Electronic Supplementary Material (ESI) for CrystEngComm.
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High-pressure phase transitions with group–subgroup disagreement in metal guanidinium formates

Supplementary information

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Experimental information

Bulk samples of fully-deuterated MnGF/CoGF were synthesised as described in reference [1]. with slight modifications. Guanidinium chloride along with potassium carbonate, instead of guanidinium carbonate, was used due to its unavailability in a deuterated form. The samples dried in a vacuum furnace were contained in TiZr alloy gasket (molar ratio of Ti:Zr = 67.6:32.4 %), a null coherent scattering alloy. The high-pressure diffraction experiments were done with the PEARL diffractometer [2] in ISIS Pulsed Neutron and Muon Source, UK. Perdeuterated methanol–ethanol in 4:1 volume ratio, which remains hydrostatic to almost 10 GPa at room temperature, is used as the pressure transmitter [3]. A small amount of Pb was used as a pressure marker. It is included as a second phase in the refinement, whose cell-volume determines the pressure using the P-T equation of state [4]. Ceramic anvils made from zirconia toughened alumina (ZTA) are used in these experiments as they possess an advantage of better neutron transparency in comparison to WC. ZrO_2 and Al_2O_3 are also included in the refinement. Rietveld refinements were done using GSAS [5].

Rietveld refinement process

The free variables in the refinements are: (a) the lattice parameters; (b) the atomic coordinates; (c) a polynomial background function, (d) a scale factor; (e) peak shape parameters; and (f) displacement parameters (isotropic). All the refinements were implemented with a TOF profile function 3 (in GSAS) featuring a convolution of back-to-back exponentials with a pseudo-Voigt function. Backgrounds were modelled using the shifted Chebyshev polynomials.

The following soft restraints were implemented both along and across the bonds of the formate and guanidinium moiety, as described in reference [1]. These implementations resulted in meaningful structural features.

Table S1: Rietveld refinement results of target compounds.

	Manganese guanidinium formate: $[C(ND_2)_3]Mn(DCOO)_3$			
Pressure (GPa)	0.14	1.13	1.61	3.01
Crystal system	Orthorhombic		Rhombohedral	
Space group	*Pnna*		$R\bar{3}c$	
a, *b*, *c* (Å)	8.4946 (11), 11.9561(20), 9.0564(17)	8.2686(12), 11.7753(22), 9.0554(19)	9.0092(3), 9.0092(3), 18.2070(5)	8.9780(3), 8.9780(3), 17.4763(4)
V (Å^3)	919.79(18)	881.68(20)	1279.81(8)	1219.93(7)
σ_{calc} (g cm^{-3})	1.871	1.952	2.017	2.116
R_p (%)	3.05	3.17	5.14	4.29
wR_p (%)	2.58	2.67	4.05	3.45

	Cobalt guanidinium formate: $[C(ND_2)_3]Co(DCOO)_3$			
Pressure (GPa)	0.01	1.86	2.66	4.02
Crystal system	Orthorhombic		Rhombohedral	
Space group	*Pnna*		$R\bar{3}c$	
a, *b*, *c* (Å)	8.3237(5), 11.7502(8), 8.9071(8)	8.0212(4), 11.4967(7), 8.8927(7)	8.8346(4), 8.8346(4), 17.4844(5)	8.8061(4), 8.8061(4), 17.0340(6)
V (Å^3)	871.16(7)	820.06(7)	1181.82(9)	1143.97(7)
σ_{calc} (g cm^{-3})	2.006	2.131	2.218	2.291
R_p (%)	4.21	3.81	4.26	3.91
wR_p (%)	3.59	3.10	3.67	3.35

Table S2: Crystallographic details of $[C(ND_2)_3]$ Mn $(DCOO)_3$ at 1.61 GPa.

Space group	*a* (Å)	*b* (Å)	*c* (Å)	V (Å^3)	
$R\bar{3}c$	9.0092(3)	9.0092(3)	18.2070(5)	1279.81(8)	
Site	*x*	*y*	*z*	U_{iso} (Å^2)	Fractional occupancy
Mn	0	0	0	0.012(6)	1.0
C1	0.1192(7)	0.333333	0.083333	0.0208(16)	1.0
D1	0.2415(7)	0.333333	0.083333	0.0794(18)	1.0
O1	0.9879(7)	0.2010(3)	0.0601(3)	0.0094(14)	1.0
C2	0	0	0.25	0.0117(16)	1.0
N1	0.147492(5)	0	0.25	0.0267(16)	1.0
D2	0.259823(5)	0.112372(4)	0.25093(12)	0.0596(18)	1.0

Table S3: Crystallographic details of $[C(ND_2)_3]$ Co $(DCOO)_3$ at 2.66 GPa.

Space group	*a* (Å)	*b* (Å)	*c* (Å)	V (Å^3)	
$R\bar{3}c$	8.8346(4)	8.8346(4)	17.4844(5)	1181.82(9)	
Site	*x*	*y*	*z*	U_{iso} (Å^2)	Fractional occupancy
Co	0	0	0	0.055(14)	1.0
C1	0.1241(5)	0.333333	0.083333	0.0132(15)	1.0
D1	0.2488(5)	0.333333	0.083333	0.0965(16)	1.0
O1	0.9901(7)	0.1982(3)	0.0593(3)	0.0129(13)	1.0
C2	0	0	0.25	0.0183(15)	1.0
N1	0.150408(6)	0	0.25	0.0218(12)	1.0
D2	0.264963(6)	0.114597(5)	0.25085(16)	0.0434(16)	1.0

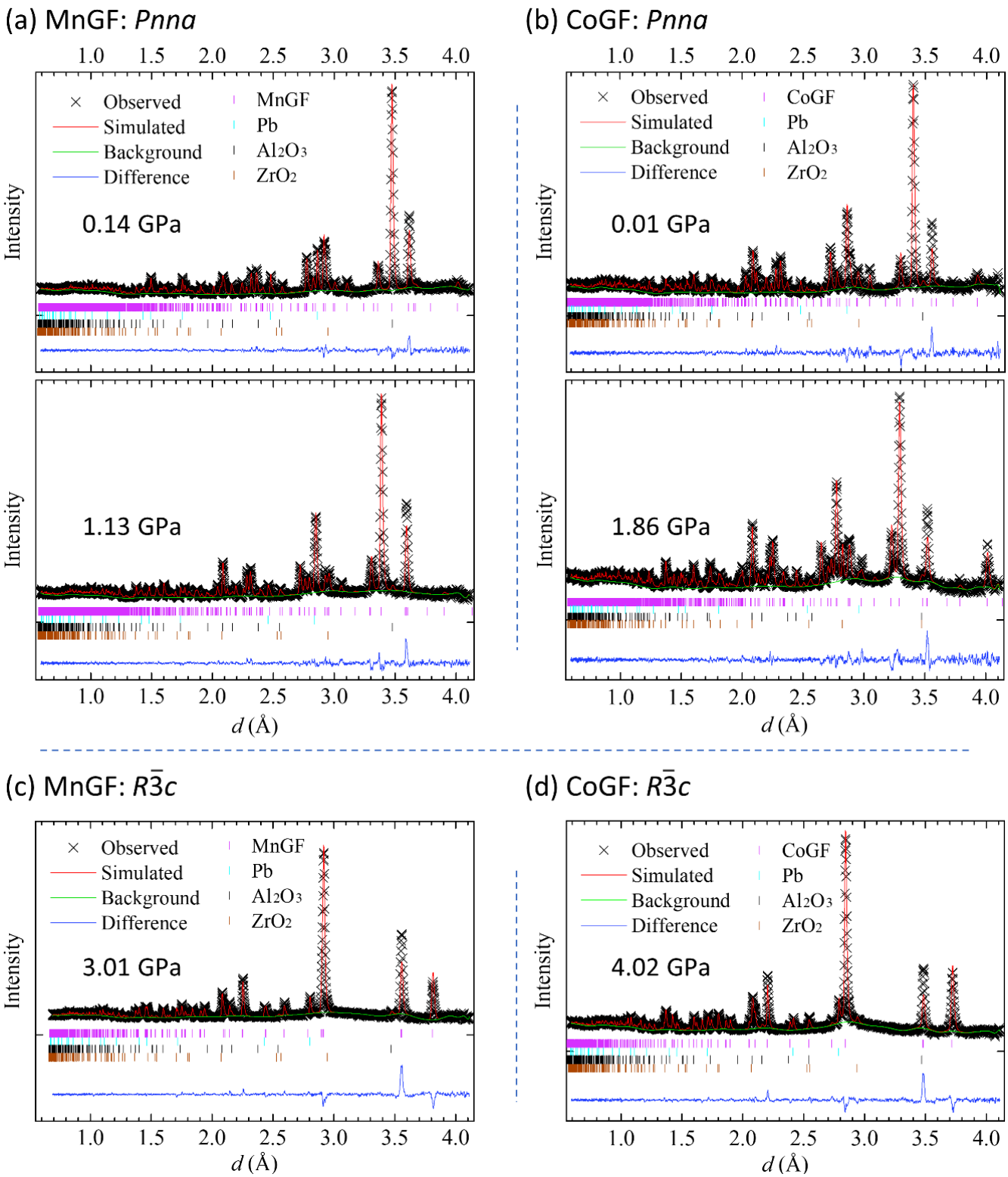

Fig. S1 Rietveld refinements of MnGF and CoGF in (a,b) orthorhombic phase; (c,d) rhombohedral phase.

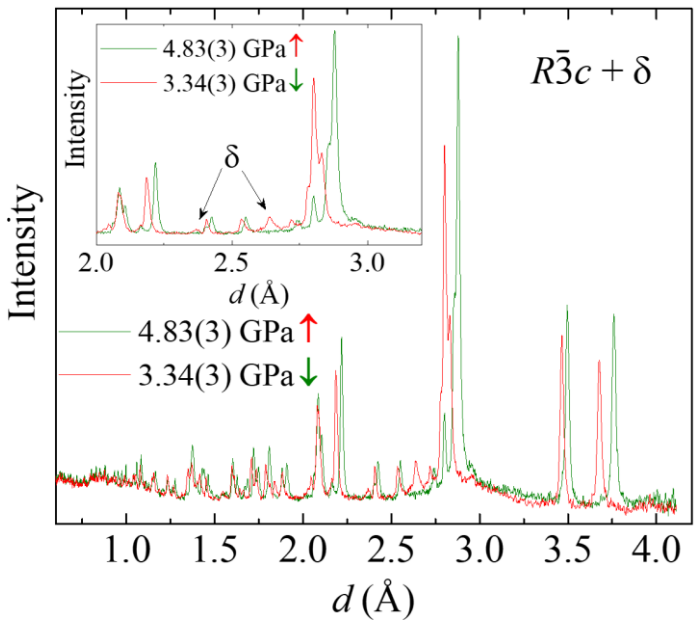

Fig. S2 Indication of a subsequent phase transition ($R\bar{3}$c + δ) experienced at 4.83 GPa with an onset between 4.02 and 4.26 GPa. Inset shows the peaks of the δ phase and the retrieval of "$R\bar{3}$c + δ" from "$R\bar{3}$c + δ" on the reduction of pressure. Diffraction patterns also include other phases (Pb, Al_2O_3 & ZrO_2).

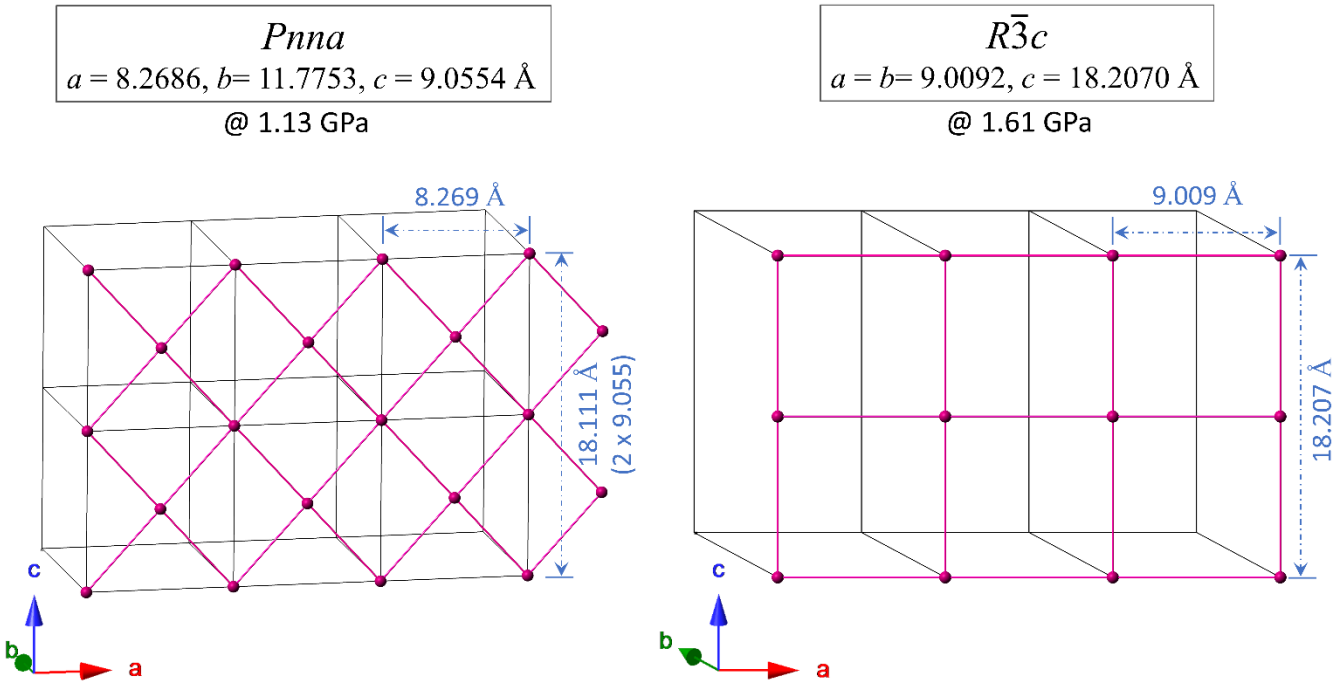

Fig. S3 A comparison of MnGF in the *Pnna* and $R\bar{3}c$ showing a near doubling of one of the unit cell axes. For clarity, only Mn atoms are shown.

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