



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



N.K. Singh ^a, S. Gupta ^{b,*}, V.K. Pecharsky ^b, V.P. Balema ^{a,b,**}

^a Aldrich Materials Science, Sigma Aldrich Corp., 6000 N. Teutonia Avenue, Milwaukee, WI, 53209, USA

^b The Ames Laboratory, Iowa State University, Ames, IA, 50011, USA

ARTICLE INFO

Article history:

Received 10 May 2016

Received in revised form

14 November 2016

Accepted 16 November 2016

Available online 17 November 2016

Keywords:

Mechanochemical synthesis

Metal-organic frameworks

Magnetic properties

Magnetocaloric

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 $34.1 \text{ J kg}^{-1}K^{-1}$ for a field change (ΔH) of 50 kOe. For the same ΔH the maximum values of ΔS_M for $R = Tb$ and Dy are $5.5 \text{ J kg}^{-1}K^{-1}$ and $8.5 \text{ J kg}^{-1}K^{-1}$ 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 [1] 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 M 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

* Corresponding author. The Ames Laboratory, Iowa State University, Ames, IA, 50011, USA.

** Corresponding author. Current address: The Ames Laboratory, Iowa State University, Ames, IA, 50011, USA.

E-mail addresses: Shalabh@ameslab.gov (S. Gupta), vbalema@ameslab.gov (V.P. Balema).

hardened steel vial using a SPEX 8000 M mill. The ball-to-powder mass ratio was consistently kept at about 20:1 for all experiments. The precursors TMA and $\text{Gd}_2(\text{CO}_3)_3 \cdot 1.2\text{H}_2\text{O}$ were obtained from MilliporeSigma or other commercial sources ($\text{Tb}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$ and $\text{Dy}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$) and used as received [21]. Three heterometallic MOFs were synthesized by milling the TMA and rare earth carbonates in following molar ratios:

- TMA/ $\text{Gd}_2(\text{CO}_3)_3 \cdot 1.2\text{H}_2\text{O}$ / $\text{Tb}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$: 2.0/0.5/0.5;
- TMA/ $\text{Gd}_2(\text{CO}_3)_3 \cdot 1.2\text{H}_2\text{O}$ / $\text{Dy}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$: 2.0/0.5/0.5;
- TMA/ $\text{Gd}_2(\text{CO}_3)_3 \cdot 1.2\text{H}_2\text{O}$ / $\text{Tb}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$ / $\text{Dy}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$: 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 $\text{Cu K}\alpha_1$ 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

Fig. 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

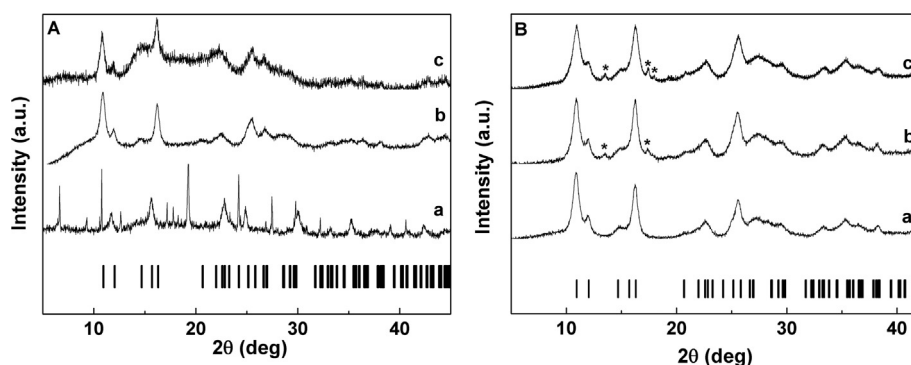
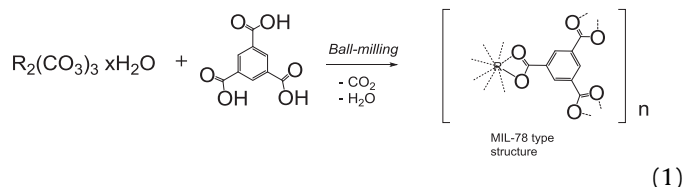


Fig. 1. A) Room temperature x-ray diffraction (XRD) patterns of a) 2:1 M mixture of $\text{C}_6\text{H}_3(\text{COOH})_3$ (TMA) and $\text{Gd}_2(\text{CO}_3)_3 \cdot 1.2\text{H}_2\text{O}$, and b) the mixture milled for 3 h 'c' represents the XRD pattern of the milled sample after heat treatment at 300 °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/ $\text{Gd}_2(\text{CO}_3)_3 \cdot 1.2\text{H}_2\text{O}$ / $\text{Tb}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$: 2.0/0.5/0.5; (b) TMA/ $\text{Gd}_2(\text{CO}_3)_3 \cdot 1.2\text{H}_2\text{O}$ / $\text{Dy}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$: 2.0/0.5/0.5; (c) TMA/ $\text{Gd}_2(\text{CO}_3)_3 \cdot 1.2\text{H}_2\text{O}$ / $\text{Tb}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$ / $\text{Dy}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$: 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. 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 CO_2 – 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

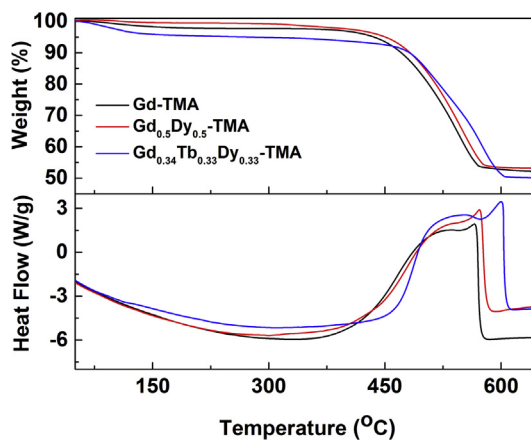


Fig. 2. The thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) data for the materials synthesized by ball milling of the Gd, Tb and Dy carbonates with trimesic acid (TMA, $\text{C}_6\text{H}_3(\text{COOH})_3$), i.e. Gd-TMA, $\text{Gd}_{0.5}\text{Dy}_{0.5}$ -TMA and $\text{Gd}_{0.34}\text{Tb}_{0.33}\text{Dy}_{0.34}$ -TMA.

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