d). In parallel, there is not any overshoot of  $n > 2$  near the MPT for  $\Delta H$  of 0–6.5 T, indicating that the nature of SOPT, as shown in Fig. 10(e) and (f). These results are consistent well with those obtained by Banerjee criterion.

#### 4. Conclusions

In summary, high quality single phased polycrystalline  $Gd_2MgTiO_6$  oxide with a B-site ordered monoclinic  $P2_1/n$  (No. 14) DP type crystal structure has been successfully fabricated. A combined theoretical and experimental investigation have been carried out in detail in terms of the crystal structure, magnetism, MPT and MC performances. The  $Gd_2MgTiO_6$  oxide is belonging to a B-site ordered monoclinic double perovskite (DP) type structure and has AFM interaction and semi-conductor characteristic at ground state. Moreover, a giant reversible cryogenic MC effect together with outstanding MC performances at around  $T_N$  of 3.3 K have been found in  $Gd_2MgTiO_6$  DP oxide with the  $-\Delta S_M^{\max}$ ,  $TEC(2\text{ K})$ ,  $RCP$  and  $RC$  values as high as 46.21 and 44.15 J/kgK,

399.04 and 300.27 J/kg with  $\Delta H$  of 0–7 T, respectively. Evidently, these MC parameters of  $Gd_2MgTiO_6$  is better than those of recently reported famous cryogenic MC materials and also the commercial gadolinium gallium garnet (GGG), making the  $Gd_2MgTiO_6$  DP oxide attractive for practical cryogenic MR application.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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