

# Remarkable resilience of the formate cage in multiferroic metal organic framework material: Dimethyl Ammonium Manganese Formate (DMAMnF).

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## SUPPLEMENTARY INFORMATION

### X-RAY DIFFRACTION

The figures shown below are the axes ratios determined by fitting the powder x-ray diffraction data of DMAMnF with the help of Rietveld refinement using the software GSAS. From these figures it can be seen that the 'c' axes is more compressible than the 'a' axes in the trigonal phase.

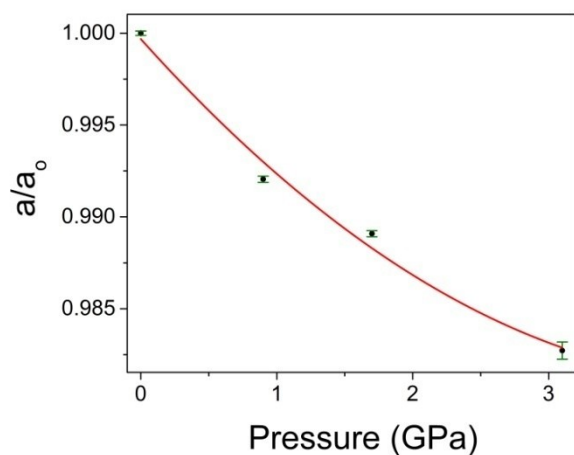


Figure S1: a/a<sub>0</sub> or b/b<sub>0</sub> versus Pressure

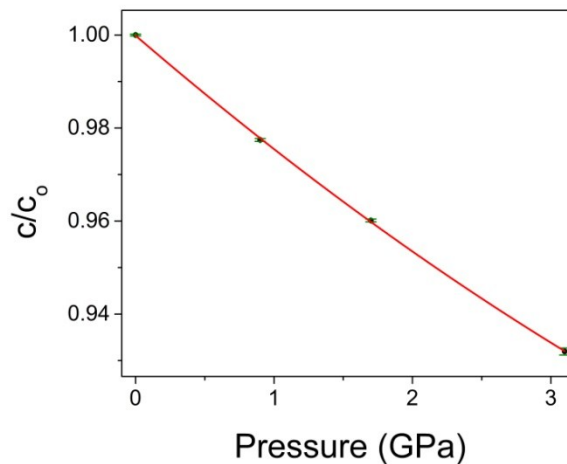
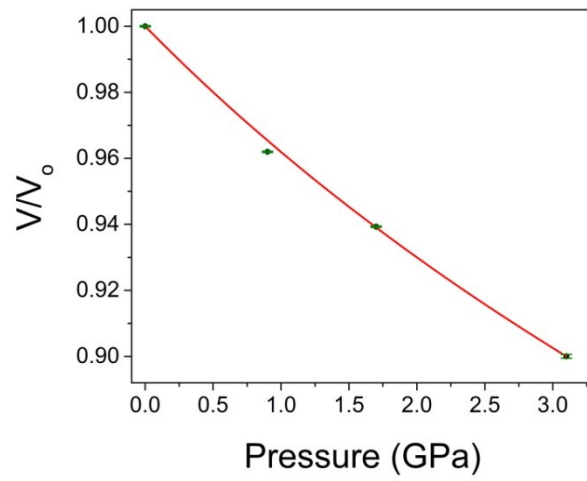


Figure S2: c/c<sub>0</sub> versus Pressure



**Figure S3:**  $V/V_0$  versus Pressure. The solid line gives the fit of the data to the 2<sup>nd</sup> order BM equation of state.

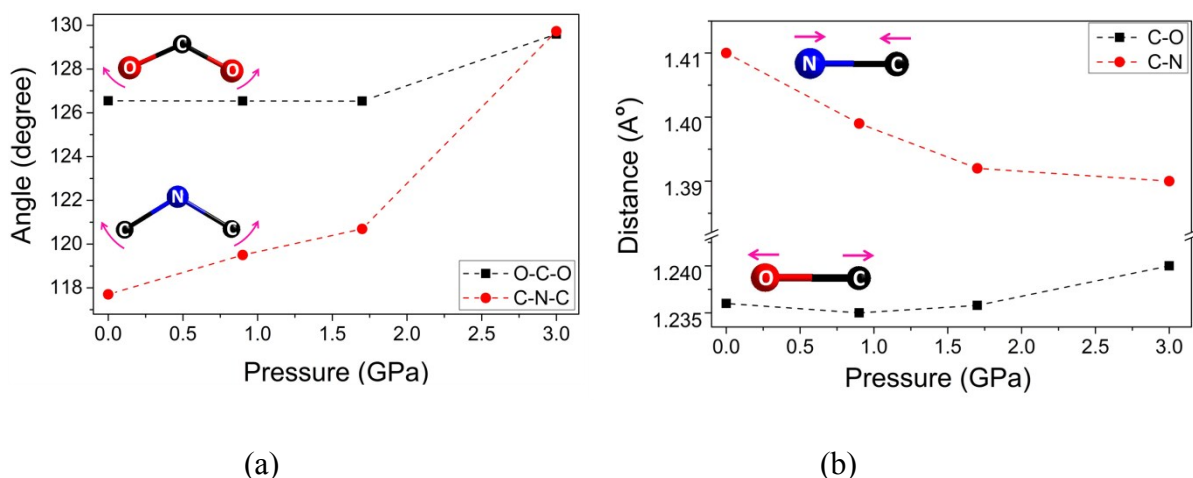
**Table S1:** The Rietveld refinement was carried out on the x-ray diffraction data upto the transition pressure. The refinement was carried out only on the coordinates of the C, O, and N atoms. Since the diffraction peaks are not very intense the atom distances were initially constrained and then once all the parameters were refined the weight on the constrains was reduced from 50000 to 10. The background was treated by the Chebyshev function. The goodness of fit parameters, crystallographic data, bond lengths and bond angles of DMAMnF at 0.1 MPa and 3.1 GPa are also given in this table.

<b>Pressure</b>		<b>0.1 MPa</b>	<b>3.1 GPa</b>
Space group		R-3c	R-3c
Unit Cell Parameters	a (Å)	8.3164(7)	8.1727(38)
	b (Å)	8.3164(7)	8.1727 (38)
	c (Å)	22.8552(33)	21.3003(17)
	$\alpha$ (°)	90	90
	$\beta$ (°)	90	90
	$\gamma$ (°)	120	120
Volume (Å) <sup>3</sup>		1368.95(15)	1232.11(80)
Density (gm/cm <sup>3</sup> )		1.07	1.200
Octahedral Volume(MnO <sub>6</sub> ) (Å) <sup>3</sup>		13.88	11.67
Bond Angle Variance (degree) <sup>2</sup>		0.5637	9.7495
Bond Length (Å)	C-O	1.236	1.240
	C-N	1.410	1.390
Bond Angle (°)	O-C-O	126.55	129.60
	C-N-C	117.70	129.73
Goodness of Fit( $W_{rp}$ )		1.77%	4.24%
C2	<b>x</b>	0.0000	0.0000
	<b>y</b>	0.0000	0.0000
	<b>z</b>	0.6971(1)	0.6908 (1)
N	<b>x</b>	0.0878 (8)	0.0723(9)
	<b>y</b>	0.0000	0.0000
	<b>z</b>	0.2500	0.2500
Mn	<b>x</b>	0.0000	0.0000
	<b>y</b>	0.0000	0.0000
	<b>z</b>	0.0000	0.0000
O	<b>x</b>	-0.21069(17)	-0.2023 (12)
	<b>y</b>	-0.22087(17)	-0.2137 (9)
	<b>z</b>	0.05433(5)	0.0534(5)

C1	<b>x</b>	0.5488(3)	0.5477(12)
	<b>y</b>	0.0000	0.0000
	<b>z</b>	0.2500	0.2500

**Table S2:** DMAMnF is in the trigonal R3-c phase at 3.1 GPa. At 4.3 GPa it transforms to the Cc phase. The lattice parameters of the trigonal phase were transformed to the monoclinic Cc phase and have been shown in this table.

<b>Pressure (GPa)</b>	<b>a (Å)</b>	<b>b (Å)</b>	<b>c (Å)</b>	<b><math>\beta</math> (°)</b>
3.1	44.8900(56)	8.1727(38)	35.8100(56)	169.19
4.3	43.680 (37)	8.3400(78)	34.630(28)	169.160(2)



**Figure S4:** The pressure dependency of bond angles and bond length are plotted in (a) and (b) respectively.

## SPECTROSCOPIC STUDIES

DMAMnF crystallizes in trigonal structure with  $R\bar{3}c$  space group. In this structure  $MnO_6$  octahedra are connected by formate linkers. The  $DMA^+$  cation is situated in the cavity formed by framework. The vibrational modes of DMAMnF are divided into internal vibrations of formate linkers and DMA cation in addition with lattice vibrations. The modes corresponding to  $HCOO^-$  linkers are six in number and are as follows, C-O symmetric stretch ( $\nu_2$ ), C-O antisymmetric stretch ( $\nu_4$ ), O-C-O bend ( $\nu_3$ ), C-H stretch ( $\nu_1$ ), C-H in plane bend ( $\nu_5$ ), C-H out of plane bend ( $\nu_6$ ). Since primitive cell of ambient ( $R\bar{3}c$ ) phase contains six  $HCOO^-$  ions, it gives rise to 36 internal modes.

Free  $DMA^+$  cation contributes 27 internal modes which are distributed among the irreducible representation:  $\Gamma = 9A_1 + 5A_2 + 7B_1 + 6B_2$ . These modes can be further subdivided into three categories;

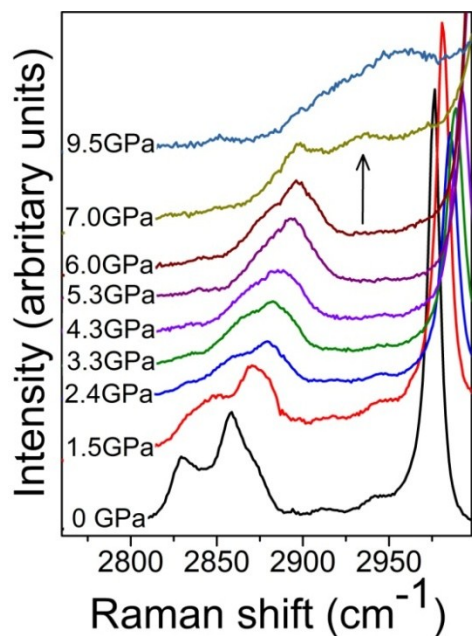
1. Three modes correspond to the C-N-C group:  
C-N symmetric stretch ( $\nu_s(CNC)$ ), C-N antisymmetric stretch ( $\nu_{as}(CNC)$ ), C-N-C bend ( $\delta(CNC)$ ),
2. Six modes correspond to  $NH_2$  group:  
N-H symmetric stretch ( $\nu_s(NH_2)$ ), N-H antisymmetric stretch ( $\nu_{as}(NH_2)$ ), scissoring ( $\delta(NH_2)$ ), rocking ( $\rho(NH_2)$ ), wagging ( $\omega(NH_2)$ ), twisting ( $\tau(NH_2)$ )
3. Remaining 18 modes correspond to two the  $CH_3$  groups:  
C-H symmetric stretch ( $\nu_s(CH_3)$ ), C-H antisymmetric stretch ( $\nu_{as}(CH_3)$ ), bending ( $\delta(CH_3)$ ), rocking ( $\rho(CH_3)$ ), torsion ( $\tau(CH_3)$ ).

We have observed most of the modes as shown in the table below. However, a few of the modes which were almost degenerate, weak or overlapped by the vibrational mode of the diamond, or were at wavenumbers lower than the limit of detection of our present experiments could not be observed.

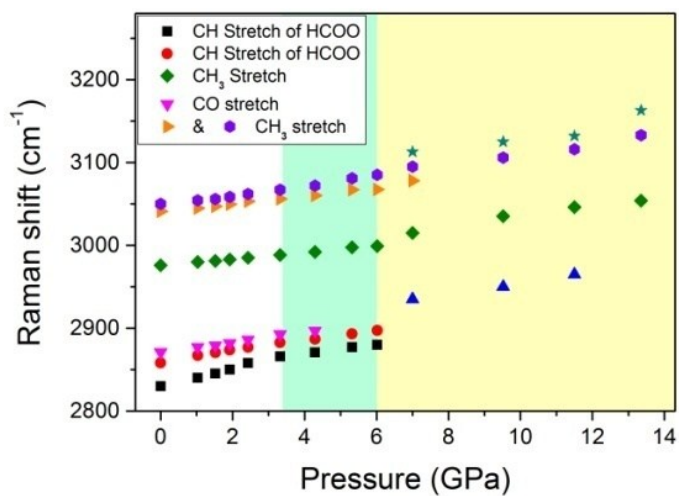
**Table S3:** Assignment of various modes of DMAMnF (in  $\text{cm}^{-1}$ ) at ambient as well as high pressure.

RAMAN			IR			Mode
Ambient	Mix Phase (~ 3.4 to 6 GPa)	High pressure Phase (> 6GPa)	Ambient	Mix Phase (~ 3.4 to 6 GPa)	High pressure Phase (> 6GPa)	
181	187	Disappears				L(HCOO <sup>-</sup> )
235	263	Disappears				T'(M <sup>2+</sup> ) and T'(HCOO <sup>-</sup> )
410	414	Disappears				$\delta$ (CNC)
794	797, 801,	774, 782, 802	793	776, 792, 805	776, 796, 809	$\nu_3$ (HCOO <sup>-</sup> )
798	809	Disappears				
894	909	927, 934				$\nu_s$ (CNC)
1032	1040, 1044	1053, 1057	1025	1038	1047, 1072, 1097	$\nu_{as}$ (CNC)
1071		Disappears				$\nu_6$ (HCOO <sup>-</sup> )
1076	1081	1103				$\nu_6$ (HCOO <sup>-</sup> )
#1101	1107	1128	1091	1106	1112	$\rho$ (CH <sub>3</sub> )
			1350	1362	1369	$\nu_2$ (HCOO <sup>-</sup> )
			1372	1380	1393	$\nu_5$ (HCOO <sup>-</sup> )
			1441	1440 1445	Disappears 1447	$\delta_{as}$ (CH <sub>3</sub> )
			1459	1459 1464	Disappears 1472	$\delta_{as}$ (CH <sub>3</sub> )
			1471	1473 1479	Disappears 1485	$\delta_{as}$ (CH <sub>3</sub> )
			1589	1595	1614 1554	$\nu_4$ (HCOO <sup>-</sup> )
			1639	1650	1671	$\delta$ (NH <sub>2</sub> )
			2802	2800	2809	$\nu$ (NH <sub>2</sub> )
2830	2866	Disappears	2831			$\nu_1$ (HCOO <sup>-</sup> )
2858	2883	Disappears	2853			$\nu_1$ (HCOO <sup>-</sup> )
2871	2893		2866			$\nu_4$ (HCOO <sup>-</sup> ) + $\nu_2$ (HCOO <sup>-</sup> )
		2935 broad				
2976	2988	3015				$\nu_s$ (CH <sub>3</sub> )
			3030			$\nu$ (NH <sub>2</sub> )
3041	3056	Disappear				$\nu_{as}$ (CH <sub>3</sub> )
3050	3067	3095, 3113				$\nu_{as}$ (CH <sub>3</sub> )

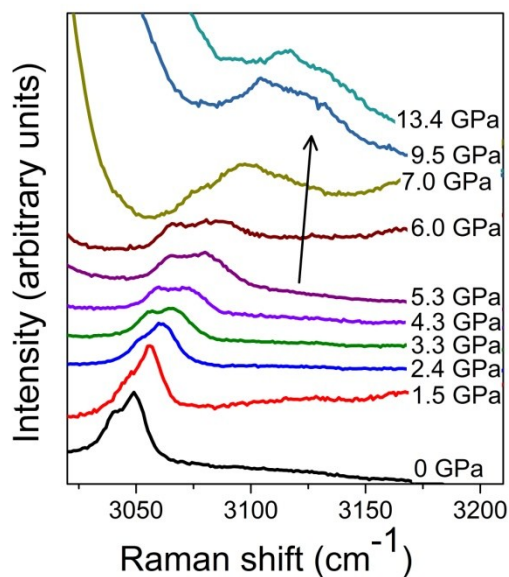
# 1101  $\text{cm}^{-1}$  appeared at ~1.5 GPa



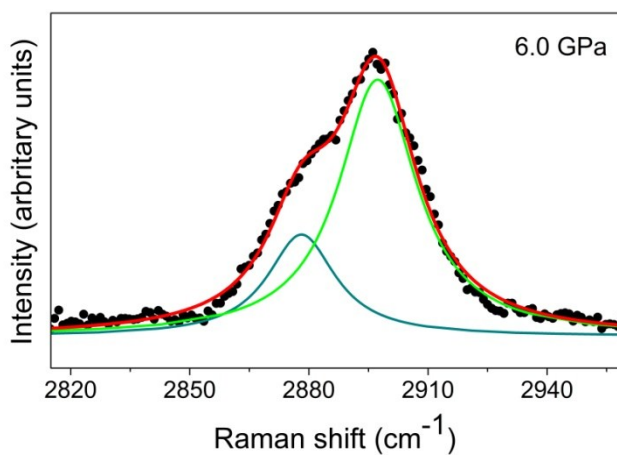
(a)



(c)



(b)



(d)

**Figure S5:** Both the C-O symmetric and asymmetric stretch modes could not be observed in the Raman spectra, as the former gets overlapped with the strong mode from the diamond anvil and the latter has a poor Raman activity. However, we could observe the combination mode of C-O stretch at  $2871\text{ cm}^{-1}$  in the Raman spectra as shown above. **(a)** Raman spectra of the combination mode of C-O stretch modes **(b)**  $\text{CH}_3$  asymmetric stretch mode **(c)** Pressure evolution of some of



the Raman vibrational modes, like the C-O and C-H stretch modes of HCOO<sup>-</sup> anion and the stretch mode of CH<sub>3</sub> of the DMA<sup>+</sup> cation. Shaded area shows the zone of transition. **(d)** Peak fitting of the  $\nu_1(\text{HCOO}^-)$  band shows that 2 modes can be fitted even at 6 GPa.