Solvent-free mechanochemical synthesis and magnetic properties of rare-earth based metal-organic frameworks

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Abstract

Mechanical milling of benzene 1,3,5-tricarboxylic acid [$C_6H_3(COOH)_3$], both with the single and mixed rare earth carbonates [$R_2(CO_3)_3 \cdot xH_2O$; $R = Gd, Tb$ and Dy], leads to the formation of metal-organic frameworks [$R\{C_6H_3(COO)_3\}$] that adopt MIL-78 type structure. $M(T)$ data of the investigated MOFs do not show any apparent onset of long range magnetic ordering down to 2 K. The $M(H)$ data for $Gd\{C_6H_3(COO)_3\}$ collected at 2 K show deviations from the magnetization behavior expected for non-interacting Gd^{3+} ions. For the Gd based MOF the temperature dependence of the isothermal magnetic entropy change (i.e. magnetocaloric effect, ΔS_M) exhibits a monotonous increase with decreasing temperature and at $T = 3.5$ K it reaches $34.1 \text{ J kg}^{-1} \text{ K}^{-1}$ for a field change (ΔH) of 50 kOe. For the same ΔH the maximum values of ΔS_M for $R = Tb$ and Dy are $5.5 \text{ J kg}^{-1} \text{ K}^{-1}$ and $8.5 \text{ J kg}^{-1} \text{ K}^{-1}$ at 9.5 K and 4.5 K, respectively.

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1. Introduction

Metal organic frameworks (MOFs) represent an attractive class of hybrid organic–inorganic crystalline materials with applications extending from luminescent materials [2] and advanced gas absorbers,[2,3] to sensors,[4] drug delivery systems[5] and materials for biomedical applications [6–8]. Usually MOFs are synthesized in solution using conventional synthetic approaches, whereby organic linker molecules and metals sources are dissolved in appropriate solvents and exposed to elevated temperatures, microwave or ultrasonic irradiation or electrical current [9,10]. Another recently developed approach to synthesize MOFs is based on the ability of solid metal salts to react with molecular organic solids upon liquid assisted or solvent-free mechanical treatment, which leads to the formation of metal complexes adopting two- or three-dimensional framework structures.[11–13]

Among various MOFs, the rare earth based MOFs are of particular interest due to their potential application as magnetic [14] and luminescent materials.[15] Recently, rare earth containing MOFs have also been probed as magnetic refrigerants at cryogenic temperatures.[16–18]

Magnetic refrigerants are commonly evaluated based on their magnetocaloric effect (MCE), which is measured as isothermal magnetic entropy change and/or adiabatic temperature change. Large molar magnetic entropy [$R \ln(2J+1)$; R = gas constant and J = total angular momentum] associated with the rare earth ions makes the rare earth based MOFs attractive as potential magnetic refrigerant materials for low temperature applications, including liquefaction hydrogen.[19] In the present article we report on mechanochemical synthesis of rare earth-based MOFs with R = Gd, Tb and Dy. In view

of the enhanced photoluminescence properties of the mixed-metal rare earth materials,[20] mechanochemical synthesis of hetero-metallic MOFs has also been demonstrated. The magnetic and magnetocaloric properties of selected MOFs have been investigated.

2. Experimental

Rare earth based MOFs were synthesized by ball milling of 2:1 molar mixtures of benzene 1,3,5-tricarboxylic acid [$C_6H_3(COOH)_3$; also known as trimesic acid (TMA)] and rare earth carbonate hydrates [$R_2(CO_3)_3 \cdot xH_2O$]. In a typical reaction, about one gram of the TMA-metal carbonate mixture was ball milled for two hours in a hardened steel vial using a SPEX 8000M mill. The ball-to-powder mass ratio was consistently kept at about 20:1 for all experiments. The precursors TMA and $Gd_2(CO_3)_3 \cdot 1.2H_2O$ were obtained from MilliporeSigma or other commercial sources ($Tb_2(CO_3)_3 \cdot 4H_2O$ and $Dy_2(CO_3)_3 \cdot 4H_2O$) and used as received.[21] Three hetero-metallic MOFs were synthesized by milling the TMA and rare earth carbonates in following molar ratios:

- a) TMA/ $Gd_2(CO_3)_3 \cdot 1.2H_2O$ / $Tb_2(CO_3)_3 \cdot 4H_2O$: 2.0/0.5/0.5;
- b) TMA/ $Gd_2(CO_3)_3 \cdot 1.2H_2O$ / $Dy_2(CO_3)_3 \cdot 4H_2O$: 2.0/0.5/0.5;
- c) TMA/ $Gd_2(CO_3)_3 \cdot 1.2H_2O$ / $Tb_2(CO_3)_3 \cdot 4H_2O$ / $Dy_2(CO_3)_3 \cdot 4H_2O$: 2.0/0.34/0.33/0.33.

The milled samples were analyzed by powder X-ray diffraction (XRD) on a PANalytical X'PERT powder diffractometer using Cu $K_{\alpha 1}$ radiation. The thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) data were collected using METTLER TOLEDO STAR system. The magnetic properties were measured using the superconducting quantum interference device (SQUID, MPMS XL, Quantum Design, USA). The temperature (T) dependence of magnetization (M) data were collected under

zero field cooled (ZFC), field cooled cooling (FCC) and field cooled warming (FCW) conditions.

3. Results and discussion

Figure 1A shows the room temperature XRD patterns of the 2:1 mixture of TMA and $\text{Gd}_2(\text{CO}_3)_3 \cdot 1.2\text{H}_2\text{O}$ milled for two hours as well as the XRD data of the starting reaction mixture and the Bragg peak positions corresponding to MIL-78. [13,22] The milled material does not contain Bragg reflections corresponding to any of the precursors. The set of broad Bragg peaks produced by the milled sample matches well that of MIL-78. Similar results – the XRD patterns corresponding to the MIL-78 type structure – were also obtained upon ball milling of TMA with Tb and Dy carbonates. To prepare hetero-metallic MOFs, combinations of different rare earth carbonates were also milled with TMA, and the XRD patterns of the milled powders are shown in Fig. 1B. During milling the total metal to TMA molar ratio was kept to 1:1. We note that milling of the mixture of gadolinium and dysprosium carbonates with TMA leads to a single phase hetero-metallic rare earth trimesate [13,22] having MIL-78 type structure and a minor unidentified impurity phase.

The samples prepared by ball milling were also investigated using TGA/DSC in the temperature range between 20 and 650 °C in air. The TGA/DSC plots for representative materials are shown in Fig. 2. According to TGA, the synthesized materials are stable up to 450 °C, and their thermal decomposition profile at higher temperatures resembles that of the rare earth based MIL-78 MOFs reported earlier.[13,22] A minor weight loss in the as-synthesized products, most notably in the $\text{Gd}_{0.34}\text{Tb}_{0.33}\text{Dy}_{0.34}$ –TMA sample, observed early during the heating is attributed to the residual water that was entrapped in the

sample after the reaction. Since no thermal events or Bragg peaks related to starting materials could be detected in the samples of the ball milled material in our TGA/DSC or XRD experiments, it is safe to conclude that the formation of 3D nanostructures as described by Equation 1 was complete.

In order to remove water and CO₂ – the potential guest molecules - from the 3D network formed, the synthesized MOFs were heat treated at 300 °C for 5 h under dynamic vacuum. It has been reported previously that the removal of guest molecules may lead to the collapse of MOF structures.[23] However, no such collapse or structure change could be observed in our case (pattern ‘c’ in Fig 1A). Similar results were obtained for other single and hetero-metallic synthesized trimesates.

It is worth noting that the formation of MIL-78 structure during solvent-free ball milling of rare earth carbonates with TMA differ from the results previously reported by Yuan *et al.*[24] for similar systems, but are in nearly perfect agreement with our earlier studies on the mechanochemical transformations of YH₃ with TMA in the absence of solvents.[13] In an attempt to reproduce the results reported by Yuan *et al.*, milling of R₂(CO₃)₃•xH₂O with TMA was also performed in the presence of anhydrous dimethylformamide and diethyl ether. In both cases the reaction did not take place and no formation of ordered 3D framework structures could be detected.

The magnetic properties of single metallic rare earth trimesates [13,22] [R-TMA; R = Gd, Tb and Dy] have been investigated by measuring the temperature (T) dependencies of the magnetization (M) in the fields (H) of 500 Oe and 50 kOe under ZFC, FCC and FCW conditions and the representative $M(T)$ data set for $H = 50$ kOe for Gd-TMA is shown in Fig. 3. With decreasing temperature the $M(T)$ in FCC mode shows a monotonous increase, and no apparent onset of long range magnetic ordering is seen down to 2 K. Also, the $M(T)$ collected under ZFC, FCC and FCW modes do not exhibit thermomagnetic irreversibility, which further rules out presence of any long range magnetic order in the investigated temperature regime.[25] A similar behavior is seen in 500 Oe $M(T)$ dataset as well.

The temperature dependence of inverse susceptibility (H/M) and the Curie-Weiss fit to it for Gd-TMA is shown in the inset of Fig 3. Above 20 K, the inverse susceptibility data could be fitted to the Curie-Weiss law which yields a paramagnetic Weiss temperature (Θ_P) of -2.3 K and an effective moment (P_{eff}) of $7.97 \mu_B/\text{Gd}^{3+}$. The experimentally determined P_{eff} matches the theoretical value of $7.94 \mu_B/\text{Gd}^{3+}$. The negative Θ_P indicates that despite the lack of long range magnetic order, weak antiferromagnetic interactions may be present in the compound. We also note that below 20 K H/M exhibits deviation from the Curie-Weiss behavior, which may be attributed to the presence of short range magnetic correlations.[26] Owing to the presence of weak superexchange interactions a similar magnetic behavior has been observed in other rare earth based MOFs.[14–17] The observed value of Θ_P for Gd-TMA is in agreement with typical Θ_P 's ($|\Theta_P|$ is usually ~ 2 K) reported for other Gd-based MOFs.

For Tb-TMA and Dy-TMA, P_{eff} is $9.64 \mu_B/\text{Tb}^{3+}$ and $10.61 \mu_B/\text{Dy}^{3+}$, respectively. The P_{eff} values match the theoretically expected values of $9.72 \mu_B/\text{Tb}^{3+}$ and $10.63 \mu_B/\text{Dy}^{3+}$.

Figure 4 shows the $M(H)$ data for Dy-TMA collected at $T = 2$ K. The $M(H)$ plots collected at higher temperatures are shown as inset. Below $H = 10$ kOe the magnetization increases rather rapidly and at higher fields shows tendency towards saturation. The $M(H)$ data collected during increasing and decreasing fields exhibit no hysteresis. A similar behavior is observed in other compounds as well. A linear fit to the 2 K magnetization as a function of inverse of the field yields saturation moments of $7 \mu_B$, $4.8 \mu_B$ and $5.3 \mu_B$ per R^{3+} for the compounds with $\text{R} = \text{Gd}$, Tb and Dy , respectively. The saturation magnetization in compounds containing Gd , Tb and Dy is expected to be $7 \mu_B$, $9 \mu_B$ and $10 \mu_B$ per R^{3+} , respectively. We note that saturation moment for $\text{Gd} - \text{TMA}$ is same as the expected value whereas for Tb-TMA and Dy-TMA it is significantly lower than the expected saturation. It is well known that in rare earth containing compounds with metals other than Gd the crystalline electric field (CEF) often leads to quenching of orbital moments which causes reduction in the saturation magnetization.[27] Thus, the reduction in the saturation moment for R-TMA with $\text{R} = \text{Tb}$ and Dy may be attributed to CEF effect. Similar behavior has been observed in other rare earth based MOFs with R other than Gd .[15,17]

In view of the absence of any apparent long range magnetic ordering and low value of θ_p , the 2 K $M(H)$ isotherm of Gd-TMA was also compared with the $M(H)$ generated theoretically under the assumption of non interacting Gd^{3+} ions (Brillouin function; see Fig. 5). The Gd based compound was chosen to avoid CEF effects. At 2 K, experimental magnetization is lower than that expected from a system of non-interacting Gd^{3+} ions.

This is in accord with the observed deviation in the inverse susceptibility and negative θ_p .

The magnetocaloric effect (MCE) has been calculated as the isothermal magnetic entropy change (ΔS_M) using the $M(H)$ data collected at various temperatures and by employing Maxwell's relations.[28] Figure 6 shows the ΔS_M vs T plots for all of the compounds. For Gd-TMA the ΔS_M vs. T plots exhibit monotonous increase with decreasing temperature and at $T = 3.5$ K it reaches $14.2 \text{ J kg}^{-1}\text{K}^{-1}$ and $34.1 \text{ J kg}^{-1}\text{K}^{-1}$ for field change (ΔH) of 20 kOe and 50 kOe, respectively. In sharp contrast to Gd-TMA, the ΔS_M vs. T plots for Tb-TMA and Dy-TMA show a maximum. Generally, a maximum in the ΔS_M vs. T occurs near magnetic order-disorder transition, spin reorientation transition etc;[28] however, no signature of long range magnetic transition is seen in $M(T)$ data of any of the studied R-TMA compounds. Thus, the observation of a monotonous increase in ΔS_M vs. T plot of Gd-TMA is consistent with its $M(T)$ behavior. For Tb-TMA and Dy-TMA, the appearance of a maximum in ΔS_M vs. T plots may have origin in CEF effect.[29] For Tb-TMA the maximum values of ΔS_M are $2.7 \text{ J kg}^{-1}\text{K}^{-1}$ and $5.5 \text{ J kg}^{-1}\text{K}^{-1}$ for $\Delta H = 20$ kOe and 50 kOe, respectively, whereas for Dy-TMA it is $5.6 \text{ J kg}^{-1}\text{K}^{-1}$ and $8.5 \text{ J kg}^{-1}\text{K}^{-1}$ for $\Delta H = 20$ kOe and 50 kOe, respectively.

The theoretical magnetic entropy of R-TMA compounds with $R = \text{Gd, Tb and Dy}$ is $47.6 \text{ J kg}^{-1}\text{K}^{-1}$, $58.4 \text{ J kg}^{-1}\text{K}^{-1}$ and $62.6 \text{ J kg}^{-1}\text{K}^{-1}$, respectively. We note that for Gd-TMA in a relatively weak magnetic field change of 50 kOe, the maximum value of ΔS_M reaches an extraordinarily high value of 70% of the total available magnetic entropy, whereas for $R = \text{Tb and Dy}$ it is 9.4% and 13.6%, respectively. This reduction in the utilization of the

magnetic entropy for Tb and Dy based trimesates may be attributed to the single ion anisotropy brought about by the CEF.[29,30]

For $\Delta H = 20$ kOe, the maximum values of ΔS_M in $Gd_3Ga_5O_{12}$, $Gd_2(fum)_3(H_2O)_4 \cdot 3H_2O$, $[Gd(OAc)_3(H_2O)_2]_2 \cdot 4H_2O$ and $Gd(HCOO)_3$, which are considered important magnetic refrigerants in the liquid helium temperature regime, have been reported to be $20.4 \text{ J kg}^{-1}\text{K}^{-1}$, $18 \text{ J kg}^{-1}\text{K}^{-1}$, $32.6 \text{ J kg}^{-1}\text{K}^{-1}$ and $43.7 \text{ J kg}^{-1}\text{K}^{-1}$, respectively.[16] Thus a comparison of the ΔS_M of Gd-TMA with other known refrigerant makes it a promising candidate for applications based on MCE in cryogenic temperature region, e.g. in adiabatic demagnetization refrigeration.

4. Conclusions

In summary, mechanochemical synthesis of both mono and hetero metallic rare earth based MOFs has been demonstrated starting from rare earth carbonates and TMA as precursors. Contrary to previous report,[24] in absence of liquid assisted grinding, the milling of both single and mixed rare earth carbonates with TMA leads to formation of rare earth trimesates, which are metal organic frameworks having MIL-78 type structure. The rare earth trimesates [R - TMA; with R = Gd, Tb and Dy] show short range magnetic order below 20 K; however, no signature of long range order is observed down to 2 K. In compounds with R=Tb and Dy the crystalline electric field appears to cause the quenching of orbital moments. The magnetocaloric effect of Gd-TMA is uncommonly strong, and is comparable to some of the best known cryogenic refrigerants.

Acknowledgments

We thank Dr. Meenakshi Hardi for discussions and Dr. Shashi Jasty for support and encouragement. The work at Ames Laboratory was supported by Sigma-Aldrich

Corporation (preparation and structural characterization) and the Office of Basic Sciences of the Office of Science of the U.S. Department of Energy under contract No. DE-AC02-07CH11358 with Iowa State University of Science and Technology (magnetic property measurements).

References:

1. Y. Cui, Y. Yue, G. Qian, B. Chen, Luminescent Functional Metal–Organic Frameworks, *Chem. Rev.* 112 (2012), 1126–1162.
2. M. P. Suh, H. J. Park, T. K. Prasad, D.-W. Lim, Hydrogen Storage in Metal–Organic Frameworks *Chem. Rev.* 112 (2012) 782–835.
3. H.-C. Zhou, J. R. Long, O. M. Yaghi, Introduction to Metal–Organic Frameworks, *Chem. Rev.* (112) 2012, 673–674.
4. B. Liu, Metal–organic framework-based devices: separation and sensors *J. Mater. Chem.*, 22 (2012), 10094–10101.
5. P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Ferey, R. E. Morris, C. Serre, Metal–Organic Frameworks in Biomedicine *Chem. Rev.* 112 (2012) 1232–1268.
6. A. C. McKinlay, R. E. Morris, P. Horcajada, G. Ferey, R. Gref, P. Couvreur, C. Serre, BioMOFs: metal-organic frameworks for biological and medical applications, *Angew. Chem. Int. Ed.* 49 (2010) 6260–6266.
7. Aldrich MOF Constructor: <http://www.sigmaaldrich.com/mofconstructor>.
8. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-A. Bae J. R. Long, Carbon Dioxide Capture in Metal–Organic Frameworks, *Chem. Rev.* 112 (2012) 724–781.
9. S. R. Caskey, A. J. Matzger, Selected Applications of Metal Organic Frameworks in Sustainable Energy Technologies, *Material Matters* 4 (2009) 111–118.
10. N. Stock, S. Biswas, Synthesis of Metal–Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites, *Chem. Rev.*, 112 (2012) 933–969 and references therein.
11. V. P. Balema, J. W. Wiench, M. Pruski, V. K. Pecharsky, Solvent-free mechanochemical synthesis of phosphonium salts, *Chem Commun* (2000) 724–725.
12. S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, Mechanochemistry: opportunities for new and cleaner synthesis, *Chem. Soc. Rev.* 41 (2012) 413–447 and references therein.
13. N. K. Singh, M. Hardi, V. P. Balema, Mechanochemical synthesis of an yttrium based metal–organic framework, *Chem. Commun.* 49 (2013) 972–974.
14. G. Lorusso, M. A. Palacios, G. S. Nichol, E. K. Brechin, O. Rubeau, M. Evangelisti, Increasing the dimensionality of cryogenic molecular coolers: Gd-based polymers and metal–organic frameworks, *Chem. Commun.* 48 (2012) 7592–7594.

15. M. Fang, J.-J. Li, P.-F. Shi, B. Zhao, P. Cheng, *Dalton Trans.* 42 (2013) 6553– and references therein.
16. G. Lorusso, J. W. Sharples, E. Palacios, O. Roubeau, E. K. Brechin, R. Sessoli, A. Rossin, F. Tuna, E. J. L. McInnes, D. Collison, M. Evangelisti, A Dense Metal–Organic Framework for Enhanced Magnetic Refrigeration *Adv. Mater.* 25 (2013) 4653–4656.
17. P.-F. Shi, Y.-Z. Zheng, X.-Q. Zhao, G. Xiong, B. Zhao, F.-F. Wan, P. Cheng, 3 D MOFs Containing Trigonal Bipyramidal Ln_5 Clusters as Nodes: Large Magnetocaloric Effect and Slow Magnetic Relaxation Behavior *Chem. Eur. J.* 18 (2012), 15086–15091.
18. R. Sibille, T. Mazet, B. Malaman, M. Francois, A Metal–Organic Framework as Attractive Cryogenic Magnetorefrigerant *Chem. Eur. J.* 18 (2012) 12970–12973.
19. K. A. Gschneidner, Jr., V. K. Pecharsky, A. O. Tsokol, Recent developments in magnetocaloric materials, *Rep. Prog. Phys.* 68 (2005) 1479–1539.
20. L. Hu, R. Ma, T. C. Ozawa, T. Sasaki, Synthesis of a solid solution series of layered $\text{Eu}_x\text{Gd}_{1-x}(\text{OH})_{2.5}\text{Cl}_{0.5}\cdot 0.9\text{H}_2\text{O}$ and its transformation into $(\text{Eu}_x\text{Gd}_{1-x})_2\text{O}_3$ with enhanced photoluminescence properties, *Inorg. Chem.* 49 (2010) 2960–2968.
21. The water content in the as-received $\text{Gd}_2(\text{CO}_3)_3\cdot x\text{H}_2\text{O}$ from Aldrich was determined to be 1.2 H_2O per formula unit by performing the Thermo-Gravimetric Analysis in air using METTLER TOLEDO STAR System.
22. C. Serre, F. Millange, C. Thouvenot, N. Gardant, F. Pellé, G. Férey, Synthesis, characterization and luminescent properties of a new three-dimensional lanthanide trimesate: $\text{M}((\text{C}_6\text{H}_3)(\text{CO}_2)_3)$ ($\text{M} = \text{Y}, \text{Ln}$) or MIL-78, *J. Mater. Chem.* 14 (2004) 1540–1543.
23. M. Klimakow, P. Klobes, A. F. Thunemann, K. Rademann, F. Emmerling, Mechanochemical Synthesis of Metal–Organic Frameworks: A fast and facile approach toward quantitative yields and high specific surface areas, *Chem. Mater.* 22 (2010) 5216–5221.
24. W. Yuan, J. O'Connor, S. L. James, Mechanochemical synthesis of homo- and hetero-rare-earth(III) metal–organic frameworks by ball milling, *CrystEngComm.* 12 (2010) 3515–3517.
25. F.-S. Guo, Y.-C. Chen, J.-L. Liu, J.-D. Leng, Z.-S. Meng, P. Vrabel, M. Orendac, M.-L. Tong, A large cryogenic magnetocaloric effect exhibited at low field by a 3D ferromagnetically coupled $\text{Mn}(\text{II})$ – $\text{Gd}(\text{III})$ framework material, *Chem. Commun.* 48 (2012) 12219–12221.
26. N. K. Singh, V. K. Pecharsky, K. A. Gschneidner, Jr., Unusual magnetic properties of $(\text{Er}_{1-x}\text{Gd}_x)_5\text{Si}_4$ compounds *Phys. Rev. B* 77 (2008) 054414–054424.
27. J. M. Cadogan, D. H. Ryan, Z. Altounian, H. B. Wang, I. P. Swainson, The magnetic structures of Nd_5Si_4 and Nd_5Ge_4 , *J. Phys. : Condens. Matter* 14 (2002) 7191–7200.
28. V. K. Pecharsky, K. A. Gschneidner, Jr., $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$: An Extremum Material, *Adv. Mater.* 13 (2001) 683–686.
29. M. Evangelisti, E. K. Brechin, Recipes for enhanced molecular cooling, *Dalton Trans.* 39 (2010) 4672–4676.
30. K. A. Gschneidner, Jr., V. K. Pecharsky, Magnetic refrigeration materials, *J. Appl. Phys.* 85 (1999) 5365–5368.

Figure Captions:

Fig. 1. A) Room temperature x-ray diffraction (XRD) patterns of a) 2:1 molar mixture of $C_6H_3(COOH)_3$ (TMA) and $Gd_2(CO_3)_3 \cdot 1.2H_2O$, and b) the mixture milled for 3 hrs. 'c' represents the XRD pattern of the milled sample after heat treatment at 300 °C under vacuum. B) Room temperature XRD patterns of hetero-metallic MOFs synthesized by milling the TMA and rare earth carbonates in following molar ratios: (a) TMA / $Gd_2(CO_3)_3 \cdot 1.2H_2O$ / $Tb_2(CO_3)_3 \cdot 4H_2O$: 2.0 / 0.5 / 0.5; (b) TMA / $Gd_2(CO_3)_3 \cdot 1.2H_2O$ / $Dy_2(CO_3)_3 \cdot 4H_2O$: 2.0 / 0.5 / 0.5; (c) TMA / $Gd_2(CO_3)_3 \cdot 1.2H_2O$ / $Tb_2(CO_3)_3 \cdot 4H_2O$ / $Dy_2(CO_3)_3 \cdot 4H_2O$: 2.0 / 0.34 / 0.33 / 0.33. The '*' in panels 'b' and 'c' of 1B show the peaks corresponding to the unidentified impurity phase. The vertical bars at the bottom of both the plots show the calculated Bragg peaks corresponding to MIL-78 structure.

Fig. 2. The thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) data for the materials synthesized by ball milling of the Gd, Tb and Dy carbonates with trimesic acid (TMA, $C_6H_3(COOH)_3$), i.e. Gd-TMA, $Gd_{0.5}Dy_{0.5}$ -TMA) and $Gd_{0.34}Tb_{0.33}Dy_{0.34}$ -TMA.

Fig. 3. (Color online) Temperature (T) dependence of magnetization (M) data of Gd - TMA collected in an applied field (H) of 50 kOe under 'zero field cooled' (ZFC), 'field cooled cooling' (FCC) and, 'field cooled warming' (FCW) conditions. The inset shows the temperature dependence of inverse susceptibility (H/M) and Curie-Weiss fit to it.

Fig 4. (Color online) Field (H) dependence of magnetization (M) data of Dy-TMA collected at $T = 2$ K. The inset shows the $M(H)$ plots collected at various temperatures between 3–30 K.

Fig. 5. (Color online) Field (H) dependence of magnetization (M) isotherm of Gd-TMA collected at 2 K along with the $M(H)$ generated theoretically under the assumption of non-interacting Gd^{3+} ions (Brillouin function).

Fig. 6. (Color online) Temperature (T) dependence of isothermal magnetic entropy change (ΔS_M) for (a) Gd-TMA, (b) Tb-TMA and, (c) Dy-TMA for field changes (ΔH) of 20 and 50 kOe.

Graphical Abstract: