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Magnetocaloric Effect and Thermal Conductivity of Gd(OH)₃ and Gd₂O(OH)₄(H₂O)₂

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Magnetocaloric effect (MCE) and thermal conductivity of two gadolinium hydroxides, Gd(OH)₃ (1) and Gd₂O(OH)₄(H₂O)₂ (2) are investigated. Magnetic study indicates that both 1 and 2 exhibit antiferromagnetic interaction, and the MCE for 1 and 2 at 2 K and ΔH = 7 is 62.00 J kg⁻¹ K⁻¹ and 59.09 J kg⁻¹ K⁻¹, respectively. Investigation on their thermal conductivity shows that the thermal conductivity for 1 is significantly better than that for 2.

Since the magnetocaloric effect (MCE) was discovered by Warburg in 1881,¹ magnetic refrigeration, a cooling technology based on the MCE,² has attracted much interest in the field of magnetic materials,² due to its environmental friendliness and energy efficiency.³ Among different types of magnetic materials, metal clusters and coordination polymers are especially notable. On one hand, their structural diversity and controllability facilitate us to adjust the magnetic interaction between the metal ions, leading to their MCE significantly larger than that of lanthanide alloys and magnetic nanoparticles.⁴ On the other hand, using this kind of magnetic materials as magnetic reagents can achieve ultra-low temperature magnetic reagents. Along this line, we respectively use Gd₂O₃ and Gd(NO₃)₃ to synthesize gadolinium hydroxides, and report herein the MCE and thermal conductivity of two gadolinium hydroxides, namely, Gd(OH)₃ (1) and Gd₂O(OH)₄(H₂O)₂ (2).

Compound 1 was obtained through hydrothermal reaction of Gd₂O₃ and NaOH,¹ instead of the early reported method which needs to dissolved Gd₂O₃ in HNO₃.¹⁶ Single-crystal structure of 1 reveals that it crystallizes in hexagonal space group P6₃/m, in accord with previous research by G. W. Beall and his co-workers.¹⁴ Each
asymmetric unit in \( 1 \) consists of \( 1/6 \) \( \text{Gd}^{3+} \) ion and \( 1/2 \) \( \text{OH}^- \) ion. Each \( \text{Gd}^{3+} \) ion coordinated with nine \( \mu_3\text{-OH} \) in tetrakaidecahedron geometry (Fig. 1a), and each \( \text{OH}^- \) group bridging to three \( \text{Gd}^{3+} \) ions generates a 3D structure with 1D hexagram channel as shown in Fig. 1b. The bond lengths of \( \text{Gd-O} \) are in the range from 2.437 to 2.452 Å, the bond angles of \( \text{Gd-O-Gd} \) are 95.4° to 112.3°, while the separations of \( \text{Gd}···\text{Gd} \) are 3.606 Å and 4.059 Å respectively.

Compound \( 2 \) was obtained through hydrothermal reaction of \( \text{Gd(NO}_3)_3 \cdot 6\text{H}_2\text{O} \), \( \text{HCOONa} \cdot 2\text{H}_2\text{O} \) and glycine.\(^1\) It was mentioned that the \( \text{HCOONa} \) and glycine play an important role in the synthesis. Without the \( \text{HCOONa} \) and glycine, it is impossible to adjust the pH value of the reaction to 6.7. Single-crystal structure analysis reveals that \( 2 \) crystallizes in orthorhombic, space group \( \text{Cmcm} \). The asymmetric unit in \( 2 \) consists of 1 \( \text{Gd}^{3+} \) ion, 1/2 \( \text{O}^2^- \) ion, 2 \( \text{OH}^- \) ions and one coordination water molecule. There are two crystallography independent \( \text{Gd}^{3+} \) ions (\( \text{Gd}1 \) and \( \text{Gd}2 \)) in \( 2 \). The \( \text{Gd}1 \) is eight-coordinated with six \( \mu_3\text{-OH} \), one \( \mu_4\text{-O}_2^- \) and one \( \text{H}_2\text{O} \) in dodecahedron geometry, and the \( \text{Gd}2 \) is nine-coordinated with six \( \mu_3\text{-OH} \), two \( \mu_2\text{-O}^2^- \) and one \( \text{H}_2\text{O} \) in tetrakaidecahedron geometry. The existence of the \( \text{O}^2^- \) in \( 2 \) can be demonstrated from its average \( \text{Gd-O} \) distance and the hydrogen-bonding interaction between the \( \text{O}^2^- \) and coordination water molecules, in addition to the charge balance. In \( 2 \), the average \( \text{Gd-O} \) distance for the \( \text{O}^2^- \) is 2.390 Å, significantly shorter than that of 2.418-2.5223 Å for the \( \text{OH}^- \). Consistently, if taking the \( \mu_3\text{-O}^2^- \) in \( 2 \) as \( \mu_3\text{-OH} \), the hydrogen-bonding interaction between the \( \mu_2\text{-OH} \) and coordinated water will be unreasonable, because the distance between \( \text{H} \) atom in \( \text{OH}^- \) and the \( \text{H} \) atom in coordinated water is only about 1.9 Å.

![](image)

**Fig. 2** (a) The coordination environment of \( \text{Gd}^{3+} \) in \( 2 \). (b) The 2D structure in \( 2 \) viewed along the \( \alpha \) axis. \( \text{Gd} \): cyan; \( \text{O} \): red; \( \text{H} \): light gray. \( \text{H} \) atoms in (b) are omitted for clarity.

The 2D structure in \( 2 \) can viewed as connection of adjacent \( \text{Gd}2 \) ions through two \( \text{OH}^- \) and one \( \text{O}^2^- \) bridges, adjacent \( \text{Gd}1 \) ions through two \( \text{OH}^- \) bridges and adjacent \( \text{Gd}1 \) and \( \text{Gd}2 \) ions through three \( \text{OH}^- \) bridges as shown in Fig. 2b. The adjacent 2D structures connected through hydrogen-bonding interaction between the coordination water molecules from adjacent 2D structures generates a 3D structure of \( 2 \) (ESI, Fig. S1). The bond lengths of \( \text{Gd-O} \) are in the range from 2.324 to 2.617 Å. The bond angles of \( \text{Gd-O-Gd} \) are in the range from 93.2 to 111.3° and the \( \text{Gd}···\text{Gd} \) separations are in the range from 3.655 to 3.939 Å. These values are comparable to the corresponding values in \( 1 \).

The temperature dependence of the magnetic susceptibility for \( 1 \) and \( 2 \) was measured from 2 to 300 K in an applied magnetic field of 1000 Oe respectively. As shown in Fig. S2 (ESI), the \( \chi_M \) \( T \) for \( 1 \) at 300 K is 8.00 cm\(^3\) · K·mol\(^{-1}\), close to that of 7.88 cm\(^3\) · K·mol\(^{-1}\) calculated for one \( \text{Gd}^{3+} \) ion (\( S = 7/2, g = 2 \)). The \( \chi_M \) \( T \) for \( 2 \) at 300 K is 15.51 cm\(^3\) · K·mol\(^{-1}\), close to that of 15.75 cm\(^3\) · K·mol\(^{-1}\) calculated for two non-interacting \( \text{Gd}^{3+} \) ions. With decreasing temperature, the \( \chi_M \) \( T \) for \( 1 \) and \( 2 \) remains essentially constant and then decreases gradually from 100 K to 30 K. On further lowering the temperature, the \( \chi_M \) \( T \) drops abruptly, and reaches 3.32 cm\(^3\) · K·mol\(^{-1}\) for 1 and 5.83 cm\(^3\) · K·mol\(^{-1}\) for 2 at 2 K, suggesting existence of antiferromagnetic coupling in \( 1 \) and \( 2 \). Consistently, fitting the data in the range of 50-300 K with Curie-Weiss law yields \( C = 8.18 \) cm\(^3\) · K·mol\(^{-1}\), \( \theta = -1.69 \) K for \( 1 \) and \( C = 15.84 \) cm\(^3\) · K·mol\(^{-1}\), \( \theta = -4.58 \) K for \( 2 \). The overall magnetic coupling characterized by the Weiss constant for \( 1 \) and \( 2 \) further confirms the antiferromagnetic coupling in \( 1 \) and \( 2 \).
the volumetric entropy change larger than 210 mJ cm\(^{-3}\) K\(^{-1}\) has only observed in three compounds so far (including in the commercial magnetic refrigerant GGG\(^{19}\)), despite a great many efforts made. Based on the Tab. 1, it is clear that -\(\Delta S_m\) for I at 2 K and \(\Delta H = 7\) T is comparable to that of 66.4 J kg\(^{-1}\) K\(^{-1}\) (355 mJ cm\(^{-3}\) K\(^{-1}\)) at 1.8 K and \(\Delta H = 7\) T, the largest -\(\Delta S_m\) reported so far;\(^2\) while the -\(\Delta S_m\) for 2 at 2 K and \(\Delta H = 7\) T is comparable to that of 55.9 J kg\(^{-1}\) K\(^{-1}\) (216 mJ cm\(^{-3}\) K\(^{-1}\)) in Gd(HCOO)\(^{3}\),

Significantly, MCE for I can also get satisfying value of 26.9 J kg\(^{-1}\) K\(^{-1}\) (150 mJ cm\(^{-3}\) K\(^{-1}\)) at \(\Delta H = 2\) T. This value is significantly larger than that for the GGG (-\(\Delta S_m\approx 14.6\) J kg\(^{-1}\) K\(^{-1}\), 105 mJ cm\(^{-3}\) K\(^{-1}\), at \(\Delta H = 2\) T),\(^3\) indicating that I is a promising magnetic refrigeration materials. It was mentioned that, although the -\(\Delta S_m\) for I at 2 K and \(\Delta H = 7\) T is comparable to that for 2 at 2 K and \(\Delta H = 7\) T, the -\(\Delta S_m\) for I at 2 K and \(\Delta H = 2\) T is significantly larger than that for 2 (-\(\Delta S_m = 17.0\) J kg\(^{-1}\) K\(^{-1}\), 62 mJ cm\(^{-3}\) K\(^{-1}\)) at 2 K and \(\Delta H = 2\) T, revealing the weaker the antiferromagnetic interaction in the compound, the larger the MCE at low magnetic field.

Table 1: Magnetic Entropy Change for Selected Materials

<table>
<thead>
<tr>
<th>Compound(^{[w]})</th>
<th>(\Delta H) (T)</th>
<th>-(\Delta S_m)(_{\text{max}}) (J kg(^{-1}) K(^{-1}))</th>
<th>-(\Delta S_m)(_{\text{max}}) (mJ cm(^{-3}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mn}(\text{H}_2\text{O})_6])[\text{MnGd-}] (oda(_2)) [6\text{H}_2\text{O}](^{[17]})</td>
<td>2</td>
<td>0.51</td>
<td>114</td>
</tr>
<tr>
<td>([\text{Gd}(\text{HCOO})_2])(^{[14]})</td>
<td>7</td>
<td>55.9</td>
<td>216</td>
</tr>
<tr>
<td>([\text{Mn}(\text{glc})_2(H_2O)_2])(^{[16]})</td>
<td>7</td>
<td>60.3</td>
<td>112</td>
</tr>
<tr>
<td>([\text{Mn}(\text{glc})_2(H_2O)])(^{[16]})</td>
<td>2</td>
<td>3.49</td>
<td>85</td>
</tr>
<tr>
<td>([\text{Gd}(\text{OH})\text{CO}_3])(^{[12]})</td>
<td>7</td>
<td>66.4</td>
<td>355</td>
</tr>
<tr>
<td>([\text{Gd}(\text{OH})\text{CO}_3])(^{[12]})</td>
<td>2</td>
<td>32.4</td>
<td>173</td>
</tr>
<tr>
<td>GGG</td>
<td>7</td>
<td>38.3</td>
<td>273</td>
</tr>
<tr>
<td>1 in this work</td>
<td>2</td>
<td>14.6</td>
<td>105</td>
</tr>
<tr>
<td>2 in this work</td>
<td>2</td>
<td>62.0</td>
<td>346</td>
</tr>
<tr>
<td>2 in this work</td>
<td>2</td>
<td>14.6</td>
<td>105</td>
</tr>
</tbody>
</table>

Fig. 4: Temperature-dependent thermal conductivity for I and 2.

Because thermal conductivity property of the materials plays a key role in enhancing the thermal efficiency of the refrigeration cycle, the thermal conductivity for I and 2 was investigated respectively, so as to evaluate I and 2 as magnetic refrigeration materials. Based on the equation of \(\kappa = \alpha c_p \rho\) for non-metal materials\(^{20}\) (where \(\alpha\) is thermal diffusion coefficient, \(c_p\) is specific heat capacity, and \(\rho\) is the density of the materials), it is clear that thermal conductivity for a given non-metal material is proportional to its thermal diffusion coefficient, specific heat capacity and density respectively. As the density of I and 2 could be obtained from their crystal structures, thus, the thermal diffusion coefficient and the specific heat capacity of I and 2 were investigated respectively in the temperature range from 312 to 352 K, due to equipment limited. As shown in Fig. S4 (ESI), the specific heat capacity for I at 312 K is 0.58 J g\(^{-1}\) K\(^{-1}\). With increasing temperature, the specific heat capacity for I remains essentially constant and reaches 0.61 J g\(^{-1}\) K\(^{-1}\) at 352 K. In contrast, the specific heat capacity for 2 is significantly affected with the temperature, and it changes from 0.53 J g\(^{-1}\) K\(^{-1}\) at 312 K to 0.71 J g\(^{-1}\) K\(^{-1}\) at 352 K.

Fig. S5 (ESI) illustrated the thermal diffusion coefficient for I and 2 measured in the temperature range from 312 to 352 K. With the increase of temperature, the thermal diffusion coefficient for I decreases gradually, and reaches 0.41 mm\(^2\) s\(^{-1}\) at 312 K. However, the thermal diffusion coefficient for 2 increases with the decrease of the temperature and reaches 0.14 mm\(^2\) s\(^{-1}\) at 312 K. The thermal diffusion coefficient for I significantly better than that for 2 is attributed to the symmetry in I higher than that in 2.\(^{15}\)

Fig. 4 illustrated temperature-dependent thermal conductivity of I and 2. The thermal conductivity for I increases with the decrease of temperature, while this for 2 decreases with the decrease of the temperature in the temperature range from 312 to 352 K. At 312 K, the thermal conductivity for I and 2 is 1.32 and 0.27 W m\(^{-1}\) K\(^{-1}\), respectively. It was noted that the thermal conductivity of I at 312 K is in the same order of magnitude as that of GGG (9 W m\(^{-1}\) K\(^{-1}\)) at room temperature. Because of both the \(\Delta S_m\) and the thermal conductivity of I significantly larger than that of 2, the thermal conductivity of I in the low temperature range was further investigated theoretically according to the reported method,\(^{21}\) due to the equipment limited. Based on the specific heat capacity of I measured in the temperature range from 100 to 400 K and the low temperature specific heat of I in the temperature range from 0.43 to 5.1 K reported previously,\(^{6}\) the thermal conductivity of I at 0.93 K (the magnetic order temperature of I) is about 4.45 W m\(^{-1}\) K\(^{-1}\) (ESI). Although this value is significantly smaller than that of about 9 W m\(^{-1}\) K\(^{-1}\) at 3 K for GGG measured through its single-crystal,\(^{22}\) considered the fact that the thermal conductivity of a given material measured through its powder sample would be significantly smaller than that measured through its single-crystal,\(^{23}\) it is reasonable to conclude that I is a promising candidate for ultra-low temperature magnetic refrigeration material.

Conclusions

In this study, we have reported the magnetocaloric effect and thermal conductivity of two gadolinium hydroxides, I and 2. Study on their MCE at 2 K and \(\Delta H = 2\) T indicates that the \(\Delta S_m\) for I is significantly larger than that for 2, demonstrating the weaker the antiferromagnetic interaction in the compound, the larger the MCE at low magnetic field. Investigation on their thermal conductivity shows that the thermal conductivity for I is significantly better than that for 2, revealing that high symmetry of the compound will enhance its thermal conductivity. Considered the fact that MCE for I at \(\Delta H = 2\) T is significantly larger than that for GGG and the thermal conductivity of I at 0.94 K is up to 4.45 W m\(^{-1}\) K\(^{-1}\), I will be the most promising candidate for ultra-low temperature magnetic refrigeration reagent reported so far.
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Notes and references

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† Electronic Supplementary Information (ESI) available: [The 3D structure of 1 and 2, the temperature dependence of the magnetic susceptibility, field-dependent magnetization, specific heat capacity, thermal diffusion coefficient for 1 and 2, the calculation of thermal conductivity of 1 at low temperature, and Single-crystal X-ray structure determination of 1 and 2]. See DOI: 10.1039/b000000x/