

SUPPLEMENTARY MATERIALS

**XRD and IR structural investigations of a special breathing effect
in the MOF-type gallium terephthalate MIL-53(Ga).**

Experimental

Synthesis and characterization of as-synthesized MIL-53(Ga). Our synthesis differs from that of Jacobson *et al.*⁹ which involves shorter reaction times. MIL-53(Ga) was hydrothermally synthesized under autogenous pressure from a mixture of 1.0 g (3.9 mmol) gallium nitrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, Alfa Aesar, 99.999 %), 0.76 g (4.6 mmol) terephthalic acid ($\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$, Aldrich, >99 %) and 20 ml (1111 mmol) deionized water. The reactants are mixed together in a 125 ml Teflon-lined stainless Parr autoclave, which was heated in an oven at 210°C for 3h30 hours. After filtration and washing with N,N-dimethylformamide (Alfa Aesar, anhydrous, 99.8 %, noted DMF) in order to remove re-crystallized terephthalic acid, the resulting white product was first identified by powder X-ray diffraction and was found to be similar to the MIL-53 phase obtained with aluminium⁶ or gallium⁹. The SEM examination showed a well crystalline sample with parallelepiped-shape crystallites of 10-100 μm (Fig. 1).

One also noted that large MIL-53(Ga) crystals have been obtained by using the fluorides route together with the methyl ester form of the carboxylic acid. It was well known that the addition of fluorides anions are assumed to improve the crystallization of the final product and the use of the methyl ester carboxylate species was observed to undergo slow hydrolysis under hydrothermal conditions to form the carboxylic acid, which further reacts with metallic cations. Crystal growth of MIL-53(Ga) is observed from the hydrothermal reaction of a mixture of 1.44 g (5.6 mmol) gallium nitrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, Alfa Aesar, 99.999 %), 0.8 g (4.1 mmol) dimethyl terephthalate ($\text{CH}_3\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{CH}_3$, Aldrich, >99 %), 0.2 ml (4.6 mmol) hydrofluoric acid (RP Normapur, 48 %) and 20 ml (1111 mmol) deionized water. The reactants are placed together in a 125 ml Teflon-lined stainless Parr autoclave, which was heated in an oven at 210°C for 5 hours. This synthetic procedure is shorter compared to reaction time of 3 days described by Jacobson *et al.* The optical examination of a sample of MIL-53(Ga) showed well crystalline powder with parallelepiped-shape crystals of 100-300 μm size. Elongated needle-like crystals of crystallized terephthalic acid are also observed together with the MIL-53(Ga) solid. Suitable single crystals can be easily isolated for its structure determination with the following cell parameters $a = 17.447(1)$, $b = 6.7561(3)$, $c = 12.1663(7)$ Å, $V = 1434.1(1)$ Å³ ($Pnma$ n°62), which are similar to the phase described by Jacobson *et al.*

Infrared spectroscopy. Preliminary IR spectroscopy experiments (Versailles) of the as-synthesized MIL-53(Ga) and MIL-53(Ga){DMF} samples were performed on a Nicolet 550 FTIR spectrometer at room temperature in the range 400-4000 cm^{-1} , with samples in potassium bromide pellets. The analysis of the MIL-53(Ga) and MIL-53(Al) networks flexibility was carried out on the Nicolet Nexus spectrometer equipped with an extended KBr beam splitting device and a mercury cadmium telluride (MCT) cryodetector (Caen). The samples (2 mg) was dispersed in deionized water and spread on a silicon wafer. They were placed in a quartz cell equipped with KBr windows. Movable quartz sample holders allow for the adjustment of the pellet in the infrared beam for spectra acquisition and displace it into a furnace at the top of the cell for thermal treatments. The cell was connected to a vacuum line for evacuation, calcination steps – residual pressure 10⁻² torr). Transmission IR spectra were recorded at room temperature in the 600-5600 cm^{-1} range, with a 4 cm^{-1} resolution.

Thermogravimetric Analysis. The thermogravimetric analyses of the two different samples (MIL-53(Ga){DMF} and MIL-53(Ga){H₂O}) were performed on a TA Instrument 2050 apparatus under O₂ with a heating rate of 1°C.min⁻¹ between 30°C and 600°C.

Preparation of the hydrated form MIL-53(Ga){H₂O}. As described in previous works^{4, 6, 7, 9}, the as-synthesized MIL-53-type metal terephthalates exhibit a three-dimensional open framework with unreacted terephthalic acid species encapsulated within the pores. In order to remove these trapped molecules, the as-synthesized MIL-53(Ga) was treated with DMF (Alfa Aesar, anhydrous, 99.8 %) in hydrothermal condition at 200°C for 36 hours by using a 125 ml Teflon-lined stainless Parr autoclave (0.5 g MIL-53 in 30 ml DMF). The resulting product (noted MIL-53{DMF}) was then filtered off and washed with DMF. XRD analysis showed a new pattern (see supplementary materials). IR spectroscopy (see supplementary materials) and TGA indicated that the encapsulated terephthalic acid is exchanged by DMF species.

The IR spectrum of the as-synthesized MIL-53(Ga) phase shows specific vibrational bands at 2660 and 2530 cm⁻¹ assigned to the ν(OH), at 1695 cm⁻¹ assigned to ν(C=O) and at 1283 cm⁻¹ assigned to the ν(C-O) stretching frequency of the free terephthalic acid trapped within the tunnels. This resonance peaks disappear in the DMF-exchanged sample and other stretching vibrations are observed at 2930 and 2870 cm⁻¹ corresponding to ν(O=C-H) and at 1660 cm⁻¹ corresponding to the ν(C=O) resonance of the free DMF species within the channels. The DMF content can be estimated from the thermogravimetric analysis (Fig. 2), which shows a curve with two weight losses. The first event is assigned to the removal of DMF species from the channels (obs.: 20.4%) up to 180°C and the second one, to the decomposition of the solid with the departure of the terephthalate linker (obs.: 48.6 %; calc. 51.9%) from 360°C. Taking into account the formation of gallium oxide from 450°C (obs.: 31.0 %), it can be deduced the following DMF amount of 0.84 per Ga atom, or the chemical formula of MIL-53(Ga){DMF}: Ga(OH)[O₂C-C₆H₄-CO₂]-0.84DMF. The SEM photographs show well crystalline product with crystallites of 10-100 μm (Fig. 1).

The occluded DMF molecules are then extracted upon heating the sample MIL-53(Ga){DMF} at 280°C in air in a furnace for 24 hours. The powdered sample was then left at room temperature under ambient air and the formation of hydrated form of MIL-53(Ga){H₂O} was observed as it was reported for the parent phases prepared with aluminum or chromium. The thermogravimetric curve (Fig. 2) of the hydrated form indicates two events. The first weight loss from room temperature up to 90°C, is attributed to the evacuation of the trapped water molecules from the channels (obs.: 6.5%; calc.: 6.7 %). A plateau is then observed up to 340°C, followed by the second weight loss corresponding to the departure of the terephthalate species (obs.: 58.0 %; calc.: 58.4 %) and the formation of gallium oxide Ga₂O₃ (obs.: 35.5%; calc.: 34.9 %) from 460°C. It results in the following chemical formula of the gallium terephthalate MIL-53(Ga){H₂O}: Ga(OH)[O₂C-C₆H₄-CO₂]-H₂O. The structural transitions with temperature of the hydrated form will be discussed in the following parts. It was observed the formation of an intermediate phase (noted MIL-53(Ga)_lt) and high temperature phase (noted MIL-53(Ga)_ht).

Powder X-ray diffraction. The MIL-53(Ga)_lt phase was isolated upon heating in a furnace at 200°C for 12 hours a glass capillary filled with the hydrated form MIL-53(Ga). The latter was sealed with Araldite glue in order to prevent rehydration process and then removed from the furnace. The same heating procedure was applied for the high temperature MIL-53(Ga)_ht form (at 400-420°C) but it was not possible to isolate accurately the latter, because of its narrow thermal stability domain.

The X-ray diffraction data were collected on the beamline CRISTAL at synchrotron Soleil (France) of both MIL-53(Ga){H₂O} and MIL-53(Ga)_lt. A monochromatic beam of wavelength 0.7285 Å was extracted from the undulator beam using a double crystal Si(111) monochromator. The samples placed inside a 0.7 mm diameter glass capillary (Borokapillaren, GLAS, Schönwalde, Germany), were mounted on a two circles diffractometer equipped with a 13 crystals multi-analyzer. With this setup, it took less than

two hours in a continuous scanning mode to collect a high angular resolution diagram. The experimental data file is obtained from the precise superposition and addition of the 13 channels data.

The X-ray diffraction powder patterns have been indexed and refined by using TOPAS software suite. The structures of the parent iron terephthalates MIL-53 [MIL-53(Fe)_lt – corresponding to MIL-53(Ga){H₂O} – and MIL-53(Fe)_ht – corresponding to MIL-53(Ga)_lt] have been used as starting models in Rietveld refinements by taking the rigid bodies positions of organic moieties (terephthalate anions) and replacing iron atoms by gallium. At the final stage, the Rietveld refinement of MIL-53(Ga){H₂O} involved the following structural parameters: 15 atomic coordinates (Ga1, OH1, OH2, Ow1 and Ow2), 6 translation and 6 rotation parameters of terephthalate anions as well as 5 geometrical parameters for each organic specie (C-C distances and tilt angles of the -CO₂ functions), 4 thermal factors and 1 scale factor in comparison with 87 atomic coordinates corresponding to 31 non-hydrogen independent atoms. The same procedure was used for the Rietveld refinement of MIL-53(Ga)_lt, which involved at the final stage 1 atomic coordinate (OH1), 3 rotation parameters of the terephthalate anion as well as 4 geometrical parameters for the organic molecule (C-C distances and tilt angle of the -CO₂ functions), 3 thermal factors and 1 scale factor. In both cases, the anisotropic line broadening effect was modeled by using spherical harmonics series. Moreover, some GaO(OH) impurity was also detected on the synchrotron patterns and was taken into account in the refinements with an estimated contribution of about 1 % wt. The final Rietveld plots (Fig. 3) correspond to satisfactory model indicators ($R_B = 0.040$ and 0.056) and profile factors ($R_P = 0.094$ and 0.103 ; $R_{WP} = 0.122$ and 0.132) for MIL-53(Ga){H₂O} and MIL-53(Ga)_lt, respectively.

Thermodiffraction. X-ray thermodiffraction was performed under static air in an Anton Parr HTK16 high temperature device of a Siemens D-5000 diffractometer (θ - θ mode, CoK α radiation) equipped with a M Braun linear position sensitive detector (PSD). Each powder pattern was recorded in the range 6-36° (2θ) (at intervals of 20°C up to 560°C) with a 2s/step scan, corresponding to an approximate duration of 1 h. The temperature ramp between two patterns was 5°C.min⁻¹.

BET surface measurement. The porosity of the dehydrated MIL-53(Ga) was measured by means of a gas sorption isotherm experiment in liquid nitrogen using Micromeritics ASAP 2010 apparatus (for surface area calculations, p/p_0 range : 0.01-0.3 (BET); 0.12-0.2 (Langmuir)).

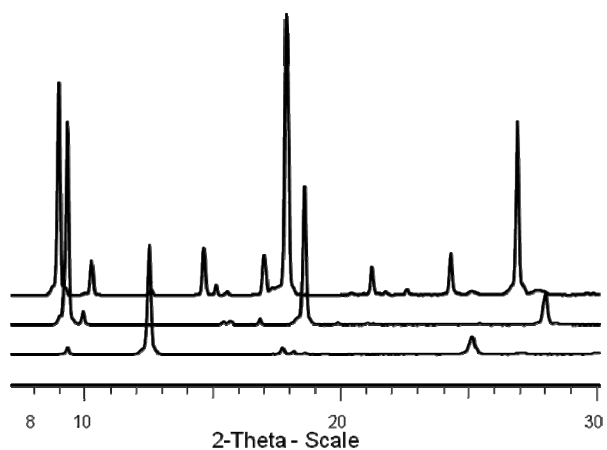


Fig. S1 XRD powder patterns of the gallium terephthalates MIL-53(Ga) showing the evolution of the Bragg peaks as a function of the nature of the trapped species within the channels (copper radiation). (top) as-synthesized MIL-53(Ga); (middle) DMF-exchanged MIL-53(Ga){DMF}; (bottom) hydrated MIL-53(Ga){H₂O}.

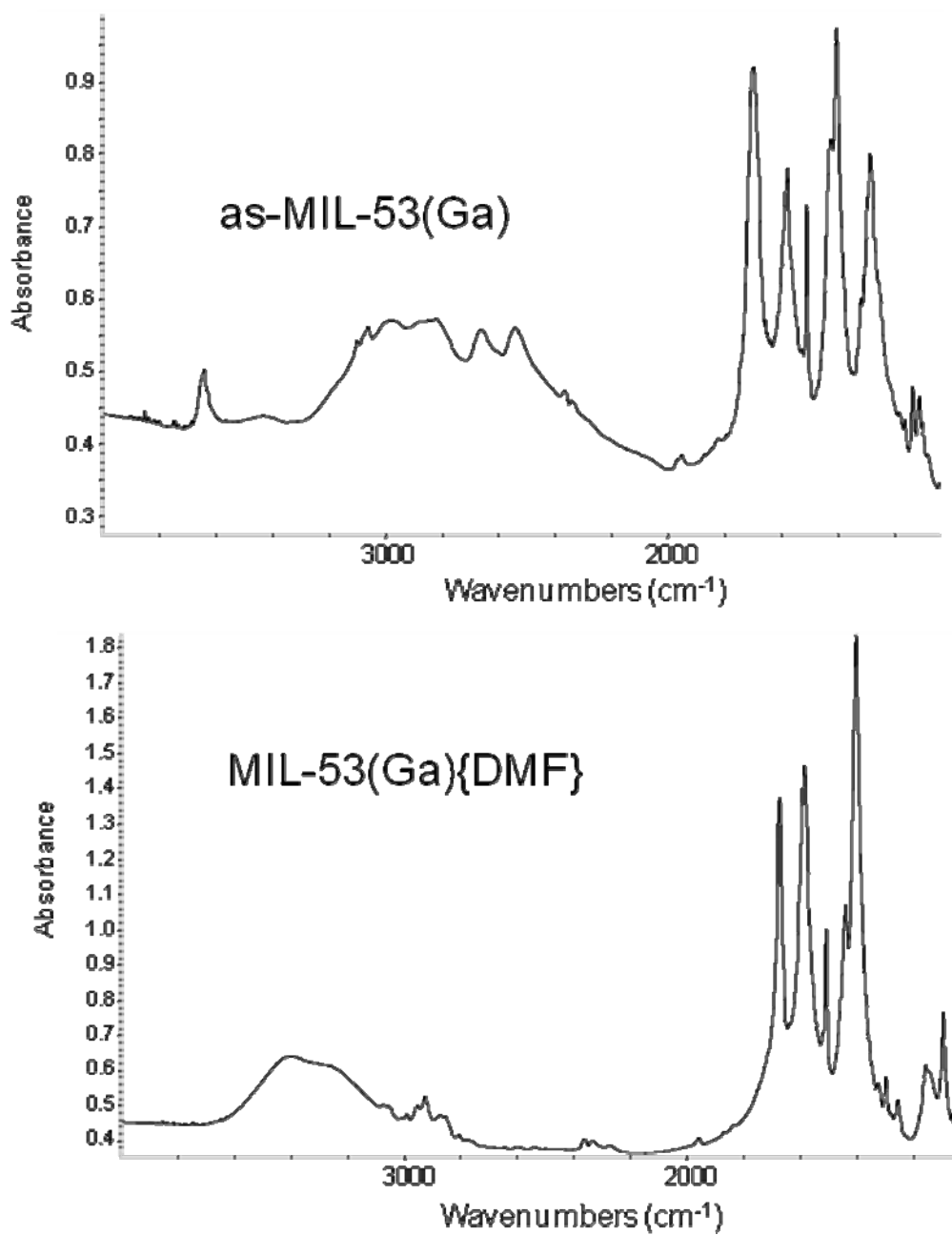


Fig. S2 IR spectra of the MIL-53(Ga) phases containing free tereapthahlic acid (top) or DMF (bottom)

Table S1: Rietveld refinements data for MIL-53(Ga)

	MIL-53(Ga){H ₂ O}	MIL-53(Ga)_lt
Radiation type	Synchrotron at Soleil	Synchrotron at Soleil
Beamline	CRISTAL	CRISTAL
Wavelength	0.7285 Å	0.7285 Å
Collection Temperature	293 K	293 K
R _{Bragg}	0.040	0.056
R _p	0.094	0.103
R _{WP}	0.122	0.132
Goodness-Of-Fit	1.94	1.73
N. Structural Parameters	42	12
N. Reflections	1750	552

Table S2: Atomic coordinates of MIL-53(Ga){H₂O}

Atom	x	y	z	Beq
Ga1	0.49568 (22)	0.25396 (53)	0.51496 (65)	1.151 (42)
Ga2	0	0.5	0	1.151 (42)
Ga3	0	0	0	1.151 (42)
O1	0.4990 (12)	0.1890 (23)	0.7708 (34)	1.58 (10)
O2	-0.0001 (13)	0.4364 (23)	0.7464 (44)	1.58 (10)
O11	0.08732169	0.5660255	-0.3777577	1.58 (10)
O12	0.06561105	0.5784208	-0.07093795	1.58 (10)
O13	0.4389728	0.6570335	0.04597103	1.58 (10)
O14	0.4169712	0.6714184	0.3519975	1.58 (10)
O21	0.4085496	0.1923123	0.367062	1.58 (10)
O22	0.4370978	0.1513548	0.08206295	1.58 (10)
O23	0.05926473	0.09746706	-0.08140812	1.58 (10)
O24	0.08870997	0.04889531	-0.3592515	1.58 (10)
C11	0.1831284	0.6001408	-0.09589053	1.25 (11)
C12	0.2291694	0.6039404	-0.2202988	1.25 (11)
C13	0.2982602	0.6220242	-0.13709	1.25 (11)
C14	0.32131	0.6363083	0.07052697	1.25 (11)
C15	0.275269	0.6325087	0.1949352	1.25 (11)
C16	0.2061782	0.6144249	0.1117265	1.25 (11)
C17	0.1084902	0.580605	-0.1857803	1.25 (11)
C18	0.3959482	0.655844	0.1604167	1.25 (11)
H12	0.2126812	0.5937225	-0.3688131	2
H13	0.3311946	0.6247421	-0.2260828	2
H15	0.2917571	0.6427265	0.3434495	2
H16	0.1732438	0.6117069	0.2007192	2
C21	0.3169716	0.1418981	0.08956288	1.25 (11)
C22	0.2673006	0.1542118	0.1996311	1.25 (11)
C23	0.1987345	0.1348211	0.1121846	1.25 (11)
C24	0.1798394	0.1031166	-0.08533021	1.25 (11)
C25	0.2295104	0.09080289	-0.1953984	1.25 (11)
C26	0.2980765	0.1101937	-0.1079519	1.25 (11)
C27	0.3910431	0.1628458	0.1840307	1.25 (11)
C28	0.105768	0.08216888	-0.179798	1.25 (11)
H22	0.2808169	0.1768909	0.3409191	2
H23	0.1632034	0.1436294	0.1909195	2
H25	0.2159942	0.06812378	-0.3366864	2
H26	0.3336076	0.1013853	-0.1866868	2
Ow1	0.5111 (14)	0.0198 (15)	0.6933 (36)	4.28 (37)
Ow2	0.9690 (10)	0.2405 (19)	0.3280 (32)	4.28 (37)

Table S3: atomic coordinates of MIL-53(Ga)_It

Atom	x	y	z	Beq
Ga	0	0	0	1.154 (40)
O1	0	-0.1457 (14)	0.75	2.092 (97)
O2	0.4137917	0.3530733	0.3641091	2.092 (97)
O3	0.4363786	0.3056234	0.06603014	2.092 (97)
C1	0.3191449	0.2813364	0.08493563	1.09 (11)
C2	0.2717039	0.3045328	0.2015445	1.09 (11)
C3	0.202559	0.2731964	0.1166088	1.09 (11)
C4	0.393358	0.3149696	0.1760969	1.09 (11)
H1	0.2872294	0.3435417	0.345715	2
H2	0.1686231	0.2897895	0.2000224	2