

Electronic Supplementary Material (ESI)
Growth of Centimeter-sized [(CH₃)₂NH₂][Mn(HCOO)₃] Hybrid Formate
Perovskite Single Crystal and Raman Evidence of
Pressure-induced Phase Transitions

Lipeng Xin^{1*}, Zhen Fan^{2,7}, Guanghui Li³, Ming Zhang⁴, Yonghao Han³, John Wang²,

Khuong P. Ong⁵, Lei Qin⁶, Yanzhen Zheng⁶, and Xiaojie Lou^{1*}

1. *Multi-disciplinary Materials Research Center (MMRC), Frontier Institute of Science and Technology(FIST), and State Key Laboratory for Mechanical Behavior of Materials , Xi'an Jiaotong University, Xi'an 710049, PR China*
2. *Department of Materials Science and Engineering, National University of Singapore, 7 Engineering Drive 1, 117574 Singapore*
3. *State Key Laboratory of Superhard Materials, Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China*
4. *Institute of Materials, China Academy of Engineering Physics, Chengdu 621907, China*
5. *Materials Science & Engineering Department, Institute of High Performance Computing, 1 Fusionopolis Way, 138632 Singapore*
6. *Centre for Applied Chemical Research (CACR), Frontier Institute of Science and Technology(FIST), Xi'an Jiaotong University, Xi'an 710049, PR China*
7. *Institute for Advanced Materials and Guangdong Provincial Key Laboratory of Quantum Engineering and Quantum Materials, South China Normal University, Guangzhou 510006, PR China*

*** Corresponding author** E-mail: ybsyh3@163.com(L.Xin) xlou03@mail.xjtu.edu.cn(X.Lou)

Tel.: +86-29-83395141 ; fax : +86-29-83395131

Table S1 The wavenumber intercepts at zero pressure (ω_0) and pressure coefficients (α) obtained from linear fitting of the Raman data

Ambient	Phase	Phase I		Phase II		Phase III		Assignment*
ω_0 (cm ⁻¹)	α (cm ⁻¹ GPa ⁻¹)	ω_0 (cm ⁻¹)	α (cm ⁻¹ GPa ⁻¹)	ω_0 (cm ⁻¹)	α (cm ⁻¹ GPa ⁻¹)	ω_0 (cm ⁻¹)	α (cm ⁻¹ GPa ⁻¹)	
				71.8	2.52	82.4	0.02	L(HCOO ⁻)
93.9	-3.25	93.7	-2.38	70.5	4.12	89.0	-0.02	L(HCOO ⁻)
97.7	9.02	109.2	0.36	93.7	3.20	90.9	2.30	L(HCOO ⁻)
115.9	3.89	122.6	1.87	100.4	5.07	143.0	-1.73	L(HCOO ⁻)
140.5	-3.64							L(DMA ⁺)
140.4	2.11							L(DMA ⁺)
147.6	7.97							L(DMA ⁺)
167.2	6.96	183.2	-5.34	150.9	5.82			L(HCOO ⁻)
180.1	1.49	182.8	0.66	185.7	0.81			L(HCOO ⁻)
		204.5	-2.92	168.2	9.14			L(HCOO ⁻)
220.4	11.67	228.2	7.71					T'(Mn ²⁺)+T'(HC OO ⁻)
231.0	11.74	243.9	5.86					T'(Mn ²⁺)+T'(HC OO ⁻)
787.7	2.78	788.3	2.16	770.7	5.93	758.4	1.83	ν_3 (HCOO ⁻)
792.6	5.09	794.2	3.13	772.9	7.75	784.2	1.87	ν_3 (HCOO ⁻)
891.2	3.11	889.6	4.22	864.8	10.18	907.3	2.78	ν_s (CNC)
						912.9	3.44	ν_s (CNC)
1023.4	2.91	1020.4	4.51					ν_{as} (CNC)
1062.4	4.28	1060.1	3.72					ν_6 (HCOO ⁻)
1067.6	2.51	1068.0	3.8					ν_6 (HCOO ⁻)
1365.6	3.14	1365.7	3.28	1371. 2	1.89	1366.9	1.84	ν_5 (HCOO ⁻)
2828.0	8.23							ν_1 (HCOO ⁻)
2854.6	5.78	2846.6	7.37	2837. 9	10.19	2852.2	8.68	ν_1 (HCOO ⁻)
2869.5	5.41	2873.8	2.95					ν_{2+4} (HCOO ⁻)
2938.6	12.73							ν_s (CH ₃)
		2959.5	3.04	2925. 1	11.58	2884.2	15.71	ν_s (CH ₃)
2971.2	3.00	2969.5	4.5	2958. 2	7.41	2995.9	2.49	ν_s (CH ₃)
						3004.3	3.59	ν_s (CH ₃)
3034.4	3.04	3038.8	3.23	3024. 3	7.21	3003.7	10.61	ν_{as} (CH ₃)
3042.5	3.18	3044.2	5.6	3050. 0	4.19	3020.6	10.92	ν_{as} (CH ₃)

* ν_1 - C-H stretching; ν_2 -symmetric C–O stretching; ν_4 -antisymmetric C–O stretching;

ν_3 -the symmetric O–C–O bending (scissor); ν_5 -the C–H in-plane bending;
 ν_6 -the C–H out-of-plane bending; L and T'- Librational (L) and translational (T');
 ν_s - symmetric stretching; ν_{as} - antisymmetric stretching.