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Unveiling the structural and magnetic properties of RENaGeO_4 (RE = Gd, Dy, and Ho) oxides and remarkable low-temperature magnetocaloric responses in GdNaGeO_4 oxide

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Low-temperature magnetocaloric (MC) responses in various types of solid-state magnets have been extensively determined, with the aim of developing high-performing MC materials for magnetic refrigeration applications and deepening our understanding of their underlying intrinsic magneto-physical characteristics. Herein, we fabricated a family of single-phase rare-earth (RE)-dominated oxides, namely, RENaGeO_4 (RE = Gd, Dy, and Ho), by applying the solid phase reaction method and unveiled their structural and magnetic properties, specifically to low-temperature MC responses through experimental determination and theoretical calculation. All RENaGeO_4 oxides crystallize in an orthorhombic olivine-type structure with the space group $Pnma$ (No. 62) and order magnetically at temperatures of 0.70, 2.28, and 2.15 K for GdNaGeO_4 , DyNaGeO_4 , and HoNaGeO_4 oxides, respectively. The consistent elements in these RENaGeO_4 oxides are distributed uniformly and present as RE^{3+} , Na^{1+} , Ge^{4+} , and O^{2-} valence states. The low-temperature MC responses in these RENaGeO_4 oxides are identified by the MC parameters of maximum magnetic entropy change and relative cooling power. These MC parameters under magnetic field changes ($\Delta\mu_0H$) of 0–2/0–5 T are as follows: 34.98/47.30 J (kg K) $^{-1}$ and 107.56/320.70 J kg $^{-1}$ for GdNaGeO_4 , 11.23/14.82 J (kg K) $^{-1}$ and 77.70/236.82 J kg $^{-1}$ for DyNaGeO_4 , and 12.21/15.37 J (kg K) $^{-1}$ and 81.18/239.47 J kg $^{-1}$ for HoNaGeO_4 . Evidently, these determined MC parameters for GdNaGeO_4 oxide, especially under relatively low $\Delta\mu_0H$, are much larger than those for the commercial MC material of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ oxide and surpass those of most updated benchmarked low-temperature MC materials, making the GdNaGeO_4 oxide an excellent candidate for low-temperature magnetic refrigeration application.

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Introduction

Solid-state magnetic refrigeration, $^{1-4}$ which leverages the magnetocaloric (MC) effect in solid-state magnets, is a distinct and prospective low-temperature cooling method $^{3-8}$ owing to its notable economic and environmental benefits. The MC effect, recognized as an inherent magneto-physical property of all solid-state magnets, $^{1-8}$ can be primarily accessed through the change in magnetic entropy (ΔS_M^{max}) under a fixed change in the magnetic field ($\Delta\mu_0H$). However, the development of practical magnetic refrigeration applications has been hindered by the lack of high-performing MC materials. $^{3-8}$ Thus, various types of solid-state magnets $^{4-16}$ have been fabricated and extensively determined regarding their MC responses over the last three decades, with the aim of exploring high-performing MC materials for practical refrigeration applications $^{4-24}$ and better understanding their underlying intrinsic magneto-physical

characters. $^{6-18}$ Consequently, several high-performance MC materials capable of operating at various temperature ranges have been achieved, $^{3-18}$ such as $(\text{Mn}, \text{Fe})_2(\text{P}, \text{X})$, $\text{Gd}_5(\text{Si}, \text{Ge})_4$, $\text{La}(\text{Fe}, \text{Si})_{13}\text{H}_y$, Ni_2MnX , $\text{Mn}_{30}(\text{Fe}, \text{Cu})_{20}\text{Al}_{50}$, and some rare earth (RE)-dominated solid-state magnets.

Among the array of achieved high-performing low-temperature MC materials, rare-earth (RE)-dominated magnetic solids $^{12-26}$ account for the highest proportions. For example, pure or partially doped $\text{RE}(\text{Co}, \text{Ni})_2$ Laves-phase compounds $^{18-21}$ have recently been reported to possess remarkable MC responses, which are considerable for hydrogen liquefaction applications. A large low-temperature MC effect in A_2GdSbO_6 oxides was reported by Koskelo *et al.*, 22 which correlates with their free-spin dominant magnetic behaviors. 22 Remarkable low-temperature MC responses were very recently reported in $\text{Gd}_2\text{Ti}_2\text{O}_7$ and SrGd_2O_4 oxides, 23,24 which correlate with their geometrically frustrated magnetic structure. 23,24 The $\text{Er}_{1-x}\text{Tm}_x\text{Ga}$ compounds were fabricated by Wang *et al.*, 25 which are reported to possess large MC responses around hydrogen liquefaction temperature. The low-temperature MC effects in

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RE(OH)₃ compounds have recently been characterized, and Dy(OH)₃ was observed to be a high-performing low-temperature MC material.²⁶ Enhanced low-temperature MC responses were recently achieved in Gd₂CuTiO₆ and GdCoC compounds,^{27,28} which are governed by 4f-3d magnetic ground state interactions. The low-temperature MC effects of RE₂CoTiO₆ oxides²⁹ were investigated, and remarkable MC responses were achieved in Gd₂CoTiO₆ oxide.²⁹ These results collectively indicate that numerous unknown RE-dominated magnetic solids hold high potential as high-performing low-temperature MC materials, warranting our in-depth investigation.

Additionally, extensive investigations have been performed on RE-dominated magnetic oxides^{22–24,27–30} owing to their benefits of being easy to fabricate and good environmental stability. Thus, we herein shift our research interest to RENaGeO₄ oxides,^{31–36} which have attracted research interest recently owing to their significant potential as luminescent phosphors.^{33–36} However, a detailed investigation of RENaGeO₄ oxides on their magnetic properties and MC responses is still lacking. Therefore, building on our previous studies^{27–30} focused on developing high-performing low-temperature MC materials and deepening our understanding of the inherent magneto-properties of RENaGeO₄ oxides, in this work, we fabricated three polycrystalline oxides of GdNaGeO₄, DyNaGeO₄, and HoNaGeO₄ and unveiled their structural and magnetic properties, specifically their cryogenic MC responses experimentally and theoretically. Our studies indicate that GdNaGeO₄ oxide possesses remarkably low-temperature MC responses, especially under relatively low $\Delta\mu_0H$, which is an exceptionally promising candidate for practical refrigeration applications.

Experimental and calculation details

Three polycrystalline samples of GdNaGeO₄, DyNaGeO₄ and HoNaGeO₄ were fabricated by applying the method of solid phase reaction using raw materials of Gd₂O₃/Dy₂O₃/Ho₂O₃, Na₂CO₃ and GeO₂ powders (purity all exceeding 99.9 wt.%). First, stoichiometric amounts of these oxide powders were weighed, hand-mixed and carefully ground. Second, the thoroughly mixed and ground powders were placed in a muffle furnace at 950 °C for 26 hours. Third, the resulting products were reground into fine powders and directly pelleted by cold pressing. Finally, the dense GdNaGeO₄, DyNaGeO₄ and HoNaGeO₄ oxides were acquired by the final thermal treatment of these pellets at 1020 °C, 1120 °C and 1170 °C for 50 hours, respectively.

The phase and structural properties of RENaGeO₄ oxides are assessed by applying a Rigaku X-ray diffractor (XRD, SmartLab). The element distributions and microstructure of RENaGeO₄ oxides were characterized by selective area electron diffraction (SAED), transmission electron microscopy (TEM, FEI-Talos-F200s) and attached energy dispersive spectroscopy (EDS). The valence states in RENaGeO₄ oxides were accessed by Thermo Scientific X-ray photoelectron spectroscopy (XPS, K-Alpha) utilizing C-1s as the reference energy. The magnetization measurements of RENaGeO₄ oxides were performed by applying

a quantum design magnetic property measurement system (MPMS-Q3) with a magnetic field and temperature sweep rates of 30 mT s⁻¹ and 3 K min⁻¹, respectively. The magnetization results of GdNaGeO₄ below 1.8 K were obtained using a dilute He-3 refrigerator with magnetic field and temperature sweep rates of 10 mT s⁻¹ and 0.3 K min⁻¹, respectively.

Atomic-level first-principles electronic and magnetic structure calculations of RENaGeO₄ oxides were conducted within the framework of spin-polarized density functional theory (DFT).^{37–39} The calculations utilized the commercial Vienna *ab initio* Simulation Package (VASP) software, employing plane waves with a cutoff energy of 520 eV to reproduce the one-electron wave function for constructing the basis set and projected augmented waves (PAW) pseudopotentials.^{37–39} The valence electron states in PAW pseudopotentials of Gd [4f⁷ 5s² 5p⁶ 5d¹ 6s²], Dy [4f¹⁰ 5s² 5p⁶ 6s²], Ho [4f¹¹ 5s² 5p⁶ 6s²], Na [2s² 2p⁶ 3s¹], Ge [3d¹⁰ 4s² 4p²], and O [2s² 2p⁴] were considered in RENaGeO₄ oxides explicitly during the calculations. The *k*-space integrations during calculation were set as 3 × 5 × 6 using the Monkhorst–Pack method.^{37–39} Structural optimizations of RENaGeO₄ oxides were conducted using a conjugate gradient algorithm until each self-consistent electronic loop and the Hellman–Feynman forces converged to below 10⁻⁷ eV per atom and -0.01 eV Å⁻¹, respectively.

Results and discussion

We first assessed the phase and structural characters of RENaGeO₄ (RE = Gd, Dy, and Ho) oxides by XRD at room temperature (RT) and Rietveld structural refinement utilizing the Fullprof suite.⁴⁰ The resulting experimental and refined XRD patterns of GdNaGeO₄, DyNaGeO₄, and HoNaGeO₄ oxides are illustrated in Fig. 1(a)–(c), respectively. All the diffraction peaks of these RENaGeO₄ oxides could be indexed and well-fitted to an orthorhombic Olivine-type structure (*Pnma* space group, No. 62). The values of fitted reliability parameters, including *R*_b, *R*_{wp} and *R*_{exp}, are as follows: 3.48%, 4.60% and 2.21% for GdNaGeO₄; 3.63%, 5.01% and 1.98% for DyNaGeO₄; and 4.05%, 6.89% and 1.67% for HoNaGeO₄; respectively. These parameters are reasonably low, indicating the reliability of the present fitting and good matching with a structural model. Additionally, the refined lattice parameters *a*, *b*, *c* and *V* are 11.5487(15), 6.5334(9), 5.3012(7) Å and 399.984 Å³ for GdNaGeO₄; 11.4400(17), 6.4839(9), 5.2764(8) Å and 391.378 Å³ for DyNaGeO₄; and 11.4167(21), 6.4488(12), 5.2748(11) Å and 388.353 Å³ for HoNaGeO₄, respectively, in which all decrease monotonically with increasing atom number of RE ions, as illustrated in Fig. 1(d), aligned well with the contraction principle of RE elemental. The schematic structural diagrams of RENaGeO₄ oxides are illustrated in Fig. 2. Generally, the RE, Na, and Ge atoms in RENaGeO₄ oxides are coordinated with six, six, and four O atoms and form irregular REO₆ octahedra, NaO₆ octahedra, and GeO₄ tetrahedra, respectively. The REO₆ and NaO₆ octahedra exhibit similar behavior, sharing two O atoms with themselves and forming octahedral chains along the *a*-axis. Within the *bc*-plane, the NaO₆ octahedra are corner shared with four equivalent REO₆ octahedra and two equivalent GeO₄

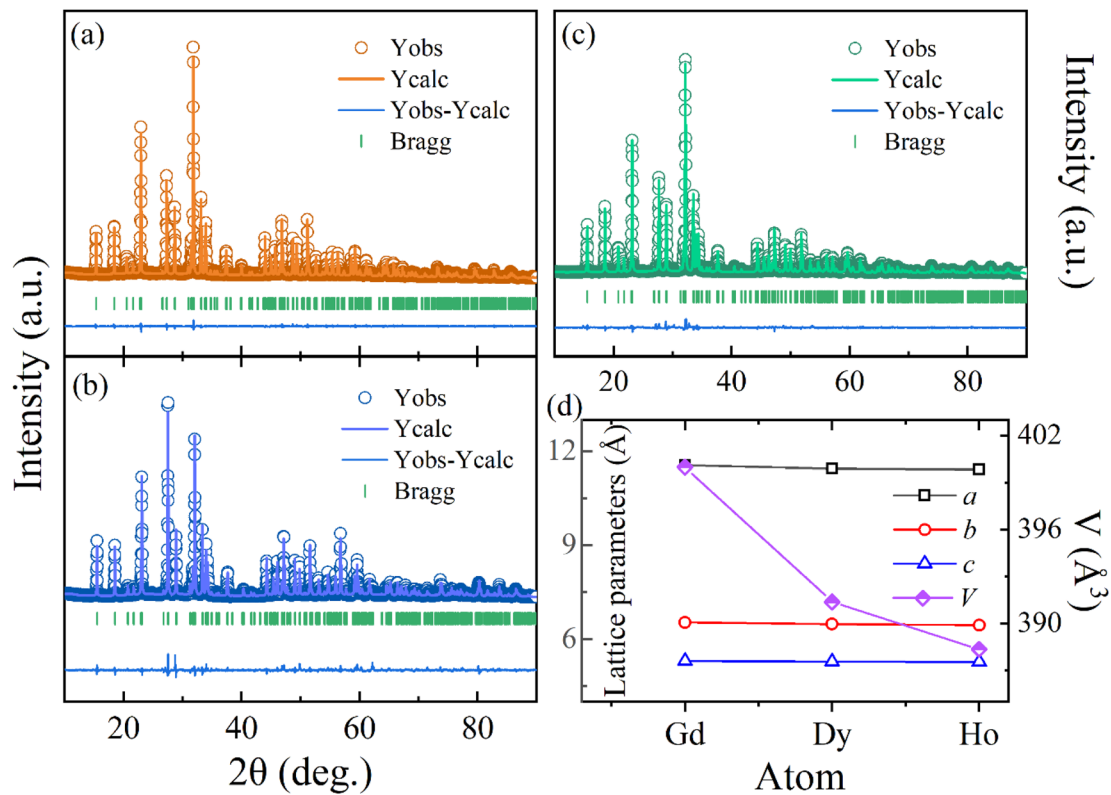


Fig. 1 Experimental and calculated XRD patterns of (a) GdNaGeO₄, (b) DyNaGeO₄, and (c) HoNaGeO₄ oxides. (d) Lattice parameter (*a*, *b*, *c*, and *V*) variations of RENaGeO₄ oxides.

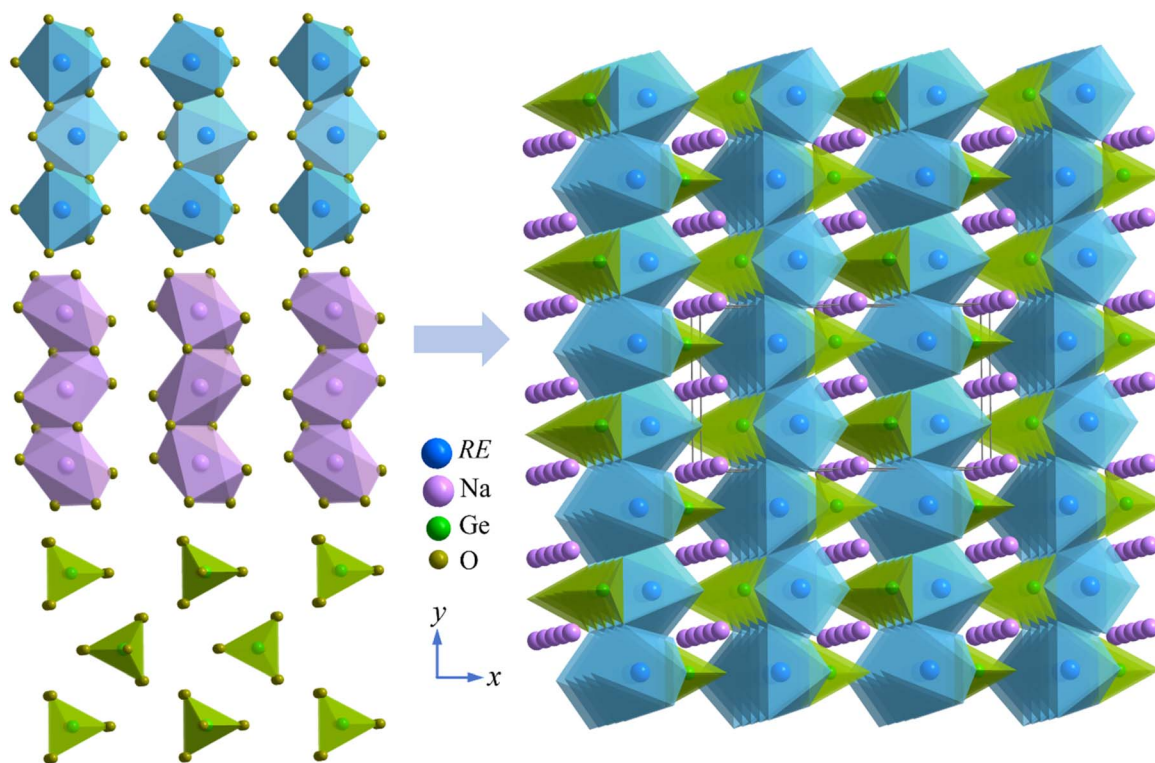


Fig. 2 Schematic of RENaGeO₄ oxides.

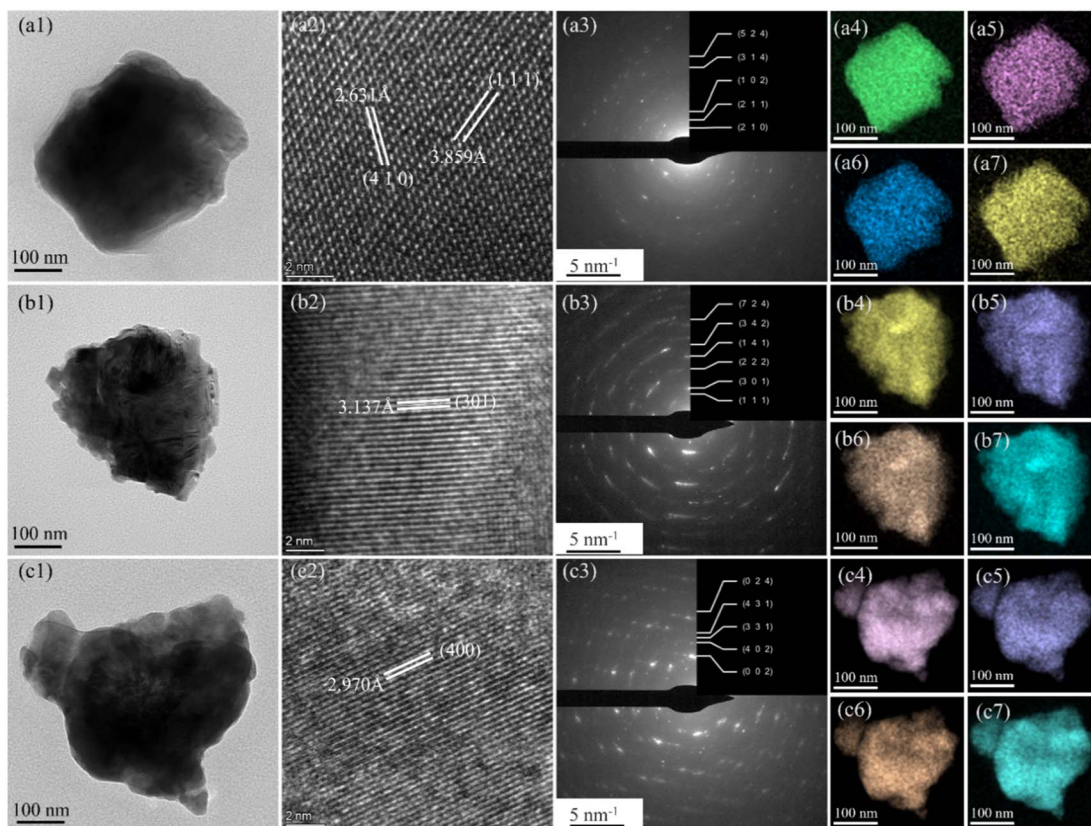


Fig. 3 TEM, SAED, and EDS results of (a1–a7) GdNaGeO_4 , (b1–b7) $\text{Dy}_2\text{NaGeO}_4$, and (c1–c7) HoNaGeO_4 oxides.

tetrahedra; it is also edge shared with two equivalent REO_6 octahedra and GeO_4 tetrahedron, resulting in a quasi-two-dimensional (2D) structural character of RENaGeO_4 oxides.

The bright-field TEM images and corresponding fast Fourier transforms of GdNaGeO_4 , DyNaGeO_4 and HoNaGeO_4 oxides are illustrated in Fig. 3. The plane spacings of GdNaGeO_4 oxide

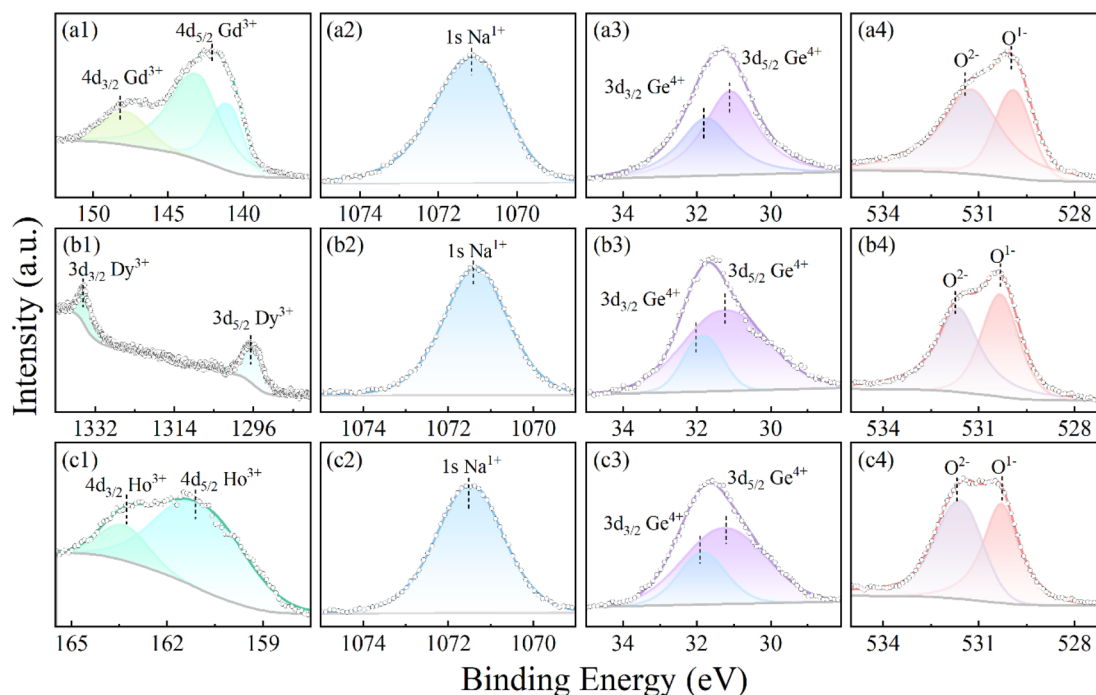


Fig. 4 XPS core-level spectra of constituent elements for (a) GdNaGeO_4 , (b) DyNaGeO_4 , and (c) HoNaGeO_4 oxides.

[Fig. 3(a2)] are deduced to be 2.631 and 3.859 Å, typically corresponding to its [410] and [111] diffraction planes, respectively. The plane spacings of DyNaGeO₄ [Fig. 3(b2)] and HoNaGeO₄ [Fig. 3(c2)] are deduced to be 3.137 and 2.970 Å, typically corresponding to their [301] and [400] diffraction planes, respectively. In addition, the observed clear ring shape in SAED patterns [Fig. 3(a3)–(c3)] of these RENaGeO₄ oxides corresponding to the lattice planes are determined as follows: (524), (314), (102), (211) and (210) for GdNaGeO₄ oxide [Fig. 3(a3)]; (724), (342), (141), (222), (301) and (111) for DyNaGeO₄ oxide [Fig. 3(b3)]; and (024), (431), (331), (402) and (002) for HoNaGeO₄ oxide [Fig. 3(c3)], respectively. The TEM-EDS mapping analysis of Gd/Dy/Ho [Fig. 3(a4)–(c4)], Na [Fig. 3(a5)–(c5)], Ge [Fig. 3(a6)–(c6)] and O [Fig. 3(a7)–(c7)] indicate the uniform distribution of all the constituent elements in RENaGeO₄ oxides up to the nanoscale without notable segregations. Thus, these results reaffirm the single-phase character of these RENaGeO₄ oxides with good homogeneity.

The chemical valence states of RE (Gd, Dy, and Ho), Na, Ge and O in RENaGeO₄ oxides were assessed using XPS at RT. The XPS spectra reveal distinct signals for C (reference), Gd/Dy/Ho, Na, Ge and O elements, which align well with those obtained from TEM-EDS analysis. The high-resolution core-level XPS spectra of Gd/Ho-4d, Dy-3d, Na-1s, Ge-3d, and O-1s in GdNaGeO₄, DyNaGeO₄, and HoNaGeO₄ oxides and the corresponding peak-fitting results are illustrated in Fig. 4(a)–(c) respectively. The XPS core-level spectra of Gd-4d [Fig. 4(a1)], Dy-3d [Fig. 4(b1)] and Ho-4d [Fig. 4(c1)] all reveal two characteristic peaks located at 142.03 and 148.16 eV for GdNaGeO₄ oxide, at 1334.75 and 1296.53 eV for DyNaGeO₄ oxide, and at 163.28 and 161.12 eV for HoNaGeO₄ oxide, respectively, indicating the presence of Gd³⁺, Dy³⁺ and Ho³⁺ valence states. The core-level XPS spectra of Na-1s [Fig. 4(a2), (b2), and (c2)] in RENaGeO₄ oxides reveal a single character peak located around 1071.17 eV, indicating the presence of the Na¹⁺ valence state. In the XPS spectra of Ge-2p core-level [Fig. 4(a3), (b3), and (c3)] in RENaGeO₄ oxides, two characteristic peaks at around 32.03 and 31.23 eV corresponding to spin-orbit splitting of Ge-3d_{3/2} and

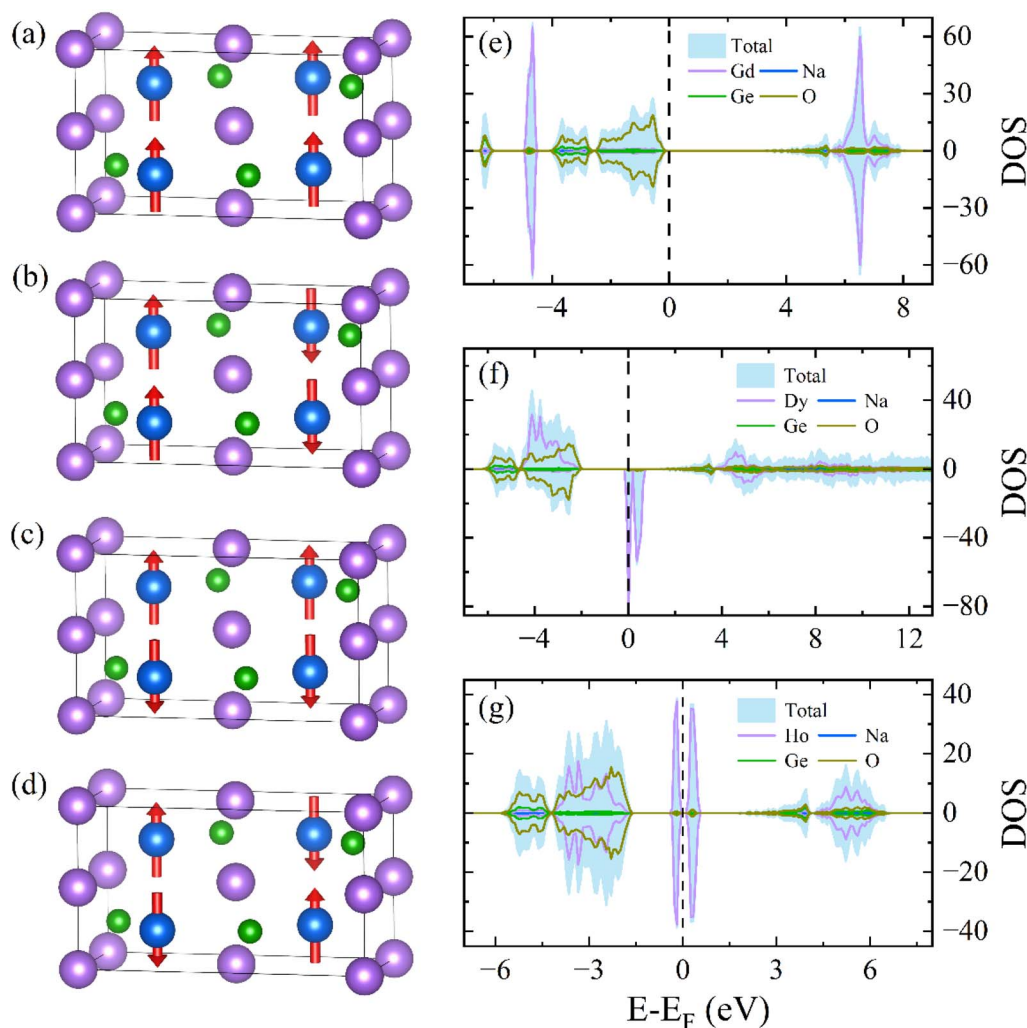


Fig. 5 Potential magnetic coupling of (a) FM and (b–d) AFM in RENaGeO₄ oxides. Spin-polarized total and partial DOS of (e) GdNaGeO₄, (f) DyNaGeO₄, and (g) HoNaGeO₄ oxides.

Ge-3d_{5/2} can be noted, indicating the presence of Ge⁴⁺ valence state. Additionally, the XPS spectra of the O-1s core level [Fig. 4(a4), (b4), and (c4)] in RENaGeO₄ oxides reveal two typical peaks at 529.98 and 531.43 eV, corresponding to the characteristic peak of O²⁻ ions in the lattices and OH⁻ on the surface, respectively.

To assess the ground-state magnetic and electronic properties of these RENaGeO₄ oxides, we performed spin-polarized first-principles DFT calculations^{37–39} using commercial VASP software with PAW pseudopotentials.^{37–39} We first evaluated the magnetic ground state of RENaGeO₄ oxides by calculating the total energy (E_{tot}) for various potential spin configurations. Parallel (FM) and three anti-parallel (AFM: AFM1, AFM2, and AFM3) states are considered, as illustrated in Fig. 5(a)–(d). The calculated E_{tot} values of E_{FM} , E_{AFM1} , E_{AFM2} and E_{AFM3} are as follows: -226.7264 , -226.7270 , -226.7299 and -226.7297 eV per f.u. for GdNaGeO₄; -210.3734 , -210.3046 , -210.3331 and -210.3344 eV per f.u. for DyNaGeO₄; and -204.3413 , -203.9209 , -204.3958 and -204.2425 eV per f.u. for HoNaGeO₄, respectively. Notably, the AFM2, FM and AFM2 states have the lowest E_{tot} in GdNaGeO₄, DyNaGeO₄ and HoNaGeO₄, respectively, illustrating that the AFM ground state is preferred for GdNaGeO₄ and HoNaGeO₄ oxides, whereas the FM ground state is preferred for DyNaGeO₄ oxide. Furthermore, we calculated the spin-polarized total density of states (DOS) and projected-orbital partial DOS for Gd(4f), Dy(4f), Ho(4f), Na(3s), Ge(4p), and O(2p) orbitals to further assess their electronic and magnetic characters, as illustrated in Fig. 5(e)–(g) for GdNaGeO₄, DyNaGeO₄ and HoNaGeO₄, respectively. Nearly identical states between spin-minority and spin-majority channels can be noted for GdNaGeO₄ and HoNaGeO₄ oxides with an evident band gap (BG) around the Fermi level, further proving their AFM ground state. However, the spin-minority and spin-majority channels in DyNaGeO₄ are asymmetric, indicating the possibility of an FM ground state. Additionally, the projected-orbital RE(4f) partial DOS predominantly governs the total DOS and exhibits significant splitting behavior in these RENaGeO₄ oxides, suggesting pronounced spontaneous polarization and large magnetic moments in RE³⁺ ions. The calculated average magnetic moment of GdNaGeO₄ oxide is $6.88\mu_{\text{B}}$, which is close to the theoretical limitation of a free Gd³⁺ ion ($7.0\mu_{\text{B}}$). However, the calculated average magnetic moments in DyNaGeO₄ and HoNaGeO₄ are 4.86 and $3.85\mu_{\text{B}}$, respectively, which are only around half of the theoretical limit of the corresponding free RE³⁺ ions. Such differences probably originate from the strong crystal field effects of Dy³⁺ and Ho³⁺ ions in RENaGeO₄ oxides.

The magnetic properties of RENaGeO₄ oxides were also experimentally determined with μ_0H up to 7 T. The resulting $M(T)$ and $1/\chi(T)$ ($\chi = M/\mu_0H$) curves of GdNaGeO₄, DyNaGeO₄ and HoNaGeO₄ oxides under $\mu_0H = 1$ T are illustrated in Fig. 6(a)–(c), respectively. Despite slight differences in values, these thermomagnetic results in RENaGeO₄ oxides exhibit similar behaviors: the values of M increase continuously as the temperature decreases, and the $1/\chi(T)$ curves above 20 K of these RENaGeO₄ oxides follow a Curie Weiss law, $\chi(T) = C/(T - \theta) + \chi_0$, in which θ_{p} and χ_0 represent paramagnetic Curie

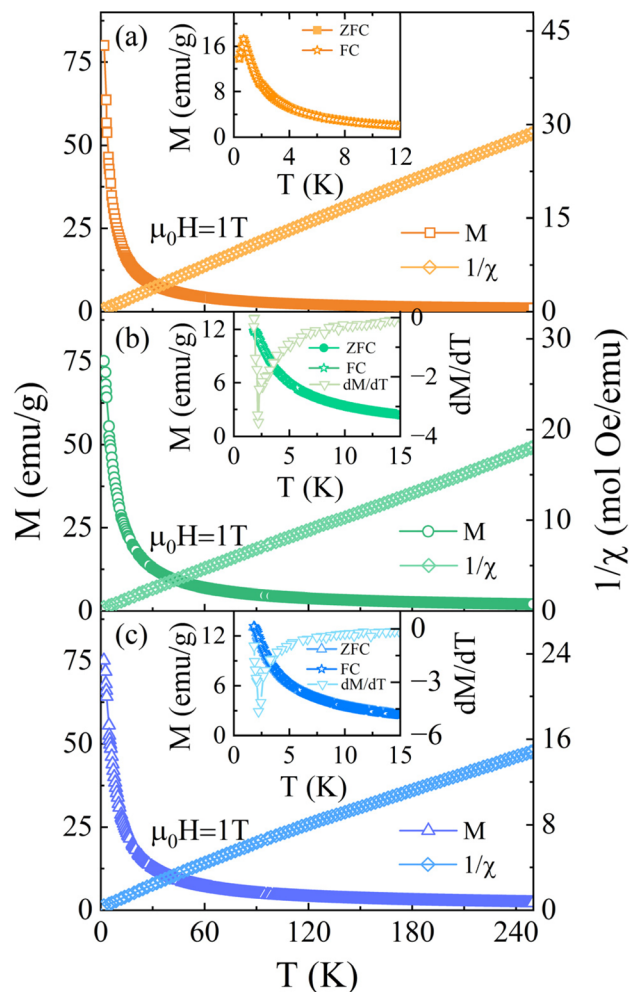


Fig. 6 $1/\chi(T)$ and $M(T)$ curves under 1 T for (a) GdNaGeO₄, (b) DyNaGeO₄, and (c) HoNaGeO₄ oxides. Insets present corresponding FC, ZFC $M(T)$ and dM/dT curves under 0.1 T.

temperature and temperature-independent part susceptibility, respectively. The Curie constant can be expressed as $C = N(\mu_{\text{B}} - \mu_{\text{eff}})^2/3k_{\text{B}}$, where μ_{eff} represents effective magnetic moment. The linear Curie Weiss fittings produce the θ_{p} values of -0.36 , 0.23 and -4.71 K for GdNaGeO₄, DyNaGeO₄, and HoNaGeO₄ oxides, respectively, indicating the possibility of ground state AFM interaction for GdNaGeO₄ and HoNaGeO₄ oxides, while FM interaction for DyNaGeO₄, which aligns with those by DFT calculations. The corresponding deduced μ_{eff} values for RENaGeO₄ oxides are 8.00 , 10.58 and $10.62\mu_{\text{B}}$ per f.u., which align well with their respective theoretical magnetic moment of free RE³⁺ ions, indicating the crucial roles of RE ions on magnetic properties in these RENaGeO₄ oxides. Additionally, the $M(T)$ curves for these RENaGeO₄ oxides are illustrated in insets in Fig. 6(a)–(c) by FC and ZFC modes, which coincide within the experimental limitations, indicating the good thermal reversibility, which is demanded for magnetic refrigeration application. Moreover, the values of M in all RENaGeO₄ oxides increase gradually as temperature decreases to 1.8 K and show a saturation tendency for DyNaGeO₄ and HoNaGeO₄

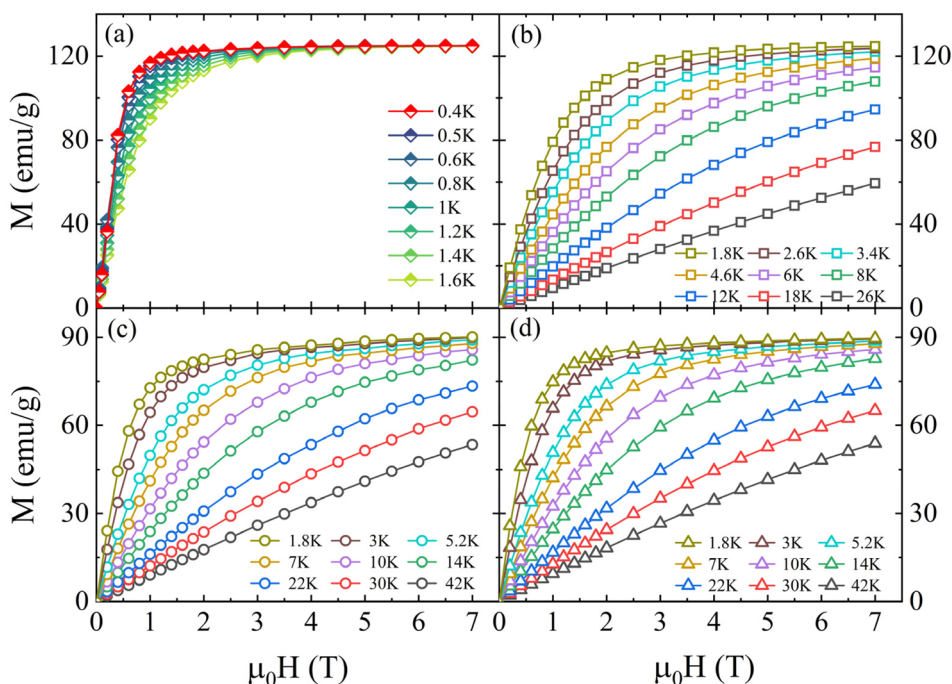


Fig. 7 $M(\mu_0H)$ curves for (a and b) GdNaGeO_4 , (c) DyNaGeO_4 , and (d) HoNaGeO_4 oxides.

oxides around 2 K, resulting in magnetic phase transition (MPT) temperatures of ~ 2.28 and 2.15 K, respectively, based on the inflection point in their $dM/dT(T)$ curves. However, the M value of GdNaGeO_4 oxide increases continuously down to 1.8 K,

indicating no distinct magnetic ordering. Thus, we further determined the thermomagnetic results of GdNaGeO_4 oxide down to 0.4 K using a dilute He-3 refrigerator, as illustrated in Fig. 6(a). A clear peak in the $M(T)$ curves of GdNaGeO_4 oxide can

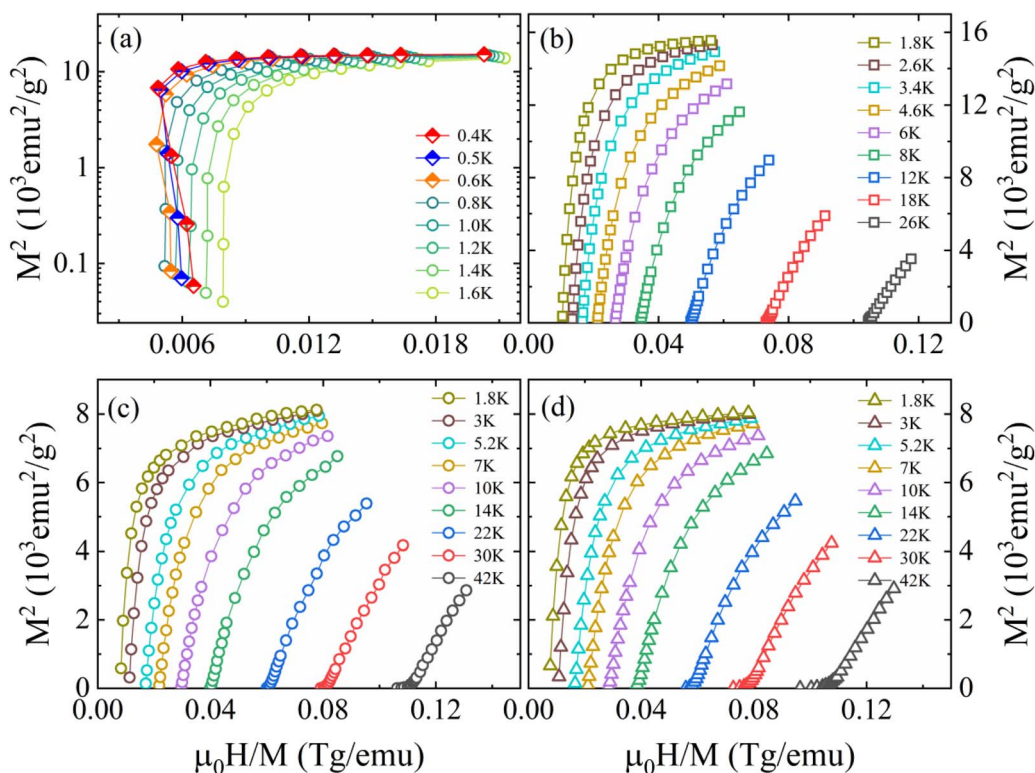


Fig. 8 Arrott-plot curves for (a and b) GdNaGeO_4 , (c) DyNaGeO_4 , and (d) HoNaGeO_4 oxides.

be noted at around 0.7 K, indicating a typical MPT from the paramagnetic (PM) to AFM state.

Moreover, a series of $M(\mu_0H)$ curves of RENaGeO_4 oxides from 1.8 to 42 K (down to 0.4 K for GdNaGeO_4) with μ_0H up to 7 T were determined to further assess their MC responses and MPT nature, as illustrated in Fig. 7(a)–(d). Except for some differences in values, the $M(\mu_0H)$ results of these RENaGeO_4 oxides exhibit similar performances. Generally, the M values increase abruptly in the low-field region, then become flat, and finally show saturation behavior in the high-field region. MC performance is known to be proportional to the saturation magnetic moment (M_s) of magnetic solids. The deduced M_s value for GdNaGeO_4 reaches $7.07\mu_B/\text{Gd}$ (0.4 K), which is close to the theoretical limitation of free Gd^{3+} ions; thus, notably low-temperature MC responses are expected. However, the M_s values are $5.20\mu_B/\text{Dy}$ (1.8 K) and $5.21\mu_B/\text{Ho}$ (1.8 K) for DyNaGeO_4 and HoNaGeO_4 , respectively, which are obviously lower than the theoretical values of the corresponding free RE^{3+} ions; such differences mainly originate from the strong crystal field effect and single-ion anisotropy for Dy^{3+} and Ho^{3+} ions. Additionally, these values align well with those obtained by the DFT calculations, further proving the vital roles of RE ions in the magnetism of these RENaGeO_4 oxides. Moreover, the MC responses in solid-state magnets are related to their corresponding MPT order types,^{27–30} which can be assessed by the slope signals in Arrott-plot (μ_0H/M versus M^2) curves, using the Banerjee criterion. The observation of a positive slope indicates the second-order type MPT,⁴¹ while the exhibition of a negative slope corresponds to first-order type MPT.⁴¹ Thus, to assess the order type of MPT in these RENaGeO_4 oxides, the Arrott plot curves were transferred based on $M(\mu_0H)$ results [Fig. 7(a)–(d)]. The resulting curves are correspondingly illustrated in Fig. 8(a)–(d), respectively. Clearly, negative slopes at low temperatures in GdNaGeO_4 oxide [Fig. 8(a)] can be observed, illustrating the occurrence of first-order type MPT. However, only positive slopes are found for DyNaGeO_4 and HoNaGeO_4 oxides [Fig. 8(c)–(d)], indicating the second-order type MPT within the experimental limitations.

Subsequently, we first assessed the MC responses of these RENaGeO_4 oxides using the temperature-dependent $-\Delta S_M$, evaluated using the equation $\Delta S_M(T, \Delta H) = \int_0^{H_{\max}} \left(\frac{\partial M(H, T)}{\partial T} \right)_H dH$,^{3–6} as illustrated in Fig. 9(a)–(c) for GdNaGeO_4 , DyNaGeO_4 , and HoNaGeO_4 oxides, respectively, which reveal a conventional MC response: only positive $-\Delta S_M(T)$ values can be observed within the experimental limitations, and the value of $-\Delta S_M$ under a fixed $\Delta\mu_0H$ increases continuously with decreases in T and reaches its maximum ($-\Delta S_M^{\max}$); after that, $-\Delta S_M$ decreases gradually by further decreasing T . Under $\Delta\mu_0H$ of 0–1, 0–2, 0–3, 0–5 and 0–7 T, the deduced $-\Delta S_M^{\max}$ values are 22.22, 34.98, 40.90, 47.30 and $50.66 \text{ J (kg K)}^{-1}$ for GdNaGeO_4 ; 7.15, 11.23, 13.00, 14.82 and $15.83 \text{ J (kg K)}^{-1}$ for DyNaGeO_4 ; and 8.21, 12.21, 13.86, 15.37 and $16.22 \text{ J (kg K)}^{-1}$ for HoNaGeO_4 , respectively. Evidently, the GdNaGeO_4 possesses larger MC responses than those in DyNaGeO_4 and HoNaGeO_4 oxides, which is probably related to

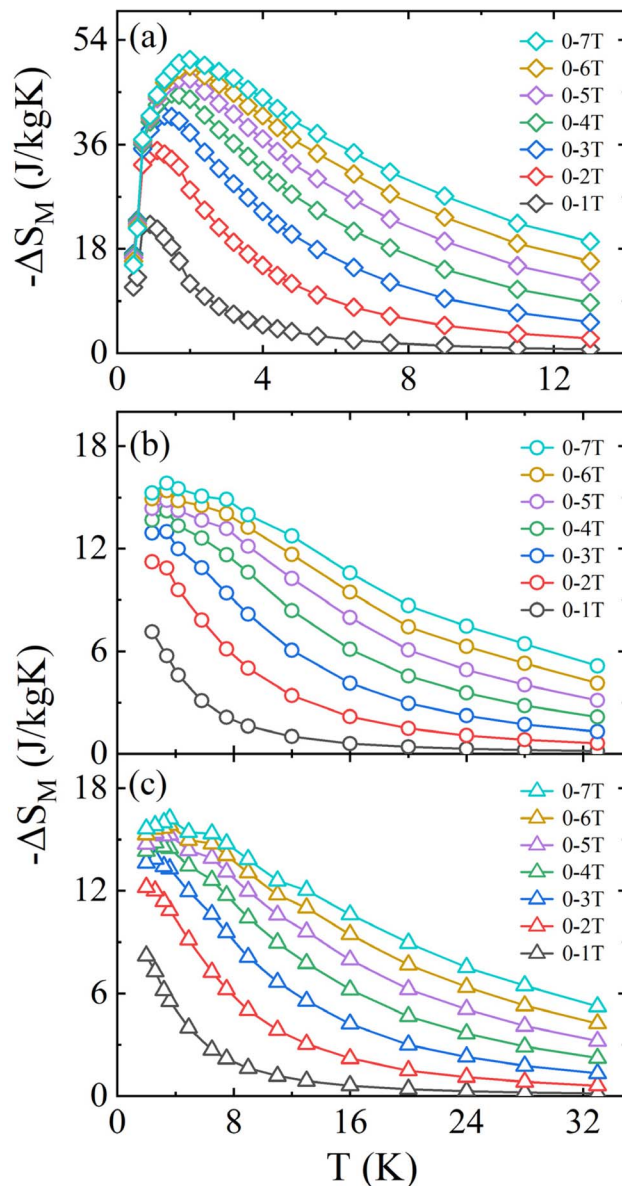


Fig. 9 $-\Delta S_M(T)$ curves for (a) GdNaGeO_4 , (b) DyNaGeO_4 , and (c) HoNaGeO_4 oxides.

its low-field induced first order MPT and largest saturation magnetic moment with low crystal field effect. In addition, the values of refrigerant capacity ($\text{RC} = \int_{T_{\text{cold}}}^{T_{\text{hot}}} |\Delta S_M(T)| dT$) and^{3–6} relative cooling^{3–6} power ($\text{RCP} = |\Delta S_M^{\max}| \times \delta T_{\text{FWHM}}$) for RENaGeO_4 oxides were deduced to further assess their MC responses. The T_{cold} and T_{hot} represent the temperatures at $\frac{1}{2} |\Delta S_M^{\max}|$ in $\Delta S_M(T)$ curves at two sides, and the δT_{FWHM} represents the absolute values of the difference between T_{hot} and T_{cold} . Consequently, the deduced $\text{RC}(\text{RCP})$ values under $\Delta\mu_0H$ of 0–1, 0–2, 0–3, 0–5 and 0–7 T are as follows: 30.35(38.64), 82.87(107.56), 137.76(178.87), 245.53(320.70) and $351.46(462.10) \text{ J kg}^{-1}$ for GdNaGeO_4 ; 21.23(28.73), 58.78(77.70), 100.02(130.92), 182.40(236.92) and $259.55(337.64) \text{ J kg}^{-1}$ for

Table 1 Summary of T_M and $-\Delta S_M^{\max}$ values of GdNaGeO₄ oxide and selected low-temperature benchmarked MC materials

Materials	T_M (K)	$-\Delta S_M^{\max}$ (0–2 T) J (kg K) ⁻¹	$-\Delta S_M^{\max}$ (0–5 T) J (kg K) ⁻¹	Ref.
GdNaGeO ₄	0.7	34.98	47.30	Present
Gd ₃ Ga ₅ O ₁₂	1.2	14.6	32.8	42 and 43
EuB ₄ O ₇	0.7	36.2	47.6	44
Gd ₂ CuTiO ₆	2.7	10.2	41.5	28
NaGdS ₂	2.5	23.5	54	45
Gd _{4.5} K _{0.5} Si ₃ O ₁₃	0.7	31.9	58.2	46
Gd ₃ TeBO ₉	2.6	20.6	50.3	47
Gd(OH)F ₂	1.31	32	65	48
Gd _{0.33} Si ₆ O ₂₆	0.65	32.5	59.5	49
Gd ₁₅₂ Ni ₁₄ @C ₁₂₄	2.5	20.5	46	50

DyNaGeO₄; and 22.92(31.09), 61.66(81.18), 101.87(133.14), 183.25(239.47) and 262.50(345.20) J kg⁻¹ for HoNaGeO₄, respectively. Evidently, the GdNaGeO₄ oxide shows the best MC responses among the RENaGeO₄ oxides, aligning with its larger saturation magnetic moment. Finally, to further identify the MC responses of GdNaGeO₄ oxide, we summarize its $-\Delta S_M^{\max}$ values under $\Delta\mu_0H$ of 0–2 and 0–5 T with the reported benchmarked low-temperature MC materials, as illustrated in Table 1. The MC responses of the present GdNaGeO₄ oxide under low $\Delta\mu_0H$ of 0–5 T are comparable to most of the reported materials. Interestingly, its MC performance under low $\Delta\mu_0H$ of 0–2 T, which could be generated by RE-dominated permanent magnets, is much larger than that of the commercialized MC material of Gd₃Ga₅O₁₂ oxide and surpasses most of the benchmarked MC materials. Although $-\Delta S_M^{\max}$ value under $\Delta\mu_0H$ of 0–2 T is lower than that of the divalent Eu-based EuB₂O₄ [44], the present GdNaGeO₄ oxide has the benefit of being easy to fabricate by applying a simple solid-state reaction process with high environmental stability. These findings highlight GdNaGeO₄ oxide as a top-level MC material that is attractive for practical low-temperature refrigeration applications.

Conclusions

In summary, three single-phased RENaGeO₄ oxides were successfully fabricated and unveiled their structural and magnetic properties, specifically for low-temperature MC responses through experimental determination and theoretical calculation. All these RENaGeO₄ oxides crystallize in an Olivine-type orthorhombic structure and order magnetically at low temperatures of 0.7, 2.28 and 2.15 K for GdNaGeO₄, DyNaGeO₄, and HoNaGeO₄ oxides, respectively. The consistent elements in NaREGeO₄ oxides are all distributed uniformly and present as Na¹⁺, RE³⁺, Ge⁴⁺, and O²⁻ valence states, respectively. Interestingly, the GdNaGeO₄ oxide possesses remarkably low-temperature MC responses with the values of $-\Delta S_M^{\max}$ reaching 22.22, 34.98, and 47.30 J (kg K)⁻¹ under $\Delta\mu_0H$ of 0–1, 0–2, and 0–5 T, respectively. These values, especially under low $\Delta\mu_0H$ that can be generated by RE-dominated permanent magnets, are much larger than those of the commercial MC material of Gd₃Ga₅O₁₂ oxide and surpass most of the updated benchmarked MC materials. These findings, in addition to their simple preparation process and high

environmental stability, make the GdNaGeO₄ oxide an excellent candidate for low-temperature magnetic refrigeration applications.

Data availability

The data supporting the findings of this study are available from the corresponding author, Yikun Zhang, upon reasonable request.

Author contributions

Y. Z.: conceptualisation, supervision, project administration, resources, writing original draft, and review and editing; Y. N., Y. X., and X. Z.: investigation, formal analysis, and data curation. All authors have reviewed and approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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