

Supporting information for: Coupling of anisotropic site substitutions in $\text{Sr}_{7-x}\text{A}_x\text{Mn}_4\text{O}_{15}$, A = Ca and Ba to acoustic instabilities and lattice distortions

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S1: Crystallographic information for room temperature refinements

Table S1.1 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82451(1)$ Å) for $\text{Sr}_6\text{CaMn}_4\text{O}_{15}$ at 300 K. Note, estimated standard deviations are not reported for the fractional coordinates due to the use of bond distance restraints in the refinements.

Composition	$\text{Sr}_6\text{CaMn}_4\text{O}_{15}$				
Space group	$P2_1/c$				
a (Å)	6.74828(11)				
b (Å)	9.58936(15)				
c (Å)	10.32346(16)				
α (°)	90				
β (°)	91.6969(12)				
γ (°)	90				
Site	x	y	z	Occupancy	B_{iso} (Å ²)
Sr1	0.997366	0.18406	0.46488	Sr 0.661(5) Ca 0.339(5)	0.626
Sr2	0.351306	0.15167	0.19500	Sr 0.903(5) Ca 0.097(5)	0.626
Sr3	0.5	0	0.5	Sr 1.000(6) Ca 0.000(6)	0.626
Sr4	0.17532	0.00200	0.83179	Sr 1.000(4) Ca 0.000(4)	0.626
Mn1	0.57545	0.16607	0.92465	1	0.600
Mn2	0.78032	0.16730	0.72063	1	0.600
O1	0.50378	0.10036	0.75185	1	0.656
O2	0.68016	0.17576	0.33544	1	0.656
O3	0.33210	0.24841	0.95186	1	0.656
O4	0.83657	0.08321	0.88560	1	0.656
O5	0.68127	0.22645	0.08326	1	0.656
O6	0.5	0	0	1	0.656
O7	0.84078	0.01447	0.62547	1	0.656
O8	0.03027	0.24415	0.71022	1	0.656

Table S1.2 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82451(1)$ Å) for $\text{Sr}_5\text{Ca}_2\text{Mn}_4\text{O}_{15}$ at 300 K. Note, estimated standard deviations are not reported for the fractional coordinates due to the use of bond distance restraints in the refinements.

Composition	$\text{Sr}_5\text{Ca}_2\text{Mn}_4\text{O}_{15}$				
Space group	$P2_1/c$				
a (Å)	6.70142(13)				
b (Å)	9.55308(18)				
c (Å)	10.28805(18)				
α (°)	90				
β (°)	91.5559(14)				
γ (°)	90				
Site	x	y	z	Occupancy	B_{iso} (Å ²)
Sr1	0.998422	0.183736	0.464038	Sr 0.450(5) Ca 0.550(5)	0.620
Sr2	0.352072	0.151882	0.194354	Sr 0.800(6) Ca 0.200(6)	0.620
Sr3	0.5	0	0.5	Sr 1.000(7) Ca 0.000(7)	0.620
Sr4	0.175680	0.001808	0.831234	Sr 1.000(5) Ca 0.000(5)	0.620
Mn1	0.575536	0.165966	0.924564	1	0.600
Mn2	0.782464	0.167474	0.720274	1	0.600
O1	0.504254	0.099674	0.75177	1	0.767
O2	0.681406	0.17527	0.33502	1	0.767
O3	0.331412	0.24756	0.952462	1	0.767
O4	0.838574	0.083014	0.88477	1	0.767
O5	0.683926	0.226352	0.083412	1	0.767
O6	0.5	0	0	1	0.767
O7	0.842704	0.014944	0.624428	1	0.767
O8	0.033318	0.244702	0.70996	1	0.767

Table S1.3 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82451(1)$ Å) for $\text{Sr}_4\text{Ca}_3\text{Mn}_4\text{O}_{15}$ at 300 K. Note, estimated standard deviations are not reported for the fractional coordinates due to the use of bond distance restraints in the refinements.

Composition	$\text{Sr}_4\text{Ca}_3\text{Mn}_4\text{O}_{15}$				
Space group	$P2_1/c$				
a (Å)	6.65959(18)				
b (Å)	9.5205(2)				
c (Å)	10.2662(2)				
α (°)	90				
β (°)	91.5044(17)				
γ (°)	90				
Site	x	y	z	Occupancy	B_{iso} (Å ²)
Sr1	0.99948	0.18341	0.46319	Sr 0.389(7) Ca 0.611(7)	0.613
Sr2	0.35284	0.1521	0.19371	Sr 0.726(7) Ca 0.274(7)	0.613
Sr3	0.5	0	0.5	Sr 1.00(1) Ca 0.00(1)	0.613
Sr4	0.17604	0.00161	0.83068	Sr 0.978(7) Ca 0.022(7)	0.613
Mn1	0.57562	0.16586	0.92448	1	0.600
Mn2	0.78461	0.16765	0.71992	1	0.600
O1	0.50473	0.09899	0.75169	1	0.878
O2	0.68265	0.17478	0.3346	1	0.878
O3	0.33073	0.24671	0.95307	1	0.878
O4	0.84058	0.08282	0.88394	1	0.878
O5	0.68658	0.22626	0.08357	1	0.878
O6	0.5	0	0	1	0.878
O7	0.84463	0.01542	0.62338	1	0.878
O8	0.03636	0.24526	0.7097	1	0.878

Table S1.4 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82638(3) \text{ \AA}$) for $\text{Sr}_3\text{Ca}_4\text{Mn}_4\text{O}_{15}$ at 300 K. Note, estimated standard deviations are not reported for the fractional coordinates due to the use of bond distance restraints in the refinements.

Composition	$\text{Sr}_3\text{Ca}_4\text{Mn}_4\text{O}_{15}$				
Space group	$P2_1/c$				
a (Å)	6.6083(14)				
b (Å)	9.4596(18)				
c (Å)	10.2498(19)				
α (°)	90				
β (°)	91.4594(13)				
γ (°)	90				
Site	x	y	z	Occupancy	B_{ISO} (Å ²)
Sr1	1.000534	0.183092	0.462346	Sr 0.201(8) Ca 0.799(8)	0.6067
Sr2	0.353604	0.152314	0.193058	Sr 0.455(7) Ca 0.545(7)	0.6067
Sr3	0.5	0	0.5	Sr 0.8852(12) Ca 0.1148(12)	0.6067
Sr4	0.1764	0.001416	0.830118	Sr 0.672(7) Ca 0.328(7)	0.6067
Mn1	0.575712	0.165762	0.924388	1	0.600
Mn2	0.786748	0.167818	0.719558	1	0.600
O1	0.505198	0.098298	0.75161	1	0.989
O2	0.683902	0.17429	0.33418	1	0.989
O3	0.330044	0.24586	0.953674	1	0.989
O4	0.842578	0.082618	0.88311	1	0.989
O5	0.689242	0.226164	0.083724	1	0.989
O6	0.5	0	0	1	0.989
O7	0.846548	0.015888	0.622336	1	0.989
O8	0.039406	0.245814	0.70944	1	0.989

Table S1.5 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82634(1)$ Å) and neutron powder diffraction for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ at 300 K.

Composition	$\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$				
Space group	$P2_1/c$				
a (Å)	6.57237(6)				
b (Å)	9.41759(8)				
c (Å)	10.24513(9)				
α (°)	90				
β (°)	91.4423(6)				
γ (°)	90				
Site	x	y	z	Occupancy	B_{ISO} (Å ²)
Sr1	1.0016(4)	0.1828(3)	0.4615(2)	Sr 0.069(5) Ca 0.931(5)	0.600(3)
Sr2	0.3543(4)	0.1525(2)	0.1924(2)	Sr 0.261(4) Ca 0.739(4)	0.600(3)
Sr3	0.5	0	0.5	Sr 0.754(7) Ca 0.246(7)	0.600(3)
Sr4	0.1768(4)	0.0012(2)	0.0012(2)	Sr 0.4313(4) Ca 0.5687(4)	0.600(3)
Mn1	0.5758(3)	0.1657(3)	0.9243(2)	1	0.600(3)
Mn2	0.7889(3)	0.1680(3)	0.7192(2)	1	0.600(3)
O1	0.5057(9)	0.0976(6)	0.7515(5)	1	1.099(3)
O2	0.685(1)	0.1738(5)	0.3338(6)	1	1.099(3)
O3	0.329(1)	0.2450(6)	0.9543(6)	1	1.099(3)
O4	0.8446(8)	0.0824(6)	0.8823(5)	1	1.099(3)
O5	0.6919(9)	0.2261(6)	0.0839(6)	1	1.099(3)
O6	0.5	0	0	1	1.099(3)
O7	0.8485(8)	0.0164(6)	0.6213(5)	1	1.099(3)
O8	0.0425(8)	0.2464(6)	0.7092(5)	1	1.099(3)

Table S1.6 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at 111 ($\lambda = 0.82453(5)$ Å) for $\text{Sr}_6\text{BaMn}_4\text{O}_{15}$ at 300 K. Note, estimated standard deviations are not reported for the fractional coordinates due to the use of bond distance restraints in the refinements.

Composition	$\text{Sr}_6\text{BaMn}_4\text{O}_{15}$				
Space group	$P2_1/c$				
a (Å)	6.85308(13)				
b (Å)	9.70834(17)				
c (Å)	10.41962(19)				
α (°)	90				
β (°)	91.6302(11)				
γ (°)	90				
Site	x	y	z	Occupancy	B_{ISO} (Å ²)
Sr1	0.99557	0.183482	0.465506	Sr 0.970(6) Ba 0.030(6)	0.744
Sr2	0.34939	0.151904	0.195266	Sr 0.983(6) Ba 0.017(6)	0.744
Sr3	0.5	0	0.5	Sr 0.599(9) Ba 0.401(9)	0.744
Sr4	0.174526	0.001792	0.833074	Sr 0.712(6) Ba 0.288(6)	0.744
Mn1	0.575224	0.166234	0.924806	1	0.700
Mn2	0.777692	0.167422	0.721418	1	0.700
O1	0.501132	0.099674	0.750704	1	0.509
O2	0.676844	0.179966	0.336934	1	0.509
O3	0.334	0.248058	0.95061	1	0.509
O4	0.832446	0.084806	0.886014	1	0.509
O5	0.672156	0.228878	0.081234	1	0.509
O6	0.5	0	0	1	0.509
O7	0.840654	0.015304	0.628222	1	0.509
O8	0.025544	0.246096	0.712186	1	0.509

Table S1.7 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at 111 ($\lambda = 0.82453(5)$ Å) for $\text{Sr}_5\text{Ba}_2\text{Mn}_4\text{O}_{15}$ at 300 K. Note, estimated standard deviations are not reported for the fractional coordinates due to the use of bond distance restraints in the refinements.

Composition	$\text{Sr}_5\text{Ba}_2\text{Mn}_4\text{O}_{15}$				
Space group	$P2_1/c$				
a (Å)	6.9023(2)				
b (Å)	9.7873(2)				
c (Å)	10.4517(2)				
α (°)	90				
β (°)	91.4689(1)				
γ (°)	90				
Site	x	y	z	Occupancy	B_{ISO} (Å ²)
Sr1	0.99483	0.182584	0.465282	Sr 1.000(6) Ba 0.000(6)	0.856
Sr2	0.34824	0.152358	0.194882	Sr 0.884(6) Ba 0.116(6)	0.856
Sr3	0.5	0	0.5	Sr 0.39(1) Ba 0.61(1)	0.856
Sr4	0.174092	0.001384	0.833798	Sr 0.443(7) Ba 0.557(7)	0.856
Mn1	0.575088	0.166298	0.924872	1	0.800
Mn2	0.777204	0.167714	0.721846	1	0.800
O1	0.498954	0.098298	0.749478	1	0.473
O2	0.674778	0.183682	0.338008	1	0.473
O3	0.33522	0.246856	0.94997	1	0.473
O4	0.830322	0.086202	0.885598	1	0.473
O5	0.665702	0.231216	0.079368	1	0.473
O6	0.5	0	0	1	0.473
O7	0.842448	0.016608	0.629924	1	0.473
O8	0.023858	0.248602	0.713892	1	0.473

Table S1.8 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82453(5)$ Å) for $\text{Sr}_4\text{Ba}_3\text{Mn}_4\text{O}_{15}$ at 300 K. Note, estimated standard deviations are not reported for the fractional coordinates due to the use of bond distance restraints in the refinements.

Composition	$\text{Sr}_4\text{Ba}_3\text{Mn}_4\text{O}_{15}$				
Space group	$P2_1/c$				
a (Å)	6.953(1)				
b (Å)	9.85372(13)				
c (Å)	10.48267(15)				
α (°)	90				
β (°)	91.4257(8)				
γ (°)	90				
Site	x	y	z	Occupancy	B_{ISO} (Å ²)
Sr1	0.99409	0.181686	0.465058	Sr 0.957(6) Ba 0.043(6)	0.967
Sr2	0.34709	0.152812	0.194498	Sr 0.738(6) Ba 0.262(6)	0.967
Sr3	0.5	0	0.5	Sr 0.205(9) Ba 0.795 (9)	0.967
Sr4	0.173658	0.000976	0.834522	Sr 0.245(6) Ba 0.755(6)	0.967
Mn1	0.574952	0.166362	0.924938	1	0.900
Mn2	0.776716	0.168006	0.722274	1	0.900
O1	0.496776	0.096922	0.748252	1	0.437
O2	0.672712	0.187398	0.339082	1	0.437
O3	0.33644	0.245654	0.94933	1	0.437
O4	0.828198	0.087598	0.885182	1	0.437
O5	0.659248	0.233554	0.077502	1	0.437
O6	0.5	0	0	1	0.437
O7	0.844242	0.017912	0.631626	1	0.437
O8	0.022172	0.251108	0.715598	1	0.437

Table S1.9 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at 111 ($\lambda = 0.82495(1) \text{ \AA}$) for $\text{Sr}_3\text{Ba}_4\text{Mn}_4\text{O}_{15}$ at 300 K. Note, estimated standard deviations are not reported for the fractional coordinates due to the use of bond distance restraints in the refinements.

Composition	$\text{Sr}_3\text{Ba}_4\text{Mn}_4\text{O}_{15}$				
Space group	$P2_1/c$				
a (Å)	7.0101(2)				
b (Å)	9.9183(3)				
c (Å)	10.5245(3)				
α (°)	90				
β (°)	91.498(16)				
γ (°)	90				
Site	x	y	z	Occupancy	B_{ISO} (Å ²)
Sr1	0.99335	0.180788	0.464834	Sr 0.8286(14) Ba 0.1714(14)	1.078
Sr2	0.34594	0.153266	0.194114	Sr 0.608(1) Ba 0.392(1)	1.078
Sr3	0.5	0	0.5	Sr 0.1000(17) Ba 0.9000(17)	1.078
Sr4	0.173224	0.000568	0.835246	Sr 0.054(11) Ba 0.946(11)	1.078
Mn1	0.574816	0.166426	0.925004	1	1.000
Mn2	0.776228	0.168298	0.722702	1	1.000
O1	0.494598	0.095546	0.747026	1	0.401
O2	0.670646	0.191114	0.340156	1	0.401
O3	0.33766	0.244452	0.94869	1	0.401
O4	0.826074	0.088994	0.884766	1	0.401
O5	0.652794	0.235892	0.075636	1	0.401
O6	0.5	0	0	1	0.401
O7	0.846036	0.019216	0.633328	1	0.401
O8	0.020486	0.253614	0.717304	1	0.401

Table S1.10 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at 111 ($\lambda = 0.82495(1)$ Å) and neutron powder diffraction for $\text{Sr}_2\text{Ba}_5\text{Mn}_4\text{O}_{15}$ at 300 K.

Composition	$\text{Sr}_2\text{Ba}_5\text{Mn}_4\text{O}_{15}$				
Space group	$P2_1/c$				
a (Å)	7.05716(2)				
b (Å)	9.9561(1)				
c (Å)	10.56867(11)				
α (°)	90				
β (°)	91.6523(6)				
γ (°)	90				
Site	x	y	z	Occupancy	B_{iso} (Å ²)
Sr1	0.9925(3)	0.1799(2)	0.46461(19)	Sr 0.646(9) Ba 0.351(9)	1.19(3)
Sr2	0.3447(3)	0.1536(2)	0.19375(20)	Sr 0.443(9) Ba 0.557(9)	1.19(3)
Sr3	0.5	0	0.5	Sr 0.056(14) Ba 0.944(14)	1.19(3)
Sr4	0.1727(3)	0.00018(18)	0.83596(20)	Sr 0.000(9) Ba 1.000(9)	1.19(3)
Mn1	0.5745(6)	0.1666(5)	0.9251(4)	1	1.10(4)
Mn2	0.7756(5)	0.1685(5)	0.7230(4)	1	1.10(4)
O1	0.491(2)	0.0935(14)	0.7453(11)	1	0.37(6)
O2	0.669(2)	0.1963(11)	0.3399(12)	1	0.37(6)
O3	0.339(2)	0.2428(16)	0.9482(11)	1	0.37(6)
O4	0.8238(18)	0.0908(14)	0.8845(12)	1	0.37(6)
O5	0.6461(21)	0.2383(17)	0.0736(14)	1	0.37(6)
O6	0.5	0	0	1	0.37(6)
O7	0.8489(18)	0.0195(13)	0.6353(10)	1	0.37(6)
O8	0.0184(20)	0.2566(14)	0.7189(11)	1	0.37(6)

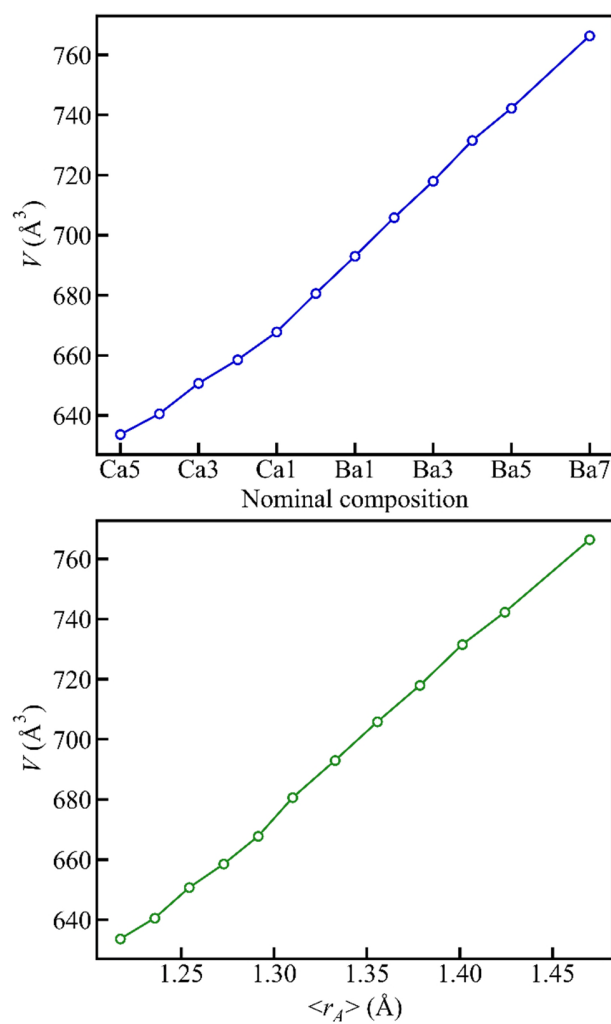


Figure S1.1 Compositional evolution of the refined unit cell volume across the $A_7Mn_4O_{15}$ series based on the nominal composition (top) and the average A-site radius $\langle r_A \rangle$ (bottom). Both clearly exhibit an overall linear variation. $\langle r_A \rangle$ was calculated assuming a coordination number of 9 for the Ca^{2+} , Sr^{2+} , and Ba^{2+} atoms.

S2: Analysis of high-pressure neutron powder diffraction data

A sample of $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ was selected for investigation in a high-pressure neutron diffraction experiment using the PEARL instrument at the ISIS Neutron and Muon Source. This phase was selected as it contained the largest amount of Ca and therefore possessed the smallest unit cell of the family of substituted $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ phases, such that it might be the most susceptible to a phase transition with applied pressure. The experimental details for this are described in the main text. A diffraction pattern recorded at 0.077 GPa is shown in Figure S2.1 with additional reflections arising due to the Paris-Edinburgh cell marked with star symbols. There is clearly a significant contamination of the diffraction pattern by the cell, which impeded data analysis and limited the results to the calculation of lattice parameters and assignment of a space group. The rest of the diffraction patterns from these measurements are shown in Figure S2.2 and Figure 2.3. The measurements at the three highest pressure points were performed using a Paris-Edinburgh press equipped with sintered diamond anvils and, as such, exhibits greater attenuation than the lower-pressure data. The plots at these pressures are on a smaller scale than the plots at lower pressures.

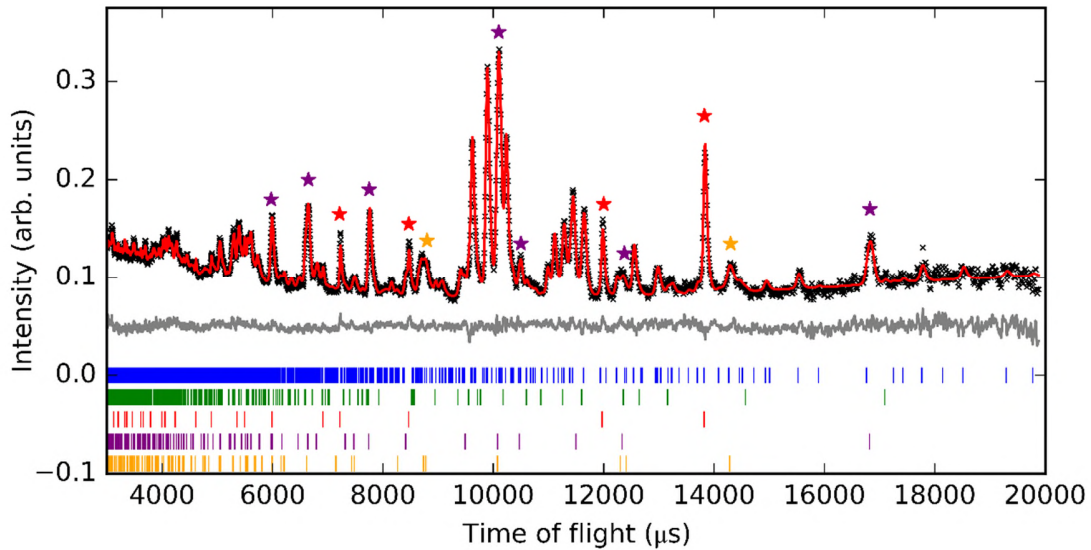


Figure S2.1 PND pattern recorded for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ at 0.077 GPa at the PEARL instrument at ISIS. Blue ticks indicate reflections present in the main phase, green ticks indicate reflections resulting from the Ca_2MnO_4 impurity, red ticks indicate reflections resulting from the lead pressure marker, purple ticks indicate reflections due to the alumina components of the Paris-Edinburgh cell and orange ticks indicate reflections due to the zirconia components of the cell. Stars above peaks in the diffraction pattern indicate strong reflections arising from these impurities, colour-coded to the colour noted for the reflection ticks. The time-of-flight range shown is approximately equivalent to a d -spacing range of 0.3–4.1 Å.

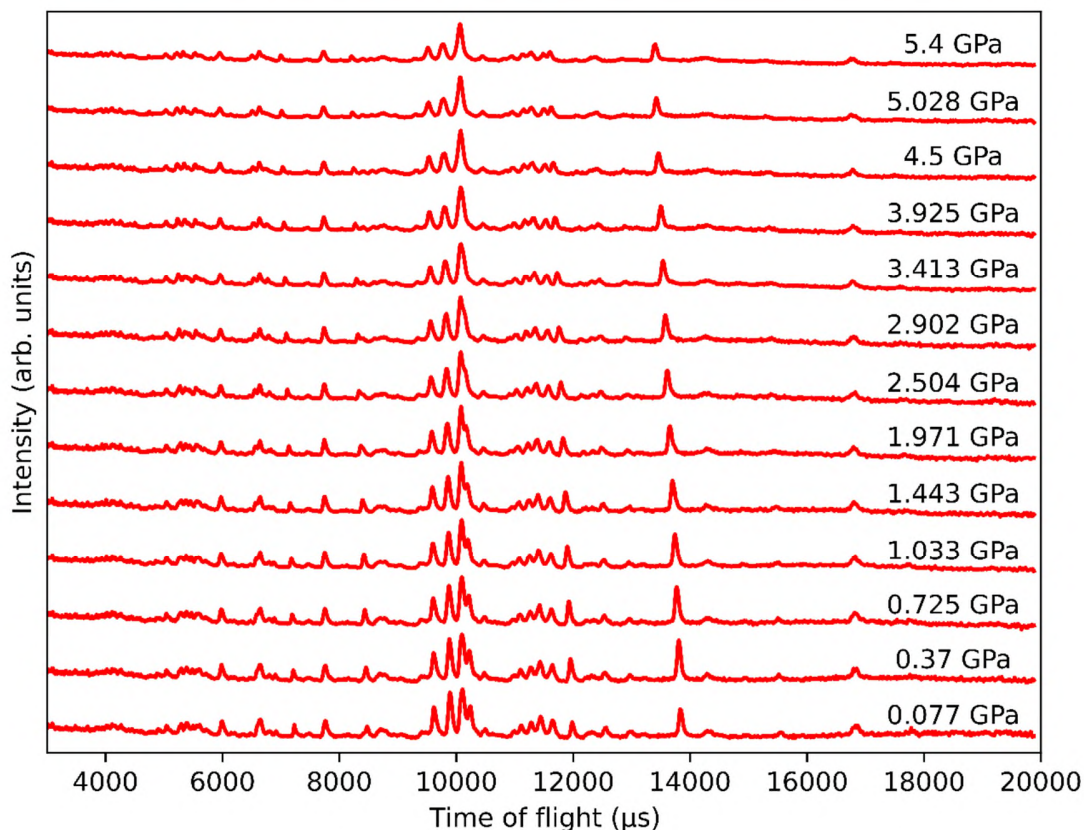


Figure S2.2 PND patterns recorded for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ with increasing pressure at the PEARL instrument at ISIS. Measurements below 5.4 GPa were performed using a Paris-Edinburgh press equipped with zirconia-toughened alumina gaskets. The time-of-flight range shown is approximately equivalent to a d -spacing range of 0.3-4.1 Å.

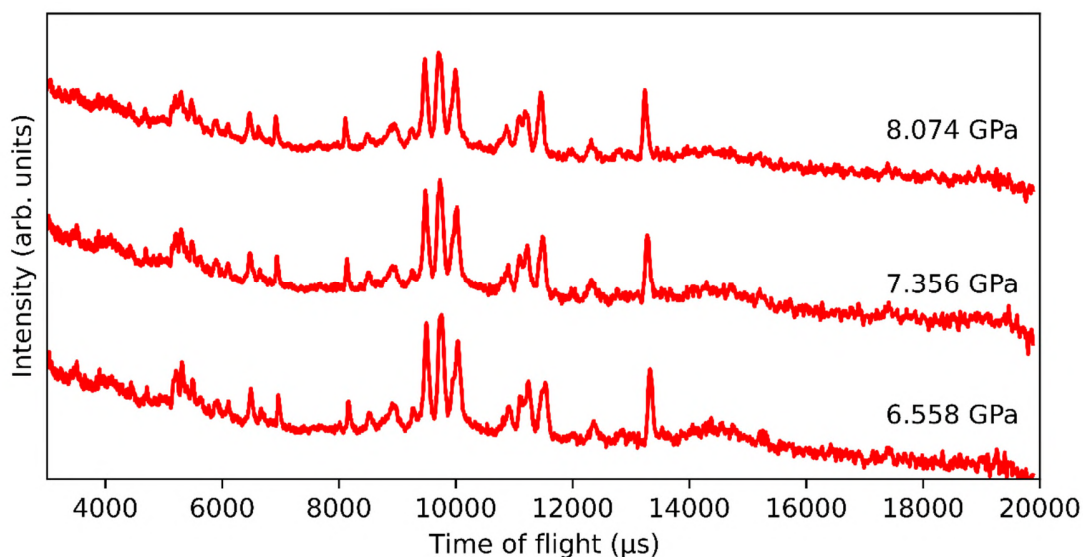


Figure S2.3 PND patterns recorded for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ with increasing pressure at the PEARL instrument at ISIS. Measurements above 5.4 GPa were performed using sintered diamond anvils and suffer from greater beam attenuation and thus reduced intensity and

resolution, and these plots are on a smaller scale than those in Figure S. The time-of-flight range shown is approximately equivalent to a d -spacing range of 0.3-4.1 Å.

There is no evidence for a phase transition up to the maximum pressure in this experiment (8.074 GPa). The variation of the lattice parameters of $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ with increasing pressure are shown in Figure . The a , b and c parameters decrease linearly with pressure, while β increases. This was unexpected as the impact of increasing Ca^{2+} content on the $\text{Sr}_{7-x}\text{Ca}_x\text{Mn}_4\text{O}_{15}$ structure was to cause β to decrease, as reported in the main text, so further reduction in the unit cell volume was naively expected to continue that trend.

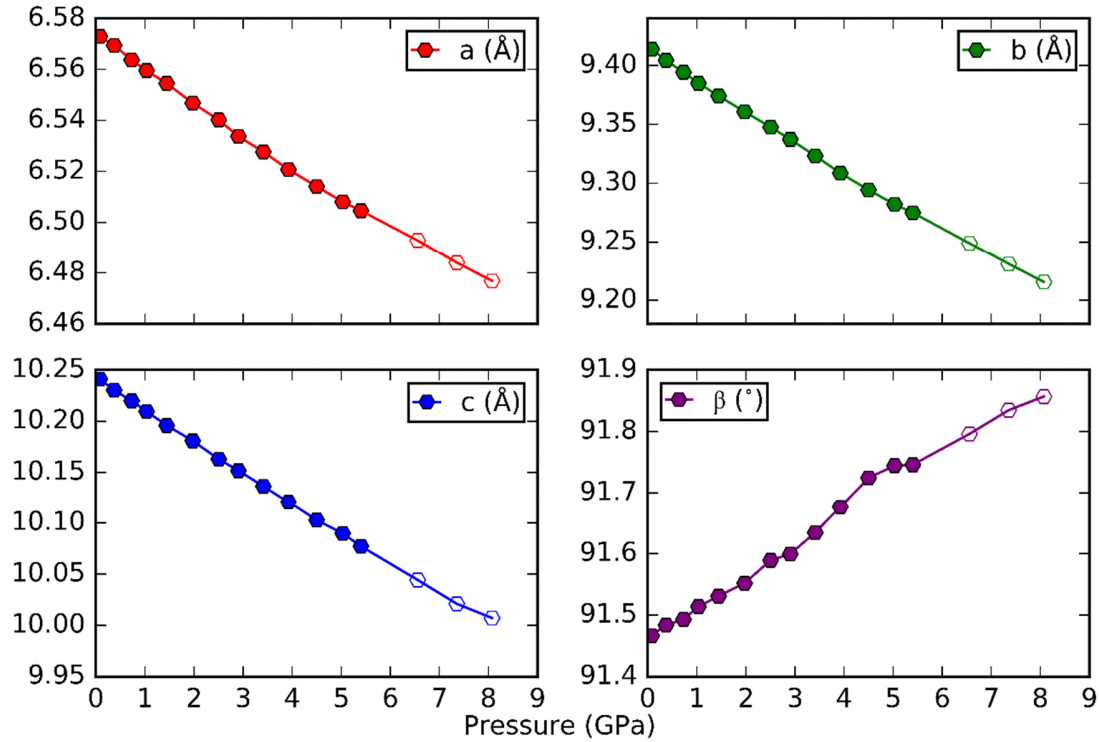


Figure S2.4 Evolution of lattice parameters of $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ with increasing isotropic pressure, measured on PEARL instrument at ISIS. Filled symbols indicate that the lattice parameters were extracted from Rietveld refinements of data measured using zirconia-toughened alumina gaskets, hollow symbols indicate that sintered diamond anvils were used. Calculated errors were within the markers and error bars are therefore omitted.

Principal axis strain calculations were performed on the PEARL PND data for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ using the Principal Axis Strain Calculator (PASCAL) web tool[40]. The resultant compressibility parameters and Birch-Murnaghan coefficients are summarised in Table S2.1 and Tabel S2.2. In line with the lattice parameter contractions with increasing pressure, the compressibilities of each principal axis decrease in the order $X_1 > X_2 > X_3$. X_2 is aligned with the crystallographic b axis and both X_1 and X_3 are split in the ac plane, with X_1 being mostly aligned with c with a large component in a and X_3 being largely aligned with a and having only a small component in c . These compressibilities can be rationalised by considering the structural motifs present in the unit cell: the Mn_2O_9 dimers are of limited compressibility, but the stacks of strings they form in a may be compressed together to a greater degree than they may be compressed in c .

Table S2.1 Compressibility parameters for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ calculated from PEARL PND data using PASCal.

Axes	K (TPa ⁻¹)	σ_K (TPa ⁻¹)	Direction			Empirical parameters			
			<i>a</i>	<i>b</i>	<i>c</i>	ϵ_0 (10 ⁻²)	λ (10 ⁻²)	P_c	V
X ₁	3.1930	0.0466	0.4905	0	0.8715	7.1190	-1.0420	-14.9668	0.7090
X ₂	2.7546	0.0486	0	1	0	6.5056	-1.8203	-11.1379	0.5274
X ₃	1.7786	0.0295	-0.9772	0	0.2125	5.0621	-2.4651	-7.9613	0.3446
V	7.6863	0.0833							

Tabel S2.2 Second- and third-order Birch-Murnaghan coefficients for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ calculated from PEARL PND data using PASCal.

	B ₀ (GPa)	σB_0 (GPa)	V ₀ (Å ³)	σV_0 (Å ³)	B'	$\sigma B'$	P _c (GPa)
2 nd	117.0395	0.4453	633.8554	0.0585	4	n/a	0
3 rd	116.7535	1.8051	633.8654	0.0869	4.1103	0.6735	0

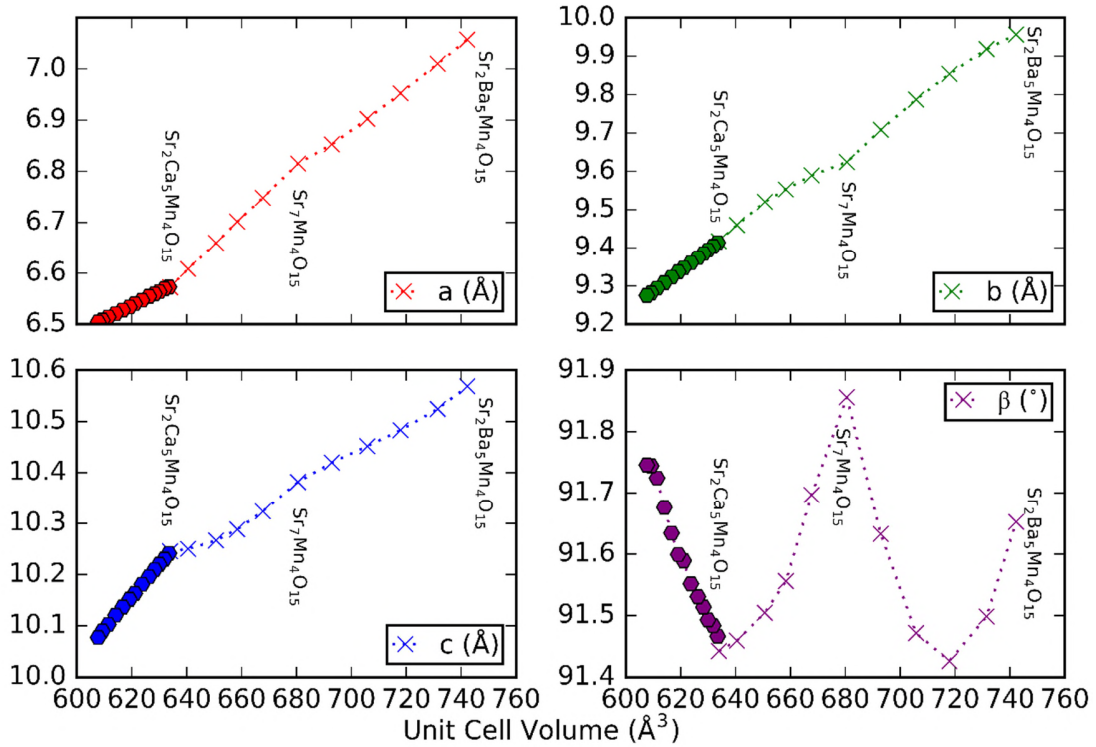


Figure S2.5 Lattice parameters of $\text{Sr}_{7-x}\text{Ca}_x\text{Mn}_4\text{O}_{15}$ ($0 \leq x \leq 5$) plotted as a function of unit cell volume. Filled symbols indicate values of the lattice parameters for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ measured with increasing pressure on PEARL instrument at ISIS (conditions the same as in Figure S2.4). Crosses indicate values measured at standard pressure for the solid solution. Markers for the end members are noted with the composition. Calculated errors were within the markers and error bars are therefore omitted.

Plotting the PEARL PND lattice parameter data as a function of the unit cell volume allows comparison with the data for the $\text{Sr}_{7-x}\text{A}_x\text{Mn}_4\text{O}_{15}$ (A: Ca, Ba; $0 \leq x \leq 5$) solid solution at standard pressure and reveals an interesting property. The *a*, *b* and *c* lattice parameters of

the $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ composition decrease as anticipated with increasing pressure. However, the β parameter increases, mirroring the behaviour of the Ba-containing compositions as the unit cell volume increases above $720 \text{ \AA}^3$. Since the application of physical pressure acts in a similar way to the addition of the smaller Ca^{2+} cation to the structure, the upturn in β with decreasing unit cell volume is unexpected.

S3: Computational Details

Table S3.1 Optimized Ba-doped ($\text{Ba}_{0.5}\text{Sr}_{6.5}\text{Mn}_4\text{O}_{15}$, $Z=2$) and Ca-doped ($\text{Ca}_{0.5}\text{Sr}_{6.5}\text{Mn}_4\text{O}_{15}$, $Z=2$) structure properties as obtained with spin-polarised PBE+U calculations. Total energy per atom; M: multiplicity/degeneracy of the crystallographic site, where the dopant sits. Energetically most favoured dopant sites are indicated in bold.

Doping site	Total E [eV/atom]	Symm	a	b	c	alpha	beta	gamma
Ba-doped								
Sr1 (M=4)	-347.02002	P1	6.940349	9.792535	10.6126	89.85446	91.53827	90.19694
Sr2 (M=4)	-347.30322	P1	6.932213	9.811298	10.58979	89.8859	91.49207	90.02144
Sr3 (M=2)	-347.65581	P-1	6.898692	9.818414	10.60582	90.1078	91.27161	89.77564
Sr4 (M=4)	-347.59155	P1	6.930538	9.806386	10.57123	89.9907	91.33431	90.16695
Ca-doped								
Sr1 (M=4)	-326.67946	P1	6.86478	9.712115	10.29588	90.36977	91.70273	89.53725
Sr2 (M=4)	-326.20560	P1	6.85748	9.694946	10.29696	90.12304	91.77105	90.20415
Sr3 (M=2)	-326.22787	P-1	6.82560	9.757593	10.28273	89.84548	91.52295	90.21095
Sr4 (M=4)	-326.42409	P1	6.82099	9.717954	10.35444	89.83176	91.1697	89.56549

Based on spin-polarised PBE+U total energies, Ba dopant prefers to sit on the Sr3 and Sr4 sites, while Ca dopant has a preference mainly for the Sr1 site, and also the S4 site.

Table S3.2. Single Ba-dopant site preference comparison using different DFT settings. Energetically most preferred sites are given in bold.

Doping site	E [eV] w/ Sconf	Symm	a	b	c	alpha	beta	gamma
GGA/PBE (closed-shell)								
Sr1 (M=4)	-360.9418	P1	6.953661	9.720639	10.33633	90	92.09124	90
Sr2 (M=4)	-361.2334	P1	6.922433	9.700883	10.20024	89.90911	91.69152	89.94977

Sr3 (M=2)	-361.5671	P-1	6.887539	9.707687	10.23393	90.1075	91.44956	89.67095
Sr4 (M=4)	-361.6036	P1	6.928582	9.700044	10.17263	89.99698	91.60957	90.17078
GGA (open-shell)								
Sr1 (M=4)	-369.13305	P1	6.927433	9.750175	10.50129	89.88274	91.52069	90.19697
Sr2 (M=4)	-369.43050	P1	6.918889	9.767303	10.48444	89.90327	91.51005	89.97018
Sr3 (M=2)	-367.88611	P-1	6.875683	9.751583	10.47599	89.61152	91.31383	89.90657
Sr4 (M=4)	-369.87001	P1	6.915435	9.746932	10.46909	89.96172	91.35044	90.17499
GGA+U (closed shell)								
Sr1 (M=4)	-325.47845	P1	6.886721	9.750272	10.43566	90.15682	91.47439	90.28921
Sr2 (M=4)	-325.83097	P1	6.889536	9.78503	10.38265	89.90903	91.54488	89.37366
Sr3 (M=2)	-325.53059	P-1	6.904132	9.735163	10.3658	90.40489	92.21132	89.65011
Sr4 (M=4)	-326.09977	P1	6.910005	9.773144	10.32337	90.32275	91.65034	90.3449
GGA+U (open-shell)								
Sr1 (M=4)	-347.02002	P1	6.940349	9.792535	10.6126	89.85446	91.53827	90.19694
Sr2 (M=4)	-347.30322	P1	6.932213	9.811298	10.58979	89.8859	91.49207	90.02144
Sr3 (M=2)	-347.65581	P-1	6.898692	9.818414	10.60582	90.1078	91.27161	89.77564
Sr4 (M=4)	-347.59155	P1	6.930538	9.806386	10.57123	89.9907	91.33431	90.16695

Table S3.3. Single Ca-dopant site preference comparison using different DFT settings.
Energetically most preferred sites are given in bold.

Doping site	E [eV] w/ Sconf	Symm	a	b	c	alpha	beta	gamma
GGA/PBE (closed-shell)								
Sr1 (M=4)	-362.20585	P1	6.868768	9.647423	10.13369	89.97843	91.57742	89.89746
Sr2 (M=4)	-361.86327	P1	6.873505	9.633166	10.15913	90.07126	91.60488	89.97539
Sr3 (M=2)	-361.64957	P-1	6.886985	9.639863	10.14719	89.93252	91.77213	90.23613
Sr4 (M=4)	-361.64061	P1	6.872313	9.630082	10.19127	90.0551	91.37594	89.94734
GGA (open-shell)								
Sr1 (M=4)	-348.06957	P1	6.875394	9.753081	10.53833	90.10718	91.35116	89.88016
Sr2 (M=4)	-347.75737	P1	6.874089	9.7507	10.5619	90.07479	91.34001	89.89323
Sr3 (M=2)	-347.58910	P-1	6.887798	9.746714	10.55415	89.8407	91.52939	90.15985
Sr4 (M=4)	-347.63743	P1	6.880754	9.743794	10.57428	90.08842	91.33454	89.90031
GGA+U (closed shell)								
Sr1 (M=4)	-370.42264	P1	6.860453	9.701188	10.41704	89.96314	91.34422	89.92369
Sr2 (M=4)	-369.92759	P1	6.862331	9.704623	10.44999	90.08688	91.39145	89.91934
Sr3 (M=2)	-369.74561	P-1	6.878444	9.702945	10.44297	89.86746	91.5537	90.18174
Sr4 (M=4)	-369.80729	P1	6.865109	9.701482	10.46941	90.09508	91.3805	89.94048
GGA+U (open-shell)								
Sr1 (M=4)	-326.67946	P1	6.86478	9.712115	10.29588	90.36977	91.70273	89.53725
Sr2 (M=4)	-326.20560	P1	6.85748	9.694946	10.29696	90.12304	91.77105	90.20415

Sr3 (M=2)	-326.22787	P-1	6.82560	9.757593	10.28273	89.84548	91.52295	90.21095
Sr4 (M=4)	-326.42409	P1	6.82099	9.717954	10.35444	89.83176	91.1697	89.56549

All DFT methods adopted here predict a clear preference for the Sr1 site by a single Ca dopant. As per total energies from different DFT variants, Ba dopant prefers to sit on the Sr4 and Sr3 sites. Due to its definition, open-shell / spin-polarised PBE+U calculations are expected to yield higher accuracy among others considered here.

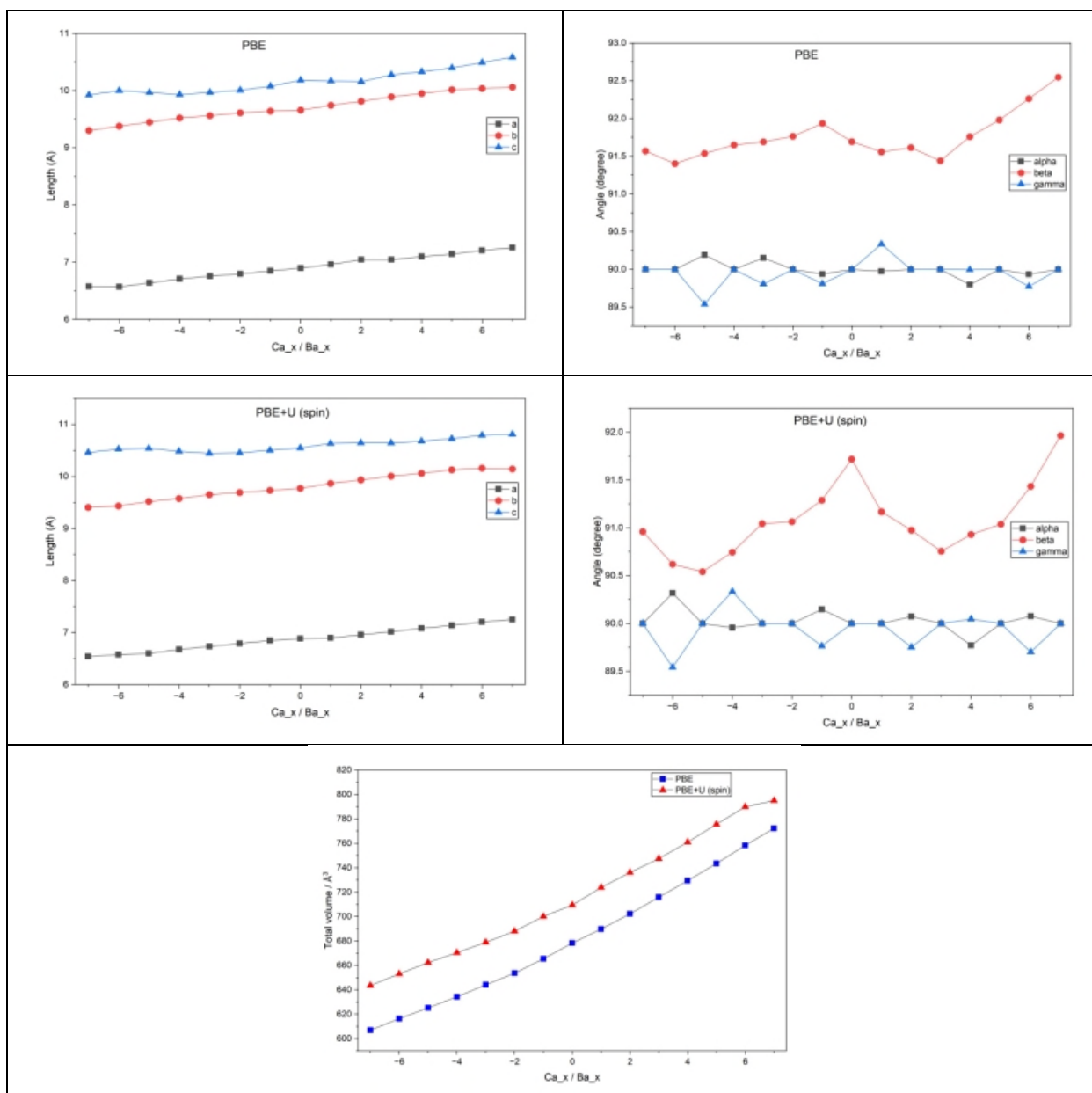


Figure S3.1. Predicted lattice parameters from the minimum-energy structures optimised by (left) GGA/PBE and (right) PBE+U (open shell) for the Ca/Ba-doped $\text{Sr}_y\text{Mn}_4\text{O}_{15}$ phases, compared to

the XRD measurements. Bottom panel compares the predicted unit cell volume as predicted by PBE and PBE+U (open-shell) calculations.

Two density functionals (PBE and PBE+U, PBE with and without Hubbard-U correction) predict similar trends for the a, b, c lengths, while PBE+U (spin-polarised) calculations overall predict larger unit cells. In terms of lattice parameters (a, b, c and also beta), **PBE+U gives a better agreement with the experiment in line with the higher accuracy of this specific DFT methodology.**

S4: Further details of the rigid-unit mode analysis

Table S4.1 RUMs of the $A_7\text{Mn}_4\text{O}_{15}$ framework were identified based on $2a_p \times 2b_p \times 2c_p$ and $3a_p \times 3b_p \times 3c_p$ superstructures with $P1$ symmetry. Each RUM has been given in terms of its corresponding symmetry mode label, which is made up of three parts: i) the $\mathbf{k}$ -point; ii) the irrep transformation with respect to the parent $P2_1/c$ structure; and iii) the order parameter direction or OPD (note that for each irrep, the general OPD is listed so that the corresponding distortion has RUM character regardless of which OPD is selected). The left-hand column encompasses all high-symmetry $\mathbf{k}$ -points of the parent $P2_1/c$ cell, while the right-hand column samples select points along low-symmetry lines of the Brillouin zone. Note that, for the low-symmetry $\mathbf{k}$ -points sampled, the RUMs are listed using only a single arm of the star of $\mathbf{k}$, but for these distortions, RUM character is retained for all symmetry-equivalent arms of the star.

$2a_p \times 2b_p \times 2c_p$	$3a_p \times 3b_p \times 3c_p$
$(\frac{1}{2}, 0, 0)Y_1^+(\mathbf{a})$	$(\frac{1}{3}, 0, 0)F_1(\mathbf{a}, \mathbf{b})$
$(\frac{1}{2}, 0, 0)Y_2^+(\mathbf{a})$	$(\frac{1}{3}, 0, 0)F_2(\mathbf{a}, \mathbf{b})$
$(0, \frac{1}{2}, 0)Z_1(\mathbf{a}, \mathbf{b})$	$(\frac{1}{3}, 0, \frac{1}{3})F_1(\mathbf{a}, \mathbf{b})$
$(0, 0, \frac{1}{2})B_1(\mathbf{a}, \mathbf{b})$	$(\frac{1}{3}, 0, \frac{1}{3})F_2(\mathbf{a}, \mathbf{b})$
$(\frac{1}{2}, \frac{1}{2}, 0)C_1(\mathbf{a}, \mathbf{b})$	$(0, \frac{1}{3}, 0)\Lambda_1(\mathbf{a}, \mathbf{b})$
$(\frac{1}{2}, 0, \frac{1}{2})A_1(\mathbf{a}, \mathbf{b})$	$(0, \frac{1}{3}, 0)\Lambda_2(\mathbf{a}, \mathbf{b})$
$(0, \frac{1}{2}, \frac{1}{2})D_1^-D_2^-(\mathbf{a}, \mathbf{b})$	$(\frac{1}{3}, \frac{1}{3}, 0)GP_1(\mathbf{a}, \mathbf{b}; \mathbf{c}, \mathbf{d})$
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})E_1^+E_2^+(\mathbf{a}, \mathbf{b})$	$(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})GP_1(\mathbf{a}, \mathbf{b}; \mathbf{c}, \mathbf{d})$

Table S4.2 Orientations of the axial vectors depicted in Fig. 8 in the main text in terms of the lattice vectors of the $P2_1/c$ parent cell. Note the uvw components have been rounded to the nearest whole number for simplicity.

RSV	Axial vector direction
$\mathbf{R}_1$	$[\bar{2} \ \bar{1} \ 3]$
$\mathbf{R}_2$	$[\bar{1} \ \bar{1} \ 5]$
$\mathbf{R}_3$	$[28 \ \bar{1} \ 9]$
$\mathbf{R}_4$	$[4 \ \bar{2} \ \bar{5}]$