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

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Abstract

Chemical substitutions offer a universal approach to tailor material properties, but the resulting chemical disorder can impose important structural responses that remain poorly understood. Here we perform a detailed investigation of the effect of chemical disorder in a low-symmetry prototype system $\text{A} = \text{Ca}$ and Ba in $\text{Sr}_{7-x}\text{A}_x\text{Mn}_4\text{O}_{15}$, through a combined high resolution X-ray and neutron powder diffraction study and first-principles density functional theory (DFT) simulations. We find that, despite the coordination environment across the 4 symmetry-unique Sr sites in the monoclinic $P2_1/c$ structure being nominally the same, a large anisotropic and asymmetric solubility preference is observed for Ca^{2+} and Ba^{2+} which have significantly smaller and larger ionic radii, respectively. We contrast this anisotropic control parameter with both experimental and computational studies of the effect of isotropic high-pressure on the evolution of the structural parameters. We show that the complex evolution of lattice parameters (strain) in this series of compounds can only be understood to arise as a result of the coupling between anisotropic site substitution with the acoustic instabilities in this material. Mechanistically, this coupling is shown to be mediated by rigid unit modes, whose composition-dependent evolution accurately reproduces the non-trivial evolution of the lattice parameters across the entire series. Since the existence of coordination polyhedra is rather ubiquitous across functional solid state materials chemistry, the clarification of the interplay between chemical disorder, acoustic instabilities and rigid unit mode distortions represents an important step in the development of approaches for the targeted design of functional materials properties.

Introduction

In materials chemistry, forming solid solutions via substitution of one or multiple formally crystallographically equivalent sites is the main way to tune structure and hence functionality. In the most common paradigm, the average ionic radius or charge of a site is modified to affect a given structural parameter or electronic doping level. Less commonly, other substitutions may be made to affect the polarisability or anisotropy of a site.¹ Additionally, the degree of disorder associated with the targeted site, sometimes characterised by the variance of its ionic radii,² may be substantially tuned. Ionic size variance has been shown to be an effective control parameter in magnetoresistive manganese oxide perovskites,³ superconductivity in doped La_2CuO_4 ⁴ and ferroelectric transitions in BaTiO_3 .^{5,6} In common to all of these examples is the assumption that the substituting cations are distributed equally and randomly across the nominally equivalent sites. While this

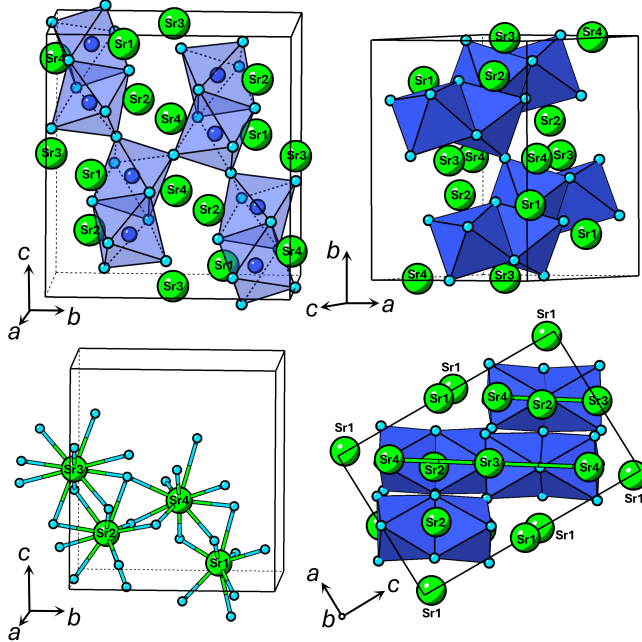


Figure 1: Crystal structure of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ in $P2_1/c$ with four different views emphasising the MnO_6 connectivity along c and the segregation of Sr3 and Sr4 sites into layers between the face sharing octahedra perpendicular to b at approximately $y = 0$ and $y = 0.5$.

is a fair assumption for materials based on ABO_3 perovskites whose aristotypical structure has only one crystallographically equivalent site per chemical species, there is growing awareness that in many functional materials, correlated disorder may persist beyond the unit cell length scale, and that it may even form an important materials design parameter.⁷

Solid-state electrolytes provide instructive examples of this complexity. In lithium argyrodites, $\text{Li}_6\text{PS}_{5x}$ and $\text{Li}_{6+x}\text{P}_{1-x}\text{Ge}_x\text{S}_5\text{I}$, disorder over distinct anion sites controls the Li^+ transport network.^{8,9} In garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, the Li sublattice comprises several tetrahedral and octahedral sites, and Al/Ga dopants display non-trivial site preferences.^{10,11} NASICON-type ($\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$), Na^+ conductors similarly contain multiple alkali-ion sites within a chemically flexible framework.¹² These cases show that substitution in functional solid electrolytes cannot generally be reduced to a random distribution over a single crystallographic site. However, despite this, the structural responses that occur as a results of such chemical disorder remain poorly understood. With this in mind, it is worthwhile to study chemically-simple yet more structurally-complex materials to gain insight into the guiding principles that govern the relationship between chemical substitution, structure and hence property. One such ternary compound is $\text{Sr}_7\text{Mn}_4\text{O}_{15}$. The $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ phase was first reported by Kriegel *et al.*, but has not received a great deal of attention compared with manganese-containing perovskites and other related structures.¹³ This phase crystallises in the monoclinic $P2_1/c$ space group and contains face-sharing MnO_6 octahedral dimers connected together in strings in the ac -plane; these strings connect to form planes which stack along the a direction to produce a quasi-2d structure (See Figure 1). Notably, there are 4 symmetry-inequivalent Sr sites in the structure, all having approximately similar 9-fold coordination with respect to the O anions.

The pseudo-symmetry imparted by the arrangement of face-sharing octahedral dimers results in an unusual magnetic behaviour.¹⁴ A transition at 370 K to short-range spin pairing within the dimers is supported by evidence from ESR spectroscopy and the Néel temperature is approximately 75 K according to neutron diffraction and SQUID experiments. Between 75-150 K the spin behaviour is unclear, with magnetisation vs field (M vs H) experiments demonstrating a separation of the zero field-cooled and field-cooled magnetisation data. This has been suggested to be the result of short-range spin clusters coalescing into long-range antiferromagnetic order with decreasing temperature.¹⁵ Another proposed explanation for the magnetic behaviour is canted antiferromagnetism resulting from a transition to a lower-symmetry space group such as $P2'_1$,¹⁶

which might be driven by coupling to inversion symmetry-breaking rigid unit mode distortions, as recently reported in 4H-SrMnO₃.¹⁷

This idea is particularly interesting as the change in space group permits a loss of centrosymmetry, which could allow Sr₇Mn₄O₁₅ to behave as a Type II multiferroic material, and is further supported by evidence from X-ray powder diffraction data suggesting that two atoms previously believed to occupy special positions are better-modelled as being slightly displaced about their mirror planes at half occupancy.¹⁸ The phase is already known to behave as an insulator from work that investigated it as a possible negative thermal coefficient thermistor material^{19–21} and high temperature dielectric,²² and so the potential exists for it to behave as a ferroelectric.

Aside from its magnetic structure, Sr₇Mn₄O₁₅ is especially interesting due to its flexibility under chemical pressure, making it a particularly suitable model system for understanding the structural responses induced by anisotropic site substitution and chemical disorder. Deintercalation of the oxide anions using sodium hydride has been shown to selectively target the apical sites of the dimers to produce Sr₇Mn₄O_{15–x} ($0 \leq x \leq 3$) and eliminate long-range magnetic ordering.^{23,24} Fluoridation of the reduced phase yields Sr₇Mn₄O₁₃F₂, a structure displaying a degree of charge-ordering wherein the fluoride anions preferentially occupy a single general position.²⁵ Saratovsky *et al.* suggest that this preference is indicative of the oxide anions possessing a large degree of mobility. It is possible that this mobility may prove useful in enhancing polarisation. Substitution of the A-site by Ca and Ba has also been shown to be readily achievable and produces anisotropic changes of the lattice parameters.¹⁸ To date, the maximum doping achieved experimentally has produced Sr_{3.5}Ca_{3.5}Mn₄O₁₅, Sr₆BaMn₄O₁₅ and Sr₅BaCaMn₄O₁₅.

We have recently sought to take advantage of the above-mentioned chemical flexibility and have succeeded in stabilising a completely A-site substituted variant Ba₇Mn₄O₁₅ which adopts a distinct magnetic ordering below 50 K, resulting in a magnetoelectric ground state.^{26,27} Since this is significantly beyond the previously reported maximum Sr₆BaMn₄O₁₅,¹⁸ and in light of the prospect of other magnetoelectric and functional phases, there is a strong motivation to revisit the complete solid solution Sr_{7–x}A_xMn₄O₁₅, A = Ca and Ba to explore both the chemical conditions that optimise it and its structure-tuning effects.

Results and Discussion

Synthesis

The solid-state powder synthesis of Sr₇Mn₄O₁₅ has been reported at temperatures ranging from 1000–1300°C.^{15,16,21} For Sr_{7–x}Ca_xMn₄O₁₅, Vente *et al.* reported requiring temperatures as high as 1400°C in order to achieve substitution to $x = 1$, with no higher substitution being possible.¹⁸ However, we showed that substitution up to $x = 3.5$ was possible, predicting a solubility limit of Ca²⁺ cations of around $x = 6$.¹⁶ Upon heating Ca-substituted samples in the range $0 \leq x \leq 5$, we found that if the temperature was allowed to exceed approximately 1100°C, the majority phase produced was Ca₂MnO₄. This phase was found to be exceedingly stable to continued heating compared with the desired compositions of Sr_{7–x}Ca_xMn₄O₁₅. We find that substitution by Ca to $x > 1$ is possible, but requires very long individual heatings to a lower temperature than has been previously described. Heating to between 1000–1050°C for 72 hours, then regrounding and repeating, allowed a controlled synthesis of the desired phases and limited the formation of perovskite and Ruddlesden-Popper phase impurities. While slow (see Table 1), this method allowed for the synthesis of phases up to $x = 5$ (See Figure 2).

Despite repeated attempts, we have not yet discovered a successful synthetic method for synthesis of SrCa₆Mn₄O₁₅ or Ca₇Mn₄O₁₅. Attempting to repeat the procedure described above resulted in the exclusive formation of Ca₂MnO₄, with little to no evidence of the desired phase formation. Other synthetic routes were attempted, including heating stoichiometric mixtures of oxides in a quartz glass tube under vacuum, solvothermal techniques and the sol-gel method described by O’Malley *et al.*²⁴ However, attempts to synthesise Sr₇Mn₄O₁₅ with a high degree of Ca- or Ba site-substitution were all unsuccessful.

As with the Ca-containing structures, there is little evidence in the literature of successful synthesis of Sr_{7–x}Ba_xMn₄O₁₅ phases. Vente *et al.* utilised a sintering temperature of 1300°C in their synthesis of Sr₆BaMn₄O₁₅, but did not report attempts to produce further samples with higher x , citing the instability of the $x = 1$ phase to humidity.¹⁸ We found that slightly milder conditions of 1050°C with intermediate regrounding could be used to synthesise pure samples up to $x = 5$ in around 3–5 days, significantly faster

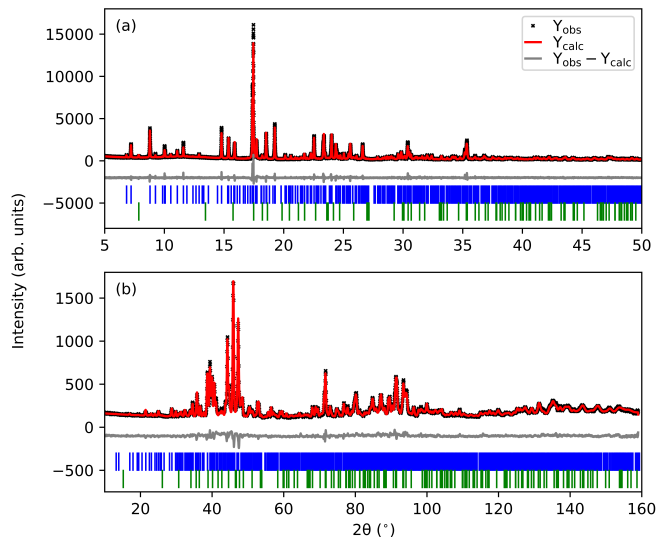


Figure 2: Representative fit of the the $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ structure-type to combined X-ray and Neutron powder diffraction data, shown for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$. Lower tick marks are for an $\tilde{5}$ % weight-fraction impurity of Ca_2MnO_4

than the analogous Ca-substituted samples. Achieving complete substitution was not possible with heating alone; we found that oxidation of the Mn(IV) centres occurred in air for samples for $x = 6$ and $x = 7$, leading to the formation of a $\text{Ba}_3\text{Mn}_2\text{O}_8$ impurity. This was eliminated through the flow of N_2 gas during both calcining and sintering steps. Repeating the same procedure as for the less-substituted Ba samples produced the desired phases containing only one major impurity phase, identified as $\text{Ba}_4\text{Mn}_3\text{O}_{10}$. This may imply that Ba undergoes a small amount of volatilisation in our reactions, however the near linear volume vs nominal composition trend (see S1.1) implies this is not a substantial effect. This $\text{Ba}_4\text{Mn}_3\text{O}_{10}$ impurity was found to form at temperatures between 800-1300°C, and was eliminated for the $x = 7$ sample via the addition of a 10% molar excess of BaCO_3 to the initial reaction mixture, followed by heating at the reduced temperature of 900°C for 48-hour periods. This method was not applicable to the $x = 6$ sample as this would offset the ratio of Sr to Ba and so produce an off-stoichiometric sample; no method has yet been discovered to produce this composition without the inclusion of some amount of impurity.

Structural analysis

With increasing substitution by either Ca or Ba, the lattice parameters of $\text{Sr}_{7-x}\text{A}_x\text{Mn}_4\text{O}_{15}$ all change in an essentially linear progression (see Figure 3). With Ca substitution, the c parameter begins to plateau as substitution reaches our experimental limit. This may hint that the upper limit of substitution is lower than previously predicted, possibly only as high as $\text{Ca} = 5.5$. The main divergence in behaviour between substituting cations is in the β -angle, where the Ca-substituted samples show a decrease in the angle with increasing substitution, reaching a plateau at $\text{Ca} = 5$ in a similar fashion to the c parameter. In contrast, the β -angle for Ba-substituted samples is curved with increasing substitution, initially decreasing before reaching a turning point around $\text{Ba} = 3$. For more highly-substituted samples, the β -angle increases rapidly and exceeds the angle for $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ around $\text{Ba} = 6$. Examining the occupancies of the Sr sites (Figure 4), it can be seen that the Ba^{2+} cations appear to substitute preferentially on to the Sr3 and Sr4 sites, which occurs within the layers of polyhedra (Figure 1). At higher Ba stoichiometries these sites are saturated by Ba^{2+} cations and the next substitutions are forced to occur on the Sr1 and Sr2 sites, which are between the octahedral layers. In contrast, Ca^{2+} cations initially substitute very easily on to the Sr1 and Sr2 sites, only substituting on the Sr4 site when these become saturated and reaching a lower maximum occupancy of the Sr3 site of around 0.33.

To understand if this anisotropic site substitution is tied to the anomalous trend in the β -angle, we

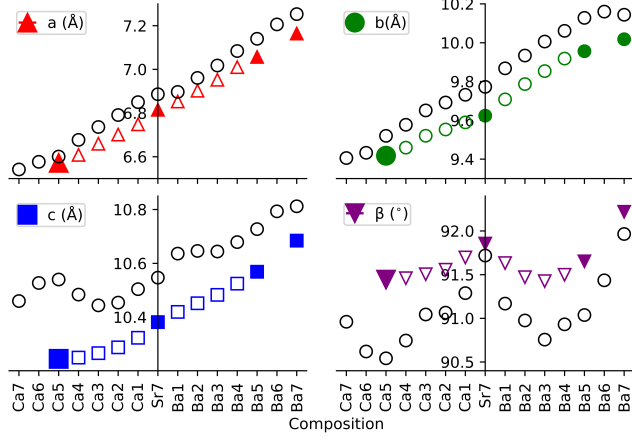


Figure 3: Experimental and calculated lattice parameters of $\text{Sr}_{7-x}\text{A}_x\text{Mn}_4\text{O}_{15}$, $\text{A} = \text{Ca}$ and Ba . Filled symbols denote values obtained from combined synchrotron X-ray and neutron powder diffraction refinements. Black symbols denote the calculated lattice parameters of the lowest-energy cation configurations from spin-polarised PBE+U relaxations. The calculated structures broadly reproduce the trends in a , b and c as well as the non-monotonic composition dependence of the monoclinic β angle.

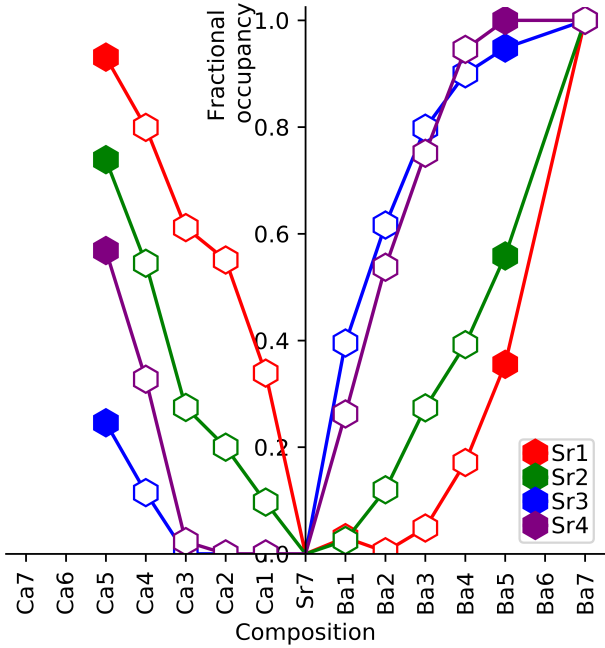


Figure 4: Occupancies of Sr sites by substituting cations. Refined occupancies from combined synchrotron and neutron diffraction data are shown as closed symbols, whereas open symbols are from synchrotron data only. Note that the site multiplicity of Sr3 is half that of the other sites and the refined Stoichiometric (x) should be calculated by weighting accordingly.

Table 1: Temperatures and total heating times required to achieve phase purity for each composition. In $\text{Sr}_3\text{Ca}_4\text{Mn}_4\text{O}_{15}$ and $\text{SrBa}_6\text{Mn}_4\text{O}_{15}$ persistent impurities Ca_2MnO_4 and $\text{Ba}_4\text{Mn}_3\text{O}_{10}$, respectively, were found.

Composition	T / °C	Time / days
$\text{Sr}_7\text{Mn}_4\text{O}_{15}$	1000	6
	1200	3
$\text{Sr}_6\text{CaMn}_4\text{O}_{15}$	1000	40
$\text{Sr}_5\text{Ca}_2\text{Mn}_4\text{O}_{15}$	1000	37
$\text{Sr}_4\text{Ca}_3\text{Mn}_4\text{O}_{15}$	1000	37
$\text{Sr}_3\text{Ca}_4\text{Mn}_4\text{O}_{15}$	1000	86
$\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$	1000	90
$\text{Sr}_6\text{BaMn}_4\text{O}_{15}$	1050	3
$\text{Sr}_5\text{Ba}_2\text{Mn}_4\text{O}_{15}$	1050	3
$\text{Sr}_4\text{Ba}_3\text{Mn}_4\text{O}_{15}$	1050	5
$\text{Sr}_3\text{Ba}_4\text{Mn}_4\text{O}_{15}$	1050	5
$\text{Sr}_2\text{Ba}_5\text{Mn}_4\text{O}_{15}$	1050	5
$\text{SrBa}_6\text{Mn}_4\text{O}_{15}$	1050	-
$\text{Ba}_7\text{Mn}_4\text{O}_{15}$	900	6

perform a conformational analysis of the total DFT ground-state energies of the solid solution. Firstly, we find that the calculated energies, when substituting one of the four Sr-sites in turn with Ba, that the Sr3 and Sr4 site-substitutions are significantly lower in energy (290-630 meV per atom) than the corresponding substitutions on Sr1 and Sr2. The pattern is somewhat reversed with Ca substitutions with the Sr1 site now favoured by 250 meV per atom. Overall, this matches the experimentally-observed trend in Figure 4, giving us confidence that the coupling between anisotropic site substitution and its effect on the average structure, that we measure via our high resolution PXRD, is accurately captured by DFT. It is worth noting in the above analysis that the single-dopant site-preference calculations were fully relaxed in $P1 / P\bar{1}$, depending on the Wyckoff position of the substituted site and were not constrained to $P2_1/c$ symmetry.

Next we perform a complete configuration analysis of $\text{Sr}_{7-x}\text{A}_x\text{Mn}_4\text{O}_{15}$ to compare with our experimental data for $\text{A} = \text{Ca}$ and Ba . For $\text{A} = \text{Ca}$, we also extend beyond $x = 5$ (Figure 3). Pleasingly, the dip in the β angle at $\text{Ba } x = 3$, and cusp at $x = 0$ accurately reproduced our experimental observations (Figure 3). A second dip centered around $x = 5$ for $\text{A} = \text{Ca}$ is predicted computationally and is consistent with our experimental results but not fully confirmed since we have been unable to prepare samples of a higher substitution level.

Since any observed lattice parameter variation can be broadly categorised into isotropic and anisotropic contributions, to decouple this feature from any evolution of the structure that is driven purely by the isotropic volume expansion / contraction, it is insightful to consider what the response of the structure would be under hydrostatic pressure. This allows one to discern if any observed anomaly in the lattice parameters, e.g. in β as we see in the present case, can be predominantly attributed to isotropic or anisotropic effects, driven through the substitution of the significantly larger / smaller ionic radii such as Ba / Ca compared to Sr . To explore this, we perform high-pressure diffraction measurement on $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$, i.e. the member of our solid solution with the smallest experimental volume. A good fit to the high-pressure neutron diffraction data was achieved via Rietveld refinement across all pressure ranges (See Figure 5). The trend in the a , b and c parameters show a more or less monotonic trend across with unit cell volume across both high pressure and composition data (Figure 6). However, the trend in the β angle seems to suggest that a purely-isotropic compression would result in an enhancement of β (Figure 6), and so can therefore not explain our trend. This point is further explored via DFT relaxation on, $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$, $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ and $\text{Ba}_7\text{Mn}_4\text{O}_{15}$ up to 10 GPa. These all show the same general trend (with a constant offset) with high pressure enhancing the β angle. To illustrate the dissimilar evolution of β , we plot in Figure 6 the evolution of the lattice parameters as function of volume determined experimentally from the high pressure study on $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ and from the solid solutions and compare them with those determined theoretically from DFT calculations. Given these results, it seems highly probable that the evolution of the β angle is explicitly controlled in some manner by the anisotropic site substitution.

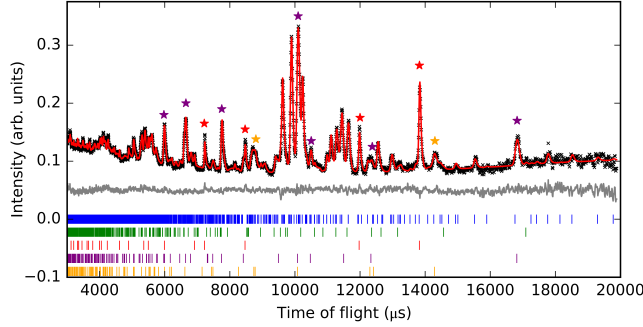


Figure 5: Rietveld fit to high pressure powder diffraction data collected on $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ at PEARL. Fit is shown for a 5 tonne load of the Paris-Edinburgh cell, corresponding to near-ambient pressure (0.077 GPa). Blue ticks indicate reflections present in the main 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 according to the reflection tick marks. The time-of-flight range shown is approximately equivalent to a d-spacing range of 0.3 - 4.1 Å. Stacked plots of the high pressure diffraction data are shown in the Figure S2.2 and S2.3.

Soft phonon modes and coupling to the monoclinic shear

To clarify this point, we investigate phonon dispersion curves at the heavily Ca-substituted end of the solid solution within the DFPT formalism (Figure 7). In $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ modes at 3 - 3.5 THz seem to predominantly involve displacements of Sr3 and Sr4. To investigate if these modes are coupled to an acoustic-like instability that may explain the trend in the β angle, we calculate the phonon dispersion $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ where we artificially constrain β to be 90°. The comparison between this and the fully relaxed structure is shown in Figure 7 where a large band of negative frequencies can be seen with a minimum around Γ -point and Y_2 -point. Next, we calculate the phonon dispersion curves for our lowest energy relaxed unstrained $\text{Ca}_5\text{Sr}_2\text{Mn}_4\text{O}_{15}$ structure. Visually, it is striking how qualitatively similar both the $\beta = 90$ degrees $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ and $\text{Ca}_5\text{Sr}_2\text{Mn}_4\text{O}_{15}$ phonon dispersion curves are. Visualizing the eigenvector components of the Sr sites (Figure 7), shows that these are strongly dominated by the Sr3 and Sr4 sites with a vanishingly small contribution from Sr1 and Sr2 (see Table 2). Furthermore, the atomic displacements are predominantly along directions expected to give a shearing between **a** and **c** lattice vectors, which would largely affect the β angle. Thus the calculations show that site substitution at Sr3 and Sr4 is key for coupling to the acoustic modes that act to tune the β angle. Qualitatively at least, β seems to track the mass disorder (size variance effect) specifically on these sites, with its experimental minimum falling close to the point of half-occupancy of Sr4.

Rigid-unit mode analysis

Our computational insights provide a microscopic basis to relate the anisotropic site substitution to the shear strain in this system. However, the driving force for the instability of this strain mode is not clear from this analysis alone. Since the structure is comprised of an interconnected network of corner-sharing Mn_2O_9 polyhedra, we considered that the strain instability must be tied to cooperative rotations of the polyhedral framework. To this end, we performed a rigid-unit mode (RUM) ^{28,29} analysis of the $\text{A}_7\text{Mn}_4\text{O}_{15}$ framework using the recently-developed ISOTILT webtool. ³⁰⁻³² In short, ISOTILT identifies the co-operative RUMs of a given framework structure by identifying the set of symmetry-allowed distortions which do not require the bond lengths of the rigid units (e.g., the Mn_2O_9 polyhedra in the $\text{A}_7\text{Mn}_4\text{O}_{15}$) to change. This information is determined through a singular value decomposition (SVD) of a linear system of equations relating changes in the positions of the pivot/passenger atoms (i.e., the Mn/O atoms, respectively) to their transformations as irreducible representations (irreps) of the parent structure. From the SVD, the RUM character of a particular distortion mode can be discerned by inspecting either its singular value (σ) or the relative root-mean-squared deviation (RrmsD) of the corresponding right-singular vector (RSV). Each RSV consists of a column vector

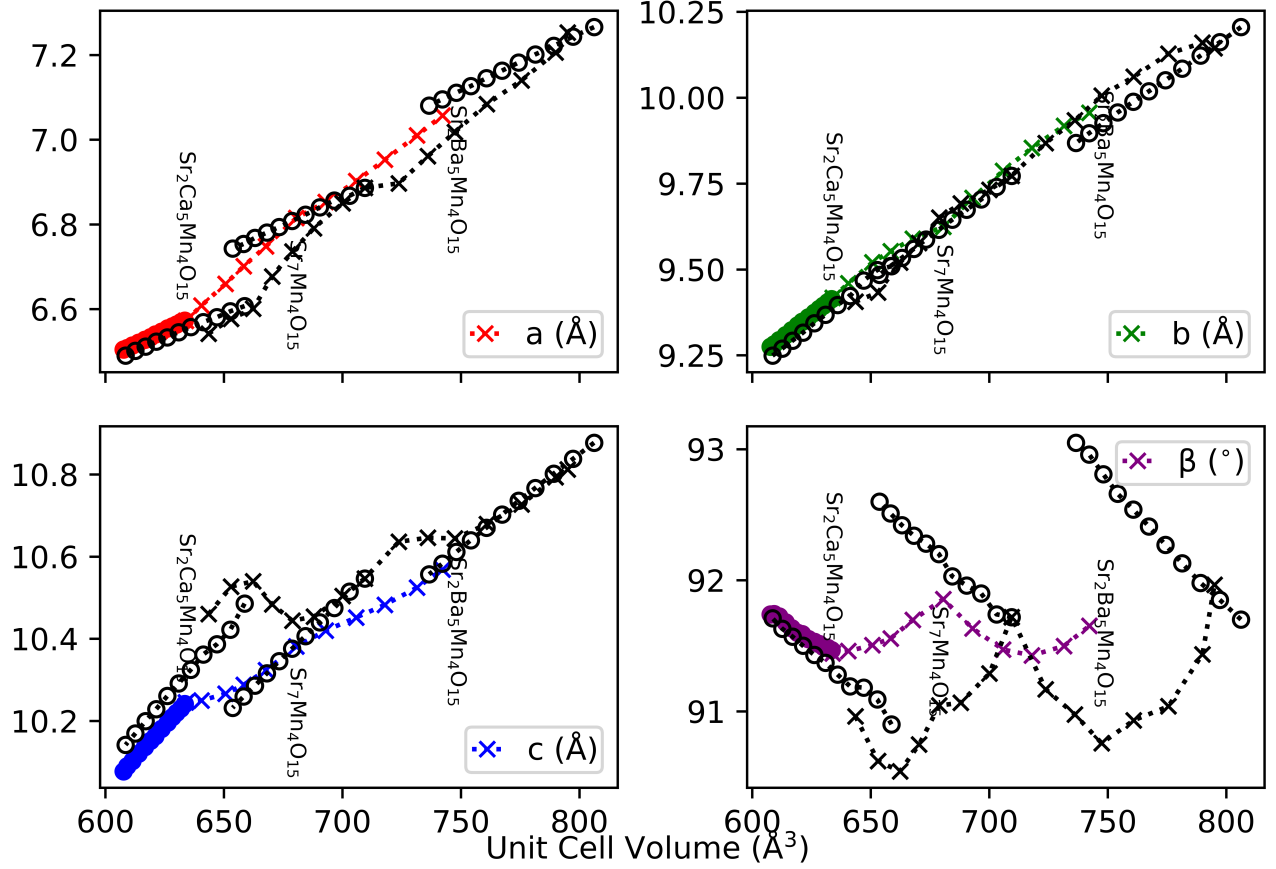


Figure 6: Trends in lattice parameters as a function of volume including both high pressure data (filled circles) on $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ and those derived from room temperature refinements (colored crosses) of the solid solutions. High pressure DFT results (up to 10 GPa) are shown as open circles while composition-dependent calculations as black crosses.

Table 2: Individual mass-weighted contributions from each crystallographic site / atom type to the normal mode for three different imaginary modes predicted for the β -strained $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ structure using open-shell PBE + U calculations. Bold numbers indicate atoms making the strongest contribution to the respective modes.

cif_label	wyckoff	#atoms	Contribution (%)		
			Mode 1 (21.9 cm^{-1})	Mode 2 (46.2 cm^{-1})	Mode 3 (50.1 cm^{-1})
Mn1	4e	8	2.56	1.66	2.40
Mn2	4e	8	0.85	0.66	0.90
O1	4e	8	2.34	3.07	3.58
O2	4e	8	0.68	1.40	1.85
O3	4e	8	12.57	17.27	20.78
O4	4e	8	2.14	2.03	3.09
O5	4e	8	3.57	7.72	5.83
O6	2b	4	38.55	30.65	31.05
O7	4e	8	3.99	6.62	3.84
O8	4e	8	1.96	3.88	6.11
Sr1	4e	8	0.05	1.16	0.28
Sr2	4e	8	0.51	3.19	1.27
Sr3	2d	4	13.84	4.69	6.87
Sr4	4e	8	16.40	16.00	12.15

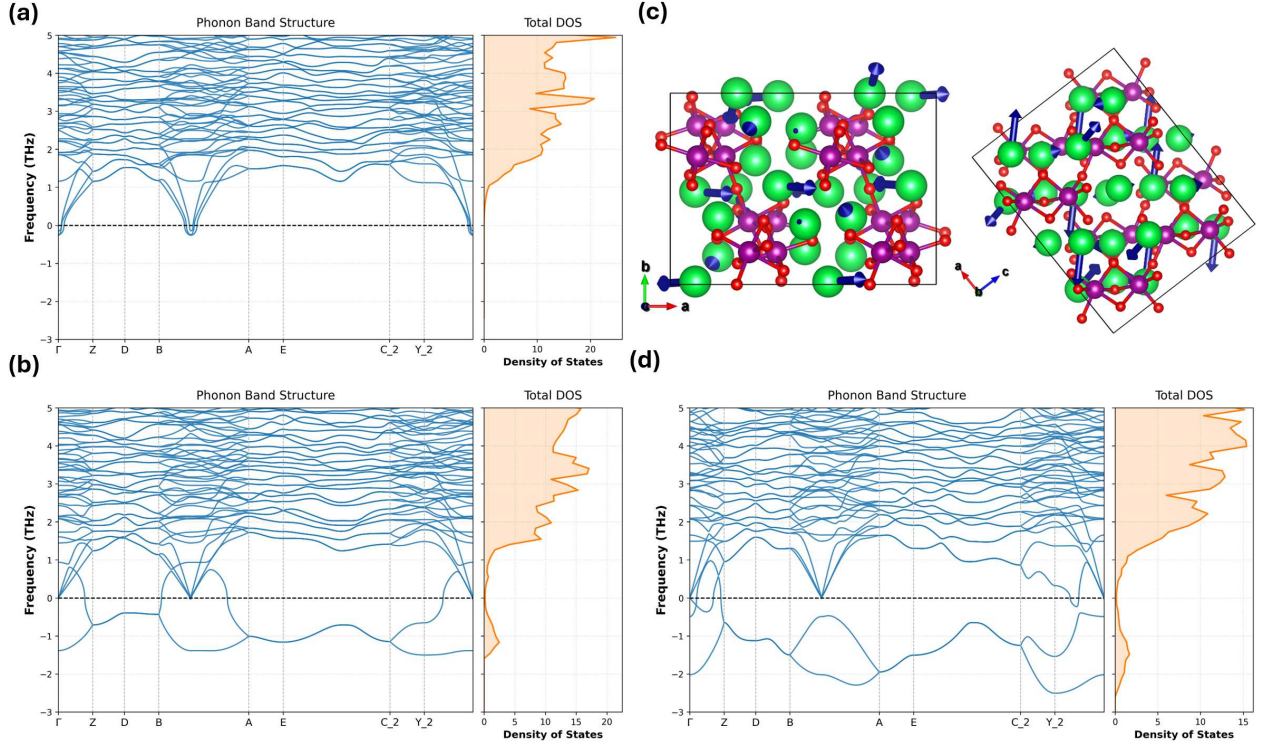


Figure 7: Calculated phonon dispersion curves and representative soft-mode eigenvectors. (a) The fully relaxed $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ structure is dynamically stable, whereas (b) constraining β to 90° produces an acoustic-like imaginary-frequency branch. The corresponding eigenvectors are dominated by Sr3/Sr4 displacements (c) and are consistent with shearing of the $\mathbf{a}$ and $\mathbf{c}$ lattice vectors, linking the soft mode to the monoclinic β distortion. (d) The phonon dispersion curves of $\text{Ca}_5\text{Sr}_2\text{Mn}_4\text{O}_{15}$ showing similar instabilities to (b), but induced by site substitution.

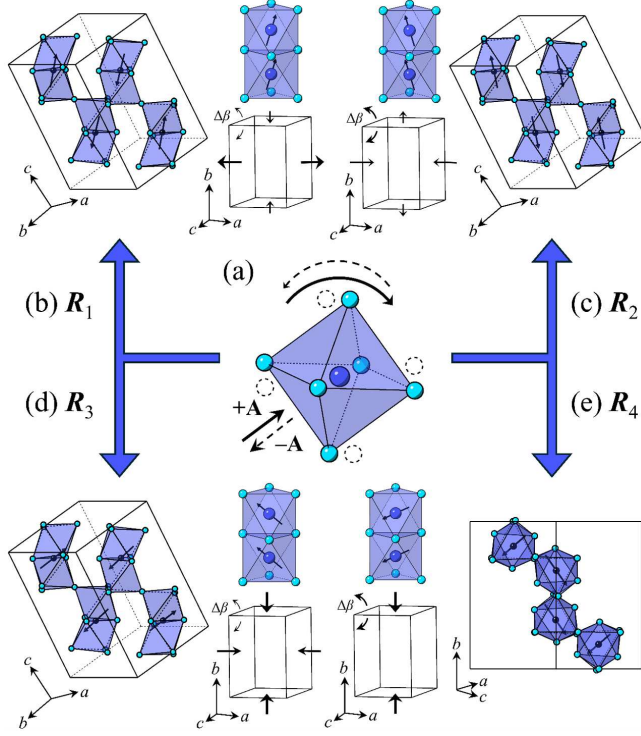


Figure 8: Visual representations of the RUMs in the $A_7Mn_4O_{15}$ framework. (a) Representation of an axial vector (A), showing how it relates to the rotational direction of an individual MnO6 octahedron. (b)-(e) Visualisations of the four Γ_1^+ RUMs. Each visualisation depicts a combined axial vector located at the centre of mass of each bioctahedral dimer, an isolated Mn_2O_9 bioctahedral dimer to better highlight the local orientations of the axial vectors (Table S4.2), and the accompanying strain states corresponding to the symmetrised strain mode components given in Table 3.

containing the symmetrised mode components describing a potential RUM-type motion, and a given RSV is classified as a RUM according to the conditions $\sigma = 0$ and / or $R_{rmsD} = 0$. Any other distortion with $\sigma > 0$ or $R_{rmsD} > 0$ is therefore discounted as a RUM, corresponding instead to some other higher-energy structural distortion that will likely not represent an incipient instability with respect to the undistorted framework structure.

The strain mode components included under each Γ_1^+ RUM provide a convenient basis to relate the experimentally-observed strain states to those expected for each RUM. Because the RUMs transform under the Γ_1^+ irrep, the symmetry analysis could be performed with respect to any of the $A_7Mn_4O_{15}$ structures; we have chosen $Ba_7Mn_4O_{15}$ as the parent under the assumption that RUM-like distortions will be favoured as the average A-site radius decreases. Our RUM analysis shows there are four RUMs which transform under the $GM1^+$ irrep in the $Sr_7Mn_4O_{15}$ structure type. These can be broadly understood in terms of two RUMs largely aligned with the local threefold axes of the Mn_2O_9 bioctahedra, with another two largely aligned orthogonal to this axis (see Fig. 8 and S4 for further details).

Each Γ_1^+ RUM is associated with a characteristic strain signature (Fig. 8) comprised of the symmetrised strain mode components listed in Table 3. All four RUMs involve changes in the monoclinic β angle, although the predicted changes are considerably larger for R_2 and R_4 than for R_1 and R_3 . Their distinct strain signatures therefore provide a useful framework to relate the experimentally-observed evolution in β across the $A_7Mn_4O_{15}$ series to the presence or absence of RUM-type distortions. However, the strains alone are insufficient to distinguish between the different RUM contributions. For this reason, we opt to decompose the full composition-dependent structural distortions evolution in terms of the RSVs given in Table 3 (see Methods section for full details).

Importantly, the resulting RUM-reconstructed β coordinate qualitatively reproduces the variation in

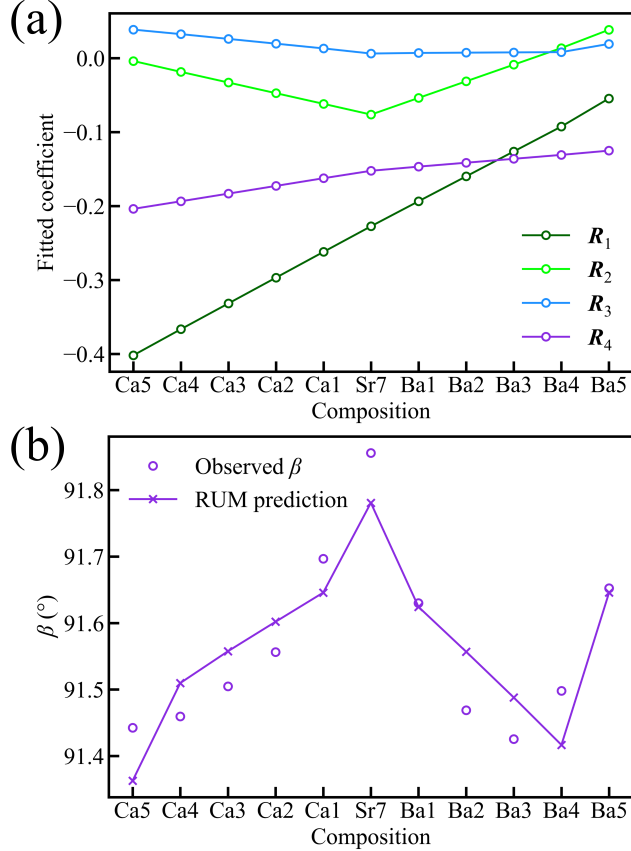


Figure 9: (a) Fitted coefficients for the four RSVs (R_n) spanning the Γ_1^+ RUM basis across the $A_7Mn_4O_{15}$ series. (b) Reconstruction of the observed variation in β based on a linear combination of the four RSVs.

β_{exp} , including the cusps observed in the intermediate solid solutions (Fig. 9(b)). Considering the linear combination of RUMs is weighted using both the displacive and strain components, and the associated errors in our refined structural models, the level of agreement between the observed and predicted β angles is particularly good. Residual deviations likely indicate contributions from additional symmetry-allowed distortions which are not represented within the Γ_1^+ RUM basis and/or nonlinear coupling of the strain to other structural distortions. Nevertheless, our analysis clearly shows that the Γ_1^+ RUMs rationalise the observed evolution of β_{exp} in this system.

We have recently shown that the large class of materials classified as hexagonal perovskites contain a large number of potential symmetry-breaking RUM distortions associated with cooperative tilting of B_2O_9 biotahedral dimers.³³ Due to the apparent ubiquitous nature of such coordination-polyhedra across materials chemistry,³⁴ we envisage our approach outlined here will be broadly applicable for investigating the phenomena in many functional materials. Crucially, our work establishes a link between the effects of chemical disorder on strain and acoustic instabilities through an understanding of the theory of rigid unit modes and the displacive instabilities to which they can couple.

Conclusion

Overall our work shows how, even in very complex and low-symmetry crystal structures, it is possible to form a mechanistic link between non-trivial site disordering and the global response this has on the lattice strain. Mechanistically, this link is formed by being able to identify anisotropic and asymmetric site substitution preferences with respect to cation sizes, through the use of high-resolution powder diffraction data and DFT-relaxed structures of the possible configuration enumerations. The influence of the mass disorder and

how this couples to acoustic phonon modes provides insight into how site disorder can be used to control lattice strain and hence functional properties. Ultimately, it is shown that a detailed understanding of the non-trivial evolution of the octahedral tilting, in response to this chemical variance, is required to accurately reproduce the strain (lattice parameters) evolutions across the full $A_7Mn_4O_{15}$ series. Since $\approx 50\%$ of all entries in the Inorganic Crystal Structure Database³⁵ exhibit some form of structural disorder,³⁶ and (quasi-rigid) rigid-unit-like motions invariably provide low energy pathways for coordination environments to relax, it is hoped our approach will inspire further investigations into the interplay between chemical site-disorder, crystallographic distortions and functionality.

Methods

Synthesis

Samples of $Sr_{7-x}A_xMn_4O_{15}$ (A: Ca, Ba; $0 \leq x \leq 5$) were synthesised using standard solid-state methods. Stoichiometric quantities of the appropriate combination of carbonates ($SrCO_3$, $CaCO_3$ and $BaCO_3$) were ground in an agate mortar with MnO_2 until homogeneous, then pressed into 13 mm-diameter pellets using 7.5 tons of pressure. These pellets were calcined at $900^\circ C$ for 20-24 hours, then reground and fired between $900-1200^\circ C$ for various time periods depending on the substituent cation and degree of substitution. Table 1 summarises the total heating times required for each composition. All samples utilised intermediate regrindings, and a continuous flow of N_2 gas was also used for samples containing larger quantities of Ba to overcome the formation of higher-oxidation state impurity phases.

Diffraction

High-resolution X-ray powder diffraction experiments were performed on all samples at Beamline I11 at Diamond Light Source, making use of the PSD and MAC detectors at room temperature at an energy of 15 keV, equating to an X-ray wavelength of approximately $0.825 \text{ \AA}$. Samples were loaded into 0.3 mm-diameter borosilicate glass capillaries. The zero-point error, wavelength and instrument contribution to the peak profile were determined against a NIST 640 Si standard and fixed for all subsequent analysis. High-resolution neutron powder diffraction experiments were performed on samples of $Sr_7Mn_4O_{15}$, $Sr_2Ba_5Mn_4O_{15}$ and $Sr_2Ca_5Mn_4O_{15}$ at ILL Beamline D2B,³⁷ using a Ge(335) monochromator to provide a neutron wavelength of $1.594 \text{ \AA}$ at 1.5, 100 and 300 K. All diffraction data were analysed using TOPAS Academic v6. The reported refined site occupancies are unconstrained and deviate substantially in some compositions from the nominal ones. This discrepancy is most notable at low Ca-substitution levels ($x = 1 - 3$) which most likely reflects the low scattering contrast of these sites at relatively small substitution levels (See Tables S1.1 - S1.10 in the Supplemental Material). The plot of the unit cell volume versus nominal composition reveals a linear trend (see Figure S1.1) confirming this is predominately an artifact of the refinements, rather than an inherent non-stoichiometry.

High pressure

High-pressure time-of-flight (TOF) neutron powder diffraction data were collected on the PEARL diffractometer at the ISIS Neutron and Muon Facility.³⁸ Details on the PEARL instrument and associated experimental and data-correction procedures are described in Bull et al.³⁹ A powder sample of $Sr_2Ca_5Mn_4O_{15}$ was loaded into a null-scattering, encapsulated titanium-zirconium alloy gasket, and a lead pellet was added to serve as a pressure calibrant. Hydrostatic compression conditions were achieved by using a methanol-ethanol pressure-transmitting medium in a 4:1 volume ratio. The gasket was loaded in a V3 Paris-Edinburgh press equipped with single-toroid zirconia-toughened alumina ceramic anvils. Data were collected at 5-tonne load increments with an additional measurement at 12 tonnes. Collection times for most load points were approximately 4 hours, except at 15 (1.01), 40 (3.41), 55 (5.03) and 60 (5.40) tonnes (GPa) which collected data for 8, 9 6 and 8 hours respectively. The unit cell volume of the lead calibrant was determined using Rietveld refinement and was used during the experiment to determine the pressure in GPa from a previously-determined Murnaghan equation of state. For additional higher-pressure measurements, the gasket was loaded into a

Paris-Edinburgh press equipped with single-toroid sintered diamond anvils. Collection times for these measurements were 8, 10 and 13 hours at 70 (6.56), 80 (7.36) and 90 (8.07) tonnes (GPa) respectively. The maximum pressure achieved in these experiments was 8.07 GPa. Principal component strain calculations and Birch-Murnaghan fits were performed on the lattice parameters extracted from Rietveld refinement using the Principal Axis Strain Calculator (PASCAL) web tool.⁴⁰

Computational details

All quantum mechanical calculations were performed using plane-wave density functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP, v. 6.4).^{41–43} The projector augmented wave (PAW) method^{44,45} was used to describe the interaction between the valence electrons and ionic cores, and the Perdew-Burke-Ernzerhof (PBE) form of the generalised gradient approximation (GGA) was used for the exchange-correlation functional.^{46,47} A plane-wave kinetic-energy cut-off of 520 eV was used, and reciprocal space was sampled using Γ -centred Monkhorst-Pack grids⁴⁸ with a spacing finer than $0.314 \text{ \AA}^{-1}$. Electronic minimisation was converged to 10^{-8} eV, and full structural relaxations were continued until all residual forces were below $0.05 \text{ eV \AA}^{-1}$. Unless otherwise stated, both atomic positions and lattice parameters were allowed to relax. To assess the effect of the correlated Mn 3d states, selected calculations were repeated using spin-polarised DFT + U within the Dudarev formalism,⁴⁹ with an effective Hubbard parameter $U_{eff} = 3.9 \text{ eV}$ applied to the Mn 3d orbitals, as previously reported.⁵⁰ The DFT + U spin-polarised results were used as the primary reference for comparison with the experimental lattice-parameter trends, because they provided the best overall agreement with the measured unit-cell metrics (Figure S3.1).

The experimentally-refined monoclinic $P2_1/c$ $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ structure was used as the parent model for generating defect configurations. Dilute substitution models were generated by replacing one Sr atom in the $Z = 2$ cell by either Ca or Ba, corresponding to $\text{Sr}_{6.5}\text{A}_{0.5}\text{Mn}_4\text{O}_{15}$. Each of the four crystallographically-distinct Sr sites was considered in turn. The resulting cells were relaxed without enforcing the parent symmetry, allowing local distortions around the dopant to develop. Relative site-preference energies were evaluated from the total energies of the relaxed cells and referenced to the lowest-energy configuration for each dopant. Effective coordination numbers, bond-valence sums, and bond distortion indices were obtained from the relaxed structures using VESTA.⁵¹

For finite dopant concentrations, symmetrically-distinct distributions of Ca or Ba over the Sr sublattice were enumerated for $\text{Sr}_{7-x}\text{A}_x\text{Mn}_4\text{O}_{15}$ (with A = Ba or Ca) using our in-house *Config-Enum* code (available upon reasonable request). At each composition, the lowest-energy relaxed structure was used to compare the calculated cell parameters with the experimental diffraction refinements. Where the experimental Ca series could not be extended beyond $x = 5$, additional Ca-rich compositions were nevertheless included computationally to test whether the lattice trends continue towards the fully substituted end member.

To separate anisotropic site-substitution effects from a purely volume-driven chemical-pressure effect, hydrostatic pressure calculations were carried out for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$, $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ and $\text{Ba}_7\text{Mn}_4\text{O}_{15}$. The cells were relaxed at fixed external pressure, and the pressure dependence of the lattice parameters and monoclinic β -angle was compared with the high-pressure neutron diffraction measurements on $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$.

Lattice-dynamical stability was examined using density functional perturbation theory (DFPT) at the spin-polarised PBE+U level. Phonon dispersion curves were calculated using $2 \times 1 \times 1$ supercells and analysed with the PHONOPY package.⁵² The eigenvectors of selected soft modes were visualised with VESTA to identify the atomic sublattices and displacement directions associated with the calculated instabilities.

Rigid-unit mode analysis

First, we enumerated all possible RUMs of the $\text{A}_7\text{Mn}_4\text{O}_{15}$ framework using a hypothetical $2a_p \times 2b_p \times 2c_p$ $P1$ superstructure of the parent $P2_1/c$ cell, where a_p , b_p , and c_p denote the lattice vectors of the parent structure. Throughout this analysis, $\text{Ba}_7\text{Mn}_4\text{O}_{15}$ is taken as the "parent" structure, and all mode analyses are performed with respect to this reference state. Initially, our RUM analysis was performed only with respect to the displacive and rotational degrees of freedom — under these constraints, we found that every zone-boundary k-point hosts at least one mode with RUM character (Table S4.1). Furthermore, analysis of a $3a_p \times 3b_p \times 3c_p$ $P1$ superstructure showed that RUM character is preserved away from the high-symmetry k-points, suggesting the corresponding distortions represent extended lines or even planes of RUMs. This

is consistent with the results from our phonon calculations, showing an imaginary-frequency phonon band spans the full k-path sampled (Fig. 7). Including the possibility of a linear strain coupling in our RUM analysis yields an additional six RUMs at the Γ -point, four of which transform under the Γ_1^+ irrep (Table 3). This is the totally symmetric representation, hence it encompasses all possible distortions which are permitted by symmetry under the parent $P2_1/c$ cell.

The A1, A2, and A3 rotational components of each Γ_1^+ RUM align with the **c**, **a**, and **b** lattice vectors, respectively. The linear combinations of these components given in Table 3 generally do not align with any of the high-symmetry directions of the monoclinic cell, making it difficult to understand the character of each RUM from the total distorted structures. For this reason, we opt to represent the polyhedral rotations in terms of their transformations as axial vectors (Fig. 8(a)). The first two RUMs (R1 and R2) contain large A1 rotational components so that they transform as axial vectors aligned approximately with the threefold axes of the individual Mn_2O_9 biotahedra (Fig. 8(b), 8(c)). R3 and R4 are dominated by larger A2 and A2 / A3 rotational components, meaning their corresponding axial vectors are largely oriented orthogonal to the threefold axis (Fig. 8(d)). Finally, R4 is almost entirely made up of A2 and A3 rotational components, meaning its axial vector is essentially entirely orthogonal to the threefold axis (Figure 8). All four RUMs are also characterised by substantial Mn displacive components (Table 3), so the rotational components alone are, strictly speaking, insufficient to describe the corresponding structural distortion. Nevertheless, the rotational degrees of freedom provide the most intuitive physical picture of each RUM, so for brevity our subsequent discussion primarily focuses on these components.

It is important to note that orthogonality of the RUM basis is only guaranteed for the full RSV basis vectors, whereas their projections onto the strain subspace do not yield an orthogonal basis. This means the basis vectors that span only the strain subspace cannot reliably distinguish the relative contributions of each RUM to the observed distortions. For this reason we opt to compare the RSVs in Table 3 against the full structural distortions.

To extract the RUM contributions to each distorted structure, we treated the RSVs in Table 3 as basis vectors and projected the distorted structures onto this basis. First, representative distortions for each RUM were generated using the atomic positions output by ISOTILT for each RSV. We then performed a mode decomposition of each distorted structure at room temperature with respect to the $\text{Ba}_7\text{Mn}_4\text{O}_{15}$ parent using ISODISTORT⁵³ to express the rotational symmetry modes in terms of the displacive degrees of freedom, essentially providing a purely displacive eigenvector for each RSV that can be compared directly against the Rietveld-refined structures. The RSV amplitudes were then obtained through a least-squares projection of the experimental distortion $\mathbf{Q}_{exp}$ onto the RSV basis:

$$\mathbf{Q}_{exp} = \mathbf{Q}_0 + \sum c_i \mathbf{R}_n$$

All four of the RSVs spanning the Γ_1^+ RUM basis are characterised by non-zero fitting coefficients (Fig. 8(a)), showing that there is a finite RUM component which evolves with composition throughout the series. R1 exhibits a linear variation across the series, while the remaining RSVs exhibit a more complex (i.e., non-linear) variation with composition. Of particular note is that no individual RSV precisely mirrors the evolution of β (Figure 3), showing no individual RUM is responsible for the shear strain instability. However, since all four RSVs are permitted under the $P2_1/c$ symmetry of the parent structure, the shear instability need not correspond to an individual RUM but may instead arise from some linear combination of them. To test this, we modelled the variation in β against the extracted RUM coefficients according to the multiple linear regression:

$$\beta_{exp} = \beta_0 + \sum w_i c_i$$

where β_{exp} is the experimental β angle, β_0 is an intercept term, and the regression coefficients w_i define a vector relating the linear combination of RUMs to the experimentally observed monoclinic angle. From the regression model, we obtained $w = 79.7, -48.0, 18.7, \text{ and } -317.8$ with $R^2 = 0.7719$.

Table 3: Mode details of the four basis RUMs in the $A_7Mn_4O_{15}$ framework. Each RUM consists of right-singular vectors (R_n) representing linear combinations of symmetry-adapted displacive (dsp), rotational (rot), and strain modes.

Mode label	Site symmetry	Irrep	R_1	R_2	R_3	R_4
Mn1:e:rot	1	A1	+0.15322	+0.44365	+0.10463	-0.07283
Mn1:e:rot	1	A2	-0.10381	-0.09061	-0.31510	-0.20712
Mn1:e:rot	1	A3	-0.04778	-0.06741	-0.00572	-0.17265
Mn2:e:rot	1	A1	+0.15322	+0.44365	+0.10463	-0.07283
Mn2:e:rot	1	A2	-0.10381	-0.09061	-0.31510	-0.20712
Mn2:e:rot	1	A3	-0.04778	-0.06741	-0.00572	-0.17265
Mn1:e:dsp	1	A1	-0.08006	-0.04332	-0.51810	-0.02901
Mn1:e:dsp	1	A2	-0.42386	-0.40945	-0.08792	+0.12463
Mn1:e:dsp	1	A3	+0.00130	-0.06850	+0.08492	+0.08764
Mn2:e:dsp	1	A1	+0.14486	+0.21743	-0.50265	+0.73678
Mn2:e:dsp	1	A2	-0.83341	+0.38834	+0.12119	+0.13291
Mn2:e:dsp	1	A3	-0.01723	+0.33875	-0.46376	-0.46650
Strain ₁			+0.15015	-0.28954	-0.07612	+0.00032
Strain ₂			-0.04957	-0.06866	-0.00545	-0.18264
Strain ₃			-0.00110	+0.07242	-0.08866	-0.09181
Strain ₄			-0.00063	-0.00101	+0.00074	-0.00278

Data Availability

The experimental neutron diffraction data underpinning this study is openly available.^{37,38} The key calculation results are available on a *GitHub* repository and the *Config-Enum* code will be made available on a reasonable request from the authors.

Supporting information

A single supporting PDF document containing 4 sections giving further details of the crystallographic information for room temperature refinements, analysis of high-pressure neutron powder diffraction, DFT calculations and rigid-unit mode analysis.

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Author Contributions

The study was designed by M.S.S. and B.K. G.R.M.C., C.R., and N.P.F. conducted the neutron diffraction experiments. G.R.M.C. carried out the sample synthesis and diffraction data analysis. B.K. conducted the DFT calculations, and S.S. performed the rigid-unit mode analysis. The manuscript was drafted by M.S.S., B.K., and S.S., with contributions from all co-authors.

Competing Interests

The authors declare no competing interests.

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