Magnetocaloric effect in gadolinium-oxalate framework
Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$·(0.6H$_2$O)

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Magnetic refrigerants incorporating Gd$^{3+}$ ions and light organic ligands offer a good balance between isolation of the magnetic centers and their density. We synthesized the framework material Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$·0.6H$_2$O by a hydrothermal route and characterized its structure. The honeycomb lattice of Gd$^{3+}$ ions interlinked by oxalate ligands in the (a,c) plane ensures their decoupling in terms of magnetic exchange interactions. This is corroborated by magnetic measurements indicating negligible interactions between the Gd$^{3+}$ ions in this material. The magnetocaloric effect was evaluated from isothermal magnetization measurements. The maximum entropy change $-\Delta S_M^{\text{max}}$ reaches 75.9 mJ cm$^{-3}$ K$^{-1}$ (around 2 K) for a moderate field change (2 T).

The magnetocaloric effect (MCE) corresponds to the adiabatic temperature change ($\Delta T_{\text{ad}}$) or the isothermal magnetic entropy change ($\Delta S_M$) of a solid in a varying magnetic field. Its use through the adiabatic demagnetization process has first focused on low temperatures. Different kinds of materials have attracted interest for their MCE in low temperature region (2-4 K), including simple paramagnetic salts, molecular nanomagnets, extended porous networks, garnets, or intermetallic alloys. For a more exhaustive insight, two recent review articles dealing with coordination compounds or molecule-based magnetic coolers can be consulted. Nowadays magnetic cooling continues attracting attention for temperatures well below liquid He temperature because of the increasing cost and scarcity of $^3$He, and in some cases as satellite applications, for its technological simplicity and independence from gravity.

Gadolinium-based compounds have been largely studied because Gd$^{3+}$ carries a large spin-only magnetic moment ($S = 7/2$) which favors a large entropy change [the maximum magnetic entropy amounts to $R \ln(2S + 1)$] together with a negligible hysteresis during the magnetization/demagnetization process. Good candidates for low temperature applications are compounds in which Gd$^{3+}$ centers are sufficiently isolated from each other to retain a paramagnetic behavior down to about 2 K. Gadolinium sulfate hydrate constitutes an historical example. For about 10 years, gadolinium-based magnetic coolers have been sought in coordination compounds with light organic molecules as ligands with the aim of combining decoupled magnetic centers with large magnetic/nonmagnetic atoms mass ratios, which are essential characteristics for obtaining good magnetocaloric properties per units of volume. It has to be noticed that, although decoupled magnetic centers are good systems for cryogenic magnetic cooling, the existence of weak ferromagnetic interactions can be taken as an advantage. A reference example is the paramagnetic salt gadolinium acetate tetrahydrate for which a remarkable moderate-field MCE was ascribed to the augmented spin of ferromagnetic dimers. Nevertheless, excellent performances in terms of MCE can also be found in compounds presenting weak...
antiferromagnetic interactions, such as the compact metal-organic framework (MOF) Gd(HCOO)$_3$, which takes advantage of formate, the lightest carboxylate. Finally, we notice the advantages of certain magnetocaloric MOF materials in terms of robustness, which can be considered as an advantage in practical applications as we emphasized in the past with the study of Gd(HCOO)(C$_3$H$_4$O$_3$)$_3$.\textsuperscript{19}

Following the above-described tendency in the research field of molecular magnetic coolers, we thought that gadolinium oxalate could be an interesting candidate. Lanthanide oxalates were studied for a long time for their optical properties and are generally prepared in the form of single crystals.\textsuperscript{20-25} They are also used as precursors for the synthesis of ceramics.\textsuperscript{26,27} The phases usually described have the composition Ln$_2$(C$_2$O$_4$)$_3$·nH$_2$O, a rich water phase presenting a weight loss of about 53\% between 25 and 650 °C (loss of water molecules and decomposition of the ligands). Gadolinium oxalate is described in two structural types: type 1, a high interstitial or “zeolitic water” content phase Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_x$·nH$_2$O with n ~2.5 (SG = P2$_1$/a, a = 10.0549(4) Å, b = 9.6066(3) Å, c = 11.0306(6) Å, β = 114.097(4)°, V = 972.63(7) Å$^3$, and D$_x$ = 2.536 g/cm$^3$),\textsuperscript{28} and type 2, free of “zeolitic water” content phase Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$ with n ~0 (SG = P2$_1$/c, a = 8.346(3) Å, b = 9.746(1) Å, c = 9.380(2) Å, β = 89.99(2)°, V = 762.9(3) Å$^3$, and D$_x$ = 2.97 g/cm$^3$).\textsuperscript{29}

Surprisingly, the MCE of gadolinium oxalate was not reported before while numerous MOF compounds with gadolinium and light organic molecules were recently investigated, for instance with oxalate-succinate mixed ligands.\textsuperscript{30} The use of such light molecules has the advantage to keep a high metal/organic ratio, so favouring the density of magnetic centers.\textsuperscript{5,18,30,31}

We have synthesized Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_x$·(nH$_2$O) by the reaction between the dry product of Gd$_2$O$_3$ dissolved in concentrated hydrochloric acid (0.5 mmol Gd$_2$O$_3$ in 10 ml HCl 6N), and an aqueous solution of Na$_2$(C$_2$O$_4$) (0.5 mmol in 10 ml distilled water). The resulting suspension is maintained under magnetic stirring for 45 min and then transferred into a Teflon-walled autoclave. After a hydrothermal treatment of 7 days at 150 °C, the hydrothermal bomb was naturally cooled in air. The as-synthesized solid product was separated from the liquid reaction medium by centrifugation and washed twice with a mixed water/ethanol (1:1) solution (yield: 80\% based on Gd). The final product was characterized by chemical analysis (Anal. (Calc.): C, 9.88 (10.33); O, 41.92 (42.68); Gd, 46.41 (45.10)) and by using Rietveld analysis of X-ray powder diffraction data collected on a D8 Advance diffractometer using monochromatized MoK$_{α1}$ radiation ($λ = 0.71076$ Å). The measurement was realized in a glass capillary (Ω = 0.3 mm) using the Debye–Scherrer geometry to minimize preferential orientation. The starting model used for Rietveld refinement was found in the literature.\textsuperscript{29} Supplementary material\textsuperscript{52} contains a Rietveld plot, a summary of the structural and refinement parameters, and the CIF (Crystallographic Information File) file resulting from the final refinement. The results of our structural analysis indicate a crystal structure of type 2, Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$(0.6H$_2$O), which is represented in Figure 1. It is a 2D structure made of sheets parallel to (010) and interconnected by hydrogen bonds (dotted lines on Fig. 1). Gd atoms are nine-O coordinated and are at the center of an almost regular tri-capped trigonal prism. Six O-atoms come from three chelating and bridging oxalate molecules while three others come from three water molecules. Bridging molecules link each “GdO$_6$” polyhedron to three others in the (a,c) plane, thus forming sheets with holes where “zeolitic” water could be present. The intra- and inter-layer Gd-Gd distances are 6.0-6.6 Å and 6.7 Å, respectively. The Rietveld refinement allows the insertion of 0.6 “zeolitic” water molecules (per formula unit) which are located in the pores of the sheets.

The water content of our type 2 phase was also investigated by thermogravimetric analysis (TGA), see Fig. 2. The TGA curve has the usual shape already reported for lanthanide oxalates.\textsuperscript{22,26} The total weight loss of 44.5 wt.% is significantly lower than the value of ~53\% observed in similar compound.\textsuperscript{22,23} This indicates a low interstitial or “zeolitic” water content phase. We can distinguish between three different weight losses: (i) 1.5 wt. % (calc.: 1.5 wt.\%) between 25 and 100 °C is attributed to the loss of 0.6 interstitial water molecules per formula unit, (ii) 15.3 wt. % (calc: 15.5 wt.\%) between 100 and 360 °C is due to the loss of the six coordinated water molecules leading to the anhydrous compound Gd$_2$(C$_2$O$_4$)$_3$, (iii) 128.0 wt. % (calc: 31 wt.\%) between 360 and 750 °C corresponds to the decomposition of Gd$_2$(C$_2$O$_4$)$_3$ in Gd$_2$O$_3$.

The magnetic properties of a polycrystalline sample of Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$(0.6H$_2$O) (M = 697.36 g/mol, D$_x$ = 3.00 g/cm$^3$) were investigated by using a PPMS-9T (Physical Property
FIG. 1. Structure of Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$·(0.6H$_2$O). (Left) View showing the slabs connected along b by hydrogen bonds (dashed lines). (Right) Detailed view of a slab.

FIG. 2. Thermogravimetric analysis of Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$·(0.6H$_2$O) recorded upon heating in air between room temperature and 750 °C (1 °C min$^{-1}$). Measurements System, Quantum Design). Data were corrected for diamagnetism originating from the sample holder, from the ligands and from the closed shells of the Gd$^{3+}$ ions. Fig. 3 shows the thermal dependence of the magnetic susceptibility ($\chi$) recorded in a 100 mT magnetic field ($\mu_0H$). The thermal variation of the inverse susceptibility is represented in the inset of Fig. 3. The Curie-Weiss law is verified with a Curie constant $C = 7.74$ cm$^3$ K mol$^{-1}$ ($\mu_{\text{eff}} = 7.87 \mu_B$) which is close to the value of $7.88$ cm$^3$ K mol$^{-1}$ expected for a free Gd (III) ion ($S = 7/2$) with a Landé factor $g = 2$. The paramagnetic temperature is, within the uncertainty of its evaluation, close to zero ($\theta_p \approx 0.75(80)$ K). This agrees with the existence of isolated magnetic centers in the structure. The compound remains paramagnetic down to 1.8 K.

Isothermal magnetization curves were measured in applied fields up to 9 T in the 2.0–35 K temperature range (Fig. 4 (top)). At the lowest available temperature, the magnetization saturates around 6.98 $\mu_B$. The magnetic entropy change $\Delta S_M$ was calculated from these magnetization data by using Maxwell equation $\int (\partial M/\partial T)H \, dH$ and integrating over various magnetic field changes $\mu_0 \Delta H = H_f - 0$ (Fig. 4 (bottom)). The magnetic entropy change increases steadily upon cooling in the explored temperature range. However, a maximum around 2.75 K is observed for field
Temperature dependence of the magnetic susceptibility ($\chi$) recorded under external field (100 mT). Inverse of magnetic susceptibility is shown in inset with the linear fit to the Curie-Weiss law.

changes higher than 7 T. Below 5 T, the maximum is observed at 2.25 K. The entropy change per unit mass reaches $-\Delta S_{M}^{\text{max}} = 46.6 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\mu_0\Delta H = 7 \text{ T}$ ($-\Delta S_{M}^{\text{max}} = 25.3 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\mu_0\Delta H = 2 \text{ T}$). The maximum magnetic entropy per mole expected for one isolated Gd$^{III}$ ion is $2.08 K = 49.2 \text{ J kg}^{-1} \text{ K}^{-1}$.

Table I gathers some of the best gadolinium magnetic coolers reported up to now ($-\Delta S_{M}^{\text{max}} > 40.0 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\mu_0\Delta H = 7 \text{ T}$). The MOFs present in this table are all made of light molecules such as acetate (CH$_3$COO$^-$),$^5$ succinate (C$_4$H$_6$O$_4^{2-}$),$^31$ oxalate (C$_2$O$_4^{2-}$),$^{39}$ formate (HCOO$^-$),$^{18}$ benzene dicarboxylate (C$_6$H$_4$O$_4^{2-}$),$^{38}$ and iminodiacetate (C$_4$H$_3$NO$_2^{2-}$).$^{32}$ One of the reported compounds is a cluster which was obtained using nicotinic linker (na = C$_6$NH$_2$O$_2$)$^-$: [Gd$_{36}$(na)$_{36}$(OH)$_{46}$O$_6$(NO$_3$)$_6$ (N$_3$)$_3$(H$_2$O)$_{20}$]Cl$_2$:28(H$_2$O).$^{34}$ In addition, two recently investigated magnetic coolers which are mineral compounds are indicated: Gd(OH)(CO$_3$)$_3$$^{35}$ and [Gd$_2$O(OH)$_{36}$(ClO$_4$)$_4$]$_4$(H$_2$O)$_8$][OH]$_4$.$^{36}$ The values indicated in the table correspond to the maximum mass and volumetric magnetic entropy variations at the temperature $T_m$ for magnetic field variations of 2 T and 7 T. The choice of a field change $\mu_0\Delta H = 2 \text{ T}$ is dictated by the fact that, for widespread applications, the interest is chiefly restricted to applied fields which can be produced by permanent magnets. Volumetric entropy changes are given since, in applications, the maximum field region has a limited volume. The benchmark gadolinium gallium garnet has, in comparison with the materials in Table I, a lower mass $-\Delta S_{M}^{\text{max}}$ but a larger volumetric $-\Delta S_{M}^{\text{vmax}}$ because of its significantly higher density.$^{14}$ Considering the volumetric entropy change $-\Delta S_{M}^{\text{vmax}}$ (mJ cm$^{-3}$ K$^{-1}$), Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$(0.6H$_2$O) occupies the 5th rank and 3rd rank for $\mu_0\Delta H = 7 \text{ T}$ and 2 T, respectively, meaning that this compound is a valuable candidate for practical applications. For the low field changes ($\mu_0\Delta H = 2 \text{ T}$), Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$(0.6H$_2$O) (75.9 mJ cm$^{-3}$ K$^{-1}$) is only overcome by the mineral compound Gd(OH)CO$_3$ (355 mJ cm$^{-3}$ K$^{-1}$) and the compact framework Gd(HCOO)$_3$ (168.5 mJ cm$^{-3}$ K$^{-1}$). It is clear that the trend was to densify Gd MOFs, as the magnetocaloric performances expressed in volumetric units are closely related to the density of the materials. The MCE of the title compound evaluated for a magnetic field change of 7 T can also be compared with the classified compounds reported in Table I of Ref. 37. With its value of 139.9 mJ cm$^{-3}$ K$^{-1}$, Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$(0.6H$_2$O) would be placed among the best compounds of this classification.

For a moderate $\mu_0\Delta H$ (3 T) Gd(CH$_3$COO)$_3$·4H$_2$O, a good reference, has a mass entropy change of 36.0 J kg$^{-1}$ K$^{-1}$ comparable with that of Gd(HCOO)$_3$C$_6$H$_5$O$_2$ (33.3 J kg$^{-1}$ K$^{-1}$) and Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$(0.6H$_2$O) (34.4 J kg$^{-1}$ K$^{-1}$). For higher field variations (7 T) the performance of Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$(0.6H$_2$O) (46.6 J kg$^{-1}$ K$^{-1}$) is better than what is reported in Gd(CH$_3$COO)$_3$·4H$_2$O (40.0 J kg$^{-1}$ K$^{-1}$).
In summary, gadolinium oxalates were known for a long time. Two crystallographic structures which are close, but present significant differences, were reported: Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$(4H$_2$O) (type 1) and Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$(type 2). Although gadolinium oxalate frameworks were good candidates for magnetic cooling because they associate Gd$^{3+}$ ions with light ligands, they were never investigated in that sense. The original hydrothermal route employed in the present work led to the formation of a low water-content phase of formula Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$·(0.6H$_2$O). This material remains paramagnetic down to 2 K and presents a valuable cryogenic MCE, especially for a moderate field change (2 T). This point is essential for practical applications using permanent magnets as source of magnetic field. In comparison with compounds in which weak Gd$^{3+}$–Gd$^{3+}$ antiferromagnetic interactions exist and limit the amplitude of the MCE for low field changes, the good capabilities of Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$·(0.6H$_2$O) for $\mu_0\Delta H = 2$ T are attributable to the good isolation of the magnetic centers from each other in the lattice.

Finally, it is interesting to note that the 0.6 interstitial water molecules per formula unit present in the investigated MOF could, in principle, be evacuated by a moderate heating at 100 °C (c.f. TGA curve on Fig. 2). Probably, this removal of residual “zeolitic water” would retain the type 2 structure which was originally described for compound Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_6$. The higher magnetic/nonmagnetic atoms mass ratio of this dehydrated compound should lead to a minor enhancement of the
| Compound and reference | $T_\text{m}$ (K) | $\Delta S_m^{\text{max}}$ (J kg$^{-1}$ K$^{-1}$) | $\Delta H_m^{\text{max}}$ (mJ cm$^{-3}$ K$^{-1}$)[b] | $D_{\lambda}$ (g cm$^{-3}$) |
|------------------------|----------------|---------------------------------|---------------------------------|----------------|
| Gd(OH)$_2$CO$_3$       | 1.8            | 54.4[2T], 66.4[7T]             | 291[2T], 355[7T]                | 5.35          |
| $\left\{ \text{Gd}_{4}(\mu_4-O)(\text{H}_2\text{O})_6(\text{H}_2\text{O})_4\text{ClO}_4\right\}_{n}$ | 2.5            | 10[2T], 17.5[3T], 46.6[7T]     | 46.3[2T], 80.9[3T], 215.6[2T]   | 4.63          |
| Gd(HCO$_2$)$_3$        | 2.0            | 43.67[2T], 55.94[7T]           | 168.5[2T], 215.7[7T]            | 3.86          |
| $\left[ \text{Gd}(\text{OH})_3\text{C}_2\text{O}_4\right]_4$ | 1.8            | 18[2T], 48.9[7T]              | 54[2T], 144[7T]                 | 3.00          |
| Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$ | 2.0            | 25.3[2T], 34.4[3T], 46.6[7T]  | 75.9[2T], 103.3[3T], 139.9[7T]  | 3.00          |
| Gd$_2$(C$_2$O$_4$)$_3$(C$_2$H$_5$O)$_2$ | 3.0            | 25[2T], 44[7T]              | 72.3[2T], 127.6[7T]             | 2.90          |
| Gd(HCOO)(C$_2$H$_2$O$_2$)$_2$ | 1.9            | 25.6[2T], 33.3[3T], 46[7T]   | 68.4[2T], 88.8[3T], 122.8[7T]   | 2.67          |
| $\left[ \text{Gd}^{2+}(\text{OH})_2\text{C}_2\text{O}_4\right]_2$ | 2.0            | 15[2T], 42.8[7T]             | 42[2T], 120[7T]                 | 2.80          |
| $\left\{ \text{Gd(ida)}_{2}\text{H}_2\text{O}_4\right\}_n$ | 2.0            | 22.5[2T], 40.6[7T]             | 75.8[2T], 100.7[7T]            | 2.48          |
| Gd$_2$(n$_3$O)$_3$ClO$_4$(NO$_2$)$_6$ | 2.0            | 12.5[2T], 39.7[7T]             | 28.8[2T], 91.3[7T]              | 2.30          |
| Gd(HCOO)$_2$-4H$_2$O | 1.2            | 36[3T], 40.8[7T]             | 671.6[3T], 79.6[7T]             | 1.99          |

MCE compared to Gd$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_2$·(0.6H$_2$O). Finally, the TGA curve for temperatures larger than about 100 °C can be considered to evaluate the thermal stability of the dehydrated framework, i.e., of the magnetocalorically active part of the material. Its stability is rather poor as the water molecules coordinating Gd$^{3+}$ ions are lost above 120 °C. The thermal stability is also, depending on the host device, a criterion of choice for a magnetocaloric substance. In that sense, benefits can be taken from robust magnetocaloric MOFs such as Gd(HCOO)(C$_2$H$_2$O)$_2$.[19]

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