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Structural Modification of the Cation-Ordered Ruddlesden-Popper Phase YSr₂Mn₂O₇ by Cation Exchange and Anion Insertion

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S Supporting Information

ABSTRACT: Calcium-for-strontium cation substitution of the $a^{-}b^{0}c^{0}/b^{0}a^{-}c^{0}$ -distorted, cation-ordered, n = 2 Ruddlesden-Popper phase, YSr₂Mn₂O₇, leads to separation into two phases, which both retain an a⁻b⁰c⁰/b⁰a⁻c⁰-distorted framework and have the same stoichiometry but exhibit different degrees of Y/ Sr/Ca cation order. Increasing the calcium concentration to form YSr_{0.5}Ca_{1.5}Mn₂O₇ leads to a change in the cooperative tilting on the MnO₆ units to a novel $a^{-}b^{-}c^{-}/b^{-}a^{-}c^{-}$ arrangement described in space group P21/n11. Low-temperature, topochemical fluorination of YSr₂Mn₂O₇ yields $YSr_2Mn_2O_5 F_{3,5}$. In contrast to many other fluorinated n = 2Ruddlesden-Popper oxide phases, YSr₂Mn₂O₅₅F₃₅ retains the $a^{-}b^{0}c^{0}/b^{0}a^{-}c^{0}$ lattice distortion and $P4_{2}/mnm$ space group



symmetry of the parent oxide phase. The resilience of the $a^{-b^{0}c^{0}/b^{0}a^{-}c^{0}}$ -distorted framework of YSr₂Mn₂O₇ to resist symmetrychanging deformations upon both cation substitution and anion insertion/exchange is discussed on the basis the A-site cation order of the lattice and the large change in the ionic radius of manganese upon oxidation from Mn³⁺ to Mn⁴⁺. The structure property relations observed in the Y-Sr-Ca-Mn-O-F system provide insight into assisting in the synthesis of n = 2Ruddlesden-Popper phases, which adopt cooperative structural distortions that break the inversion symmetry of the extended lattice and therefore act as a route for the preparation of ferroelectric and multiferroic materials.

INTRODUCTION

The chemical diversity of oxide phases that adopt ABO₃ perovskite structures can be attributed, in part, to the high mechanical flexibility of the perovskite framework. This flexibility allows the apex-linked BO₆ octahedra, which constitute the perovskite framework, to cooperatively tilt and twist to optimize the packing of the system in response to changes in the ratio of the A- and B-cation radii (conveniently parametrized by the structural tolerance factor: $t = \langle A - O \rangle /$ $\sqrt{2(B-O)}$.¹ As a result, a wide range of cation combinations can be incorporated into thermodynamically stable perovskite lattices.

A further feature of the tilting and twisting distortions of perovskite phases is that they can be harnessed to modify and tune the physical behavior of systems, particularly transitionmetal-containing phases. This is because the collective rotations of the octahedra act to distort the B-O-B bond angles from the 180° value observed in the undistorted, aristotype framework. This tightening of the B-O-B bond angles modifies the orbital interactions and thus the coupling between the local electronic states of the transition-metal B-cations, changing the electronic band widths in electronically

delocalized systems or magnetic exchange interactions in localized systems.² As a result much effort has gone into understanding the electronic and magnetic consequences of tuning the structural distortions of perovskite phases, typically via studies that make chemical substitutions on the 12coordinate A-site.^{2,3}

In addition to tuning the electronic coupling between neighboring B-cations, the collective distortions of the perovskite phases also modify the lattice symmetry of the framework. As a consequence, if the correct distortion mode is adopted, the collective deformations of perovskite lattices offer a mechanism to break the inversion symmetry of the system and thus the potential to induce ferroelectric behavior.⁴ In the specific case of the three-dimensional perovskite lattice, acentric phases can only be produced when octahedral tilting is accompanied by cation order.⁵⁻⁸ However, when equivalent structural distortions are applied to layered analogues of the perovskite structure, particularly $A_3B_2O_7$, n = 2 Ruddlesden-Popper phases, the inversion symmetry of the system can be

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broken in the absence of cation order, 9,10 as demonstrated by the observation of ferroelectric behavior in (Ca, Sr)₃Ti₂O₇.¹¹

Utilizing the distortions of the n = 2 Ruddlesden–Popper phases to prepare noncentrosymmetric lattices is highly attractive because it provides a route to polar materials without the need to include "active distortion centers", such as d⁰ transition-metal cations, which break the inversion symmetry through the action of a second-order Jahn–Teller distortion.^{12–15} The additional chemical flexibility that comes from not having to include such centers makes the incorporation of paramagnetic ions into polar frameworks much easier, and thus distorted n = 2 Ruddlesden–Popper phases offer a route to the preparation of magnetoelectric multiferroic materials.

While the distortions of n = 2 Ruddlesden–Popper phases offer an attractive route for the preparation of noncentrosymmetric phases in theory, it is hard to realize these concepts in practice because the desired "A2₁am", $a^{-}a^{-}c^{+}/a^{-}a^{-}c^{+}$ ferroelectric distortion mode is only stabilized at extremely low values of the structural tolerance factor. A recent study by Pitcher et al. highlighted these difficulties when they observed that it was not possible to induce the desired polar distortion mode in the Fe^{3+} , $Ln_2AEFe_2O_7$ (Ln = lanthanide; AE = Ba, Sr, Ca) system through A-site substitution.¹⁶ This was partly because, in compositions containing very small A-cations, $A_3B_2O_7$ n = 2 Ruddlesden-Popper phases tend to be thermodynamically less stable than a 1:1 mixture of the corresponding $A_2BO_4 n = 1$ Ruddlesden–Popper phase and the ABO₃ perovskite. Thus, in the Ln₂AEFe₂O₇ system, the A2₁amdistorted structure could only be stabilized by additional titanium-for-iron B-site substitution.16

In an attempt to circumvent these problems, we have been looking at the use of topochemical manipulation as a route to prepare noncentrosymmetric materials. Specifically, we have been utilizing the observation that fluorine insertion leads to a significant enhancement of the lattice distortions of many n = 2Ruddlesden-Popper systems, as indicated by a general tightening of the B-O-B bond angles.¹⁷⁻²⁰ Furthermore, it has also been observed that upon fluorination the largest enhancement tends to be to the rotations of the BO₆ octahedra around the crystallographic z-axis. This led us to anticipate that the fluorination of La₃Ni₂O₇, which adopts an Amam, $a^{-}a^{-}c^{0}/$ $a^{-}a^{-}c^{0}$ distortion, would lead to the formation of an oxidefluoride phase with the desired polar $A2_1am$, $a^-a^-c^+/a^-a^-c^+$ distorted structure. However, a detailed crystallographic study of $La_3Ni_2O_{5.5}F_{3.5}$ reveals that while fluorination of $La_3Ni_2O_7$ does induce a z-axis rotation of the NiX₆ octahedra, the "sense" of this rotation (clockwise or anticlockwise) alternates between adjacent perovskite sheets to yield an $a^{-}a^{-}c^{+}/a^{-}a^{-}(c^{+})$ distortion, which breaks the inversion symmetry of the lattice locally but not globally, yielding an antiferroelectric lattice with *Pnma* space group symmetry.¹⁹ While this synthesis did not achieve the desired result, it shows that the basic concept is viable and motivates us to study the fluorination of other systems to see if it is possible to prepare a fluorinated phase that is ferroelectric rather than antiferroelectric.

In this contribution, we report the effects of A-cation substitution and topochemical fluorine insertion on the structure of the A-cation-ordered, n = 2 Ruddlesden–Popper phase YSr₂Mn₂O₇. It was hoped that these chemical modifications would enhance the collective distortions of the layered perovskite phase, leading to a noncentrosymmetric, polar material.

EXPERIMENTAL SECTION

Synthesis. Samples in the $YSr_{2-x}Ca_xMn_2O_7$ series (x = 0, 0.25, 0.5, 0.5, 0.5) 1.0, and 1.5) were prepared via a citrate gel method. Suitable stoichiometric ratios of Y2O3 (99.99%, dried at 900 °C), SrCO3 (99.99%), CaCO₃ (99.99%), and MnO₂ (99.9%) were dissolved in a minimal quantity of 6 M nitric acid. Citric acid and ethylene glycol were then added, and the solution was heated with constant stirring. The gel thus formed was heated to 350 °C until a coarse black powder was obtained. The powder was ground and then heated to 1000 °C in air at a rate of 1 °C/min to remove the remaining organic components. The resulting powder was then pressed into pellets before further heat treatments. For the preparation of YSr₂Mn₂O₇ and YSr_{1.75}Ca_{0.25}Mn₂O₇, the sample pellets were heated for three periods of 48 h at 1350 °C in air and two further periods of 48 h at 1450 °C. For YSrCaMn₂O₇, the pellets were heated for three periods of 48 h at 1350 °C in air and two further periods of 48 h at 1400 °C. For YSr_{0.5}Ca_{1.5}Mn₂O₇, the pellets were heated for five periods of 48 h at 1350 °C in air. Lower synthesis temperatures were employed for the calcium-substituted samples to avoid melting. The preparation of YCa₂Mn₂O₇ was also attempted, but the phase failed to form after four heating cycles of 48 h at 1300 °C, and this composition melts at 1325 °C.

Fluorination of YSr₂Mn₂O₇ and YSr_{0.5}Ca_{1.5}Mn₂O₇ was carried out using CuF₂ as a fluorination agent, in the same manner as has been described previously.^{17,20,21} To avoid contamination of the samples with CuO, which occurs when the fluorination agent is mixed directly into the sample, CuF₂ was heated separately from the sample at 500 °C under flowing oxygen to liberate fluorine. The resulting O₂/F₂ gas mixture was then passed over a sample of YSr_{2.x}Ca_xMn₂O₇ powder held at 400 °C in an adjacent furnace. Samples were treated in this way for four periods of 48 h, with the CuF₂ reagent being replaced between heating periods.

Characterization. X-ray powder diffraction data were collected using a PANalytical X'pert diffractometer incorporating an X'celerator position-sensitive detector (monochromatic Cu K α_1 radiation). Neutron powder diffraction data were collected from samples contained within vanadium cans, using the HRPD diffractometer (ISIS neutron source, Oxon, U.K). Rietveld profile refinement was performed using the GSAS suite of programs.²² Magnetization data were collected using a Quantum Design MPMS SQUID magnetometer. Average manganese oxidation states were determined by iodometric titration. Titrations were performed by dissolving samples in a dilute HCl solution containing an excess of KI and titrating the amount of liberated I₂ with a standardized Na₂S₂O₃ solution. Powder second-harmonic-generation (SHG) measurements were performed on a modified Kurtz–Perry instrument.²³ A description of the equipment and methodology was published previously.²⁴

RESULTS

Structural Characterization of YSr₂Mn₂O₇ (0 < *x* **< 1.5). X-ray powder diffraction data collected from samples of YSr_{2-***x***}Ca_{***x***}Mn₂O₇ (***x* **= 0, 0.25, 0.5, 1, 1.5), shown in Figure 1, were initially indexed on the basis of tetragonal unit cells, consistent with the formation of** *n* **= 2 Ruddlesden–Popper phases. Structural models based on the a⁻b⁰c⁰/b⁰a⁻c⁰-distorted** *n* **= 2 Ruddlesden–Popper structure of YSr₂Mn₂O₇ (space group P4_2/mnn),²⁵ but with calcium partially replacing strontium as appropriate, were refined against these data. The refinements proceeded smoothly; however, close inspection revealed that, with the exception of the** *x* **= 0 sample, none of the fits to the data were satisfactory.**

Detailed inspection of the data from the x = 0.25, 0.5, 1 samples revealed that the poor fitting of the $P4_2/mnm$ structural model was due to a peak-shape asymmetry of the 00*l* diffraction reflections. This asymmetry could not be modeled by the addition of *hkl*-dependent broadening terms; however, the fits to the data were significantly improved by the introduction of a



Figure 1. X-ray powder diffraction data collected from $YSr_{2-x}Ca_xMn_2O_7$.

second tetragonal n = 2 Ruddlesden–Popper phase to the models.

In order to stabilize these two-phase refinements, the peak shapes and atomic positions of the two phases were constrained to be the same, with only the lattice parameters and phase fractions of the two phases allowed to refine freely. Table 1 shows the refined values of these parameters.

Table 1. Lattice Parameters from Two-Phase Refinements of $YSr_{2-x}Ca_xMn_2O_7^{\ a}$

x		a (Å)	c (Å)	volume (Å ³)	fraction (%)				
0		5.40456(6)	19.9054(2)	581.26(2)	100				
0.25	P1	5.4064(1)	19.7608(3)	577.26(1)	66.5(6)				
	P2	5.3997(1)	19.7883(5)	576.98(2)	33.5(6)				
0.5	P1	5.4106(1)	19.5848(1)	573.33(1)	83.7(2)				
	P2	5.4006(1)	19.6388(5)	572.81(2)	16.3(2)				
1	P1	5.4254(1)	19.255(1)	566.79(1)	65.8(1)				
	P2	5.4123(1)	19.325(1)	566.11(3)	34.2(1)				
^{<i>a</i>} Parameters from the $x = 0$ composition were extracted from ref 25.									

Structural Characterization of YSrCaMn₂O₇. Phase separation analogous to that observed for $YSr_{2-x}Ca_xMn_2O_7$ (0.25 < x < 1) has been observed in other manganese-containing n = 2 Ruddlesden–Popper phases.^{26–28} To further investigate the phase separation of the $YSr_{2-x}Ca_xMn_2O_7$ system, high-resolution neutron powder diffraction data were collected from $YSrCaMn_2O_7$.

In common with the X-ray data, satisfactory fits to the neutron powder diffraction data collected from $YSrCaMn_2O_7$ could only be achieved using two-phase models; however, the high resolution of the latter data set allowed the atomic coordinates and site occupancies of the two phases to be refined independently. To assist refinement stability, the thermal displacement factors of corresponding atoms in the two phases were constrained to be the same.

The origin of the observed phase separations in manganesecontaining n = 2 Ruddlesden–Popper phases has been

variously ascribed to either A-cation inhomogeneity within samples (i.e., the two phases have different chemical compositions) or to a difference in the A-cation distribution on the 9- and 12-fold A-cation coordination sites in the different phases (i.e., the two phases have the same composition but different A-cation orderings).²⁶ In order to determine which of these scenarios is responsible for the phase separation in the YSr_{2-x}Ca_xMn₂O₇ system, the structural refinement of YSrCaMn₂O₇ was initially performed with the constraint that the two tetragonal phases in the structural model had the same, ideal, chemical composition: YSrCaMn₂O₇ (neutron scattering lengths: Ca, 4.70 fm; Y, 7.75 fm; Sr, 7.02 fm).²⁹ The refinement proceeded smoothly with this constraint to give a good statistical fit (χ^2 = 5.79), producing a structural model in which the Y/Sr/Ca distributions over the 9-fold (phase 1 = 50:4:46; phase 2 = 50:10:40 and 12-fold (phase 1 = 0:91:9; phase 2 =0:80:20) A-cation sites differed between the two phases. The Acation distribution constraint was then released so that the occupancies of the A-cation sites in the two phases could vary freely and thus the chemical compositions of the two phases could vary freely. With the removal of this constraint, it was observed that none of the A-site neutron scattering powers changed by more than 1%, indicating that the principal difference between the two phases of YSrCaMn₂O₇ is their Acation ordering, not their chemical composition. A full description of the refined two-phase structural model of $YSrCaMn_2O_7$ is given in Table S1, with selected bond lengths and angles in Table S2 and plots of the observed and calculated data shown in Figure S1.

Structural Characterization of YSr_{0.5}Ca_{1.5}Mn₂O₇. Detailed inspection of the X-ray powder diffraction data collected from YSr_{0.5}Ca_{1.5}Mn₂O₇ revealed that the poor fitting of the $P4_2/mnm$ structural model was due to a splitting of diffraction peaks, consistent with a lowering of the crystallographic symmetry from tetragonal to orthorhombic. As noted above, calcium substitution into YSr2-xCaxMn2O7 will reduce the structural tolerance factor of the system, leading to an enhancement of the collective tilting and twisting distortions of the MnO₆ octahedra. The lower crystallographic symmetry of the x = 1.5 sample, therefore, suggests that it has a more distorted structure than the x < 1.5 samples. Starting from the $a^{-}b^{0}c^{0}/b^{0}a^{-}c^{0}$ distortion of the 0 < *x* < 1 phases, the symmetry analysis performed by Aleksandrov and Bartolome³⁰ indicates there are six possible collective distortions that YSr_{0.5}Ca_{1.5}Mn₂O₇ could adopt, as detailed in Table 2. Structural models were constructed for each of these six distorted n = 2Ruddlesden-Popper frameworks and then refined against neutron powder diffraction data collected from YSr_{0.5}Ca_{1.5}Mn₂O₇. It was assumed that the 12-coordinate Asites contained a 1:1 mixture of Sr:Ca and the 9-coordinate A-

Table 2. Fitting Statistics from the Structural Refinement of $YSr_{0.5}Ca_{1.5}Mn_2O_7$ Using Models Based on the Distortions of n = 2 Ruddlesden-Popper Phases

space group	distortion	χ^2	wR_p (%)	R _p (%)
<i>P</i> 2 ₁ / <i>n</i> 11 (No. 14)	$a^{-}b^{-}c^{-}/b^{-}a^{-}c^{-}$	7.63	4.74	4.95
<i>P</i> 2 ₁ <i>nm</i> (No. 31)	$a^-b^-c^+/b^-a^-c^+$	7.71	4.77	5.01
Pnnm (No. 58)	$a^{-}b^{-}c^{0}/b^{-}a^{-}c^{0}$	8.19	4.92	5.08
A2 ₁ am (No. 36)	$a^{-}a^{-}c^{+}/a^{-}a^{-}c^{+}$	17.09	7.14	6.30
A2/a (No. 15)	a ⁻ a ⁻ c ⁻ /a ⁻ a ⁻ c ⁻	17.79	7.28	6.42
Amam (No. 63)	a ⁻ a ⁻ c ⁰ /a ⁻ a ⁻ c ⁰	17.11	7.15	6.31

sites contained a 1:1 mixture of Y:Ca. Subsequent refinement of these parameters showed this to be the case, so all models were fixed with these A-site compositions. In addition, displacement parameters were constrained by element. All six refinements converged smoothly.

The goodness-of-fit parameters listed in Table 2 indicate that the three A-centered models describing $a^{-}a^{-}c^{?}/a^{-}a^{-}c^{?}$ distortions give much poorer fits to the data than the three primitive models that describe $a^{-}b^{-}c^{2}/b^{-}a^{-}c^{2}$ distortions, eliminating the former models from consideration. Of the three remaining models, the $a^{-}b^{-}c^{-}$ / $b^{-}a^{-}c^{-}$ distorted $P2_1/n11$ model has the best fitting-statistics, considerably better than the $a^{-}b^{-}c^{0}/b^{-}a^{-}c^{0}$ -distorted *Pnnm* model but only marginally better than the $a^{-}b^{-}c^{+}/b^{-}a^{-}c^{+}$ -distorted $P2_{1}nm$ model. In order to help to differentiate between the $P2_1nm$ and $P2_1/n11$ models, we investigated the SHG activity of YSr_{0.5}Ca_{1.5}Mn₂O₇ as an $a^{-}b^{-}c^{+}/b^{-}a^{-}c^{+}$ -distorted $P2_{1}nm$ structure would be noncentrosymmetric, and thus SHG-active, while a $a^{-}b^{-}c^{-}/$ $b^{-}a^{-}c^{-}$ -distorted $P2_1/n11$ structure would be centrosymmetric, and thus SHG-inactive. No SHG activity was observed for $YSr_{0.5}Ca_{1.5}Mn_2O_{72}$ consistent with this phase adopting an $a^{-}b^{-}c^{-}/b^{-}a^{-}c^{-}$ distorted $P2_{1}/n11$ structure. Full details for the refined structure of YSr_{0.5}Ca_{1.5}Mn₂O₇ are given in Table S3, with selected bond lengths and angles in Table S2 and a plot of the observed and calculated data shown in Figure S2.

Fluorination of YSr_{2-x}**Ca**_x**Mn**₂**O**₇. The fluorination of YSr₂Mn₂O₇, by the procedure outlined above, yielded a singlephase sample with an expanded *c*-lattice parameter, consistent with topochemical fluorination to form a phase of composition YSr₂Mn₂O_xF_y. In contrast, when the same procedure was applied to YSr_{0.5}Ca_{1.5}Mn₂O₇, a mixture of apparently unreacted material and a new tetragonal phase, nominally assigned as YSr_{0.5}Ca_{1.5}Mn₂O_xF_y, was observed with an approximate stoichiometric ratio of 3:1. Further fluorination cycles led to decomposition and the formation of binary fluorides (SrF₂, CaF₂, etc.), indicating that the calcium-doped phase could not be readily fluorinated via this route.

Chemical and Structural Characterization of YSr₂Mn₂O_{5.5}F_{3.5}. The crystallographic characterization of YSr₂Mn₂O_xF_y, described below, indicates that this is a fluorine-intercalated n = 2 Ruddlesden–Popper phase in which all of the anion sites were fully occupied and thus x + y = 9, as observed for other fluorinated n = 2 Ruddlesden– Popper phases.^{17–20,31} This information, combined with iodometric titration results, which revealed an average manganese oxidation state of Mn +3.75, indicates that the fluorinated phase has a chemical formula of YSr₂Mn₂O_{5.5}F_{3.5}.

Neutron powder diffraction data collected from $YSr_2Mn_2O_{5.5}F_{3.5}$ can be readily indexed using a tetragonal unit cell (a = 5.326 Å; c = 22.631 Å) with extinction conditions consistent with the $P4_2/mnm$ space group symmetry of the all-oxide starting material $YSr_2Mn_2O_7$. A structural model was constructed in the space group $P4_2/mnm$, based on the reported structure of $YSr_2Mn_2O_7$ but with additional anions inserted into the "tetrahedral" coordination sites within the rock-salt layers of the phase, in an analogy to the structures of a series of other fluorine-intercalated n = 2 Ruddlesden–Popper oxide phases.^{17,19,20} The Y/Sr distribution was set to be the cation-ordered arrangement of this model against the neutron powder diffraction data proceeded smoothly. All atomic positional and displacement parameters were refined freely.

Given the very similar neutron scattering lengths of oxide and fluoride (O, 5.80 fm; F, 5.65 fm)²⁹ no attempt was made to differentiate between the two anions at this stage, with all anion sites treated as if they were occupied by oxide. The refinement converged smoothly to give a good statistical fit ($\chi^2 = 5.43$).

The majority of previous studies that have examined analogous fluorinations of n = 2 Ruddlesden–Popper oxides observe a lowering of crystallographic symmetry upon fluorine insertion.^{17–19} Therefore, to confirm that the model in space group $P4_2/mnm$ is the best description of the structure of $YSr_2Mn_2O_{5.5}F_{3.5}$, a series of lower-symmetry models, with more distorted $Mn(O/F)_6$ networks and also with disordered $Mn(O/F)_6$ rotations, were refined against the neutron powder diffraction data. As shown in Table S5, none of these models achieves as good a statistical fit as the $P4_2/mnm$ model, confirming that this is the best structural description of $YSr_2Mn_2O_{5.5}F_{3.5}$.

As noted above, the poor neutron scattering contrast between oxide and fluoride ions prevents the anion distribution in $YSr_2Mn_2O_{5.5}F_{3.5}$ from being determined directly. However, it is possible in some cases to deduce the location of fluoride ions within oxide–fluoride lattices by examining the local bonding environments of the anion sites through bond valence sums (BVS).^{32–34} This approach has proven to be effective in locating the fluoride ions in a number of fluorinated n = 2 Ruddlesden–Popper phases.^{18–20}

Table 3 lists the BVS of the seven crystallographically distinct anion sites in the structure of $YSr_2Mn_2O_{5.5}F_{3.5}$. These BVS

Table 3. Anion BVS from YSr₂Mn₂O₇ and YSr₂Mn₂O_{5.5}F_{3.5}

YSr ₂	Mn ₂ O ₇	$YSr_{2}Mn_{2}O_{5.5}F_{3.5}$			
anion	BVS(O)	anion	BVS(O)	BVS(F)	
O(1)	1.711	X(1)/O/F(1)	1.509	1.237	
O(2)	2.225	X(2)/O(1)	2.069	1.756	
O(3)	2.227	X(3)/O(3)	2.157	1.833	
O(4)	2.236	X(4)/O(4)	1.854	1.569	
O(5)	1.974	X(5)/O(5)	2.122	1.775	
		X(6)/F(6)	1.460	1.103	
		X(7)/F(7)	1.498	1.132	

values were calculated on the basis of occupation by oxide or fluoride, and the BVS values of the corresponding anion sites in the structure of $YSr_2Mn_2O_7$ were also calculated for comparison. The anion-site labeling scheme is shown in Figure 2. These data reveal that the two smallest BVS values were calculated from the tetrahedral interstitial anion sites X(6) and X(7), consistent with the occupation of fluoride ions. Occupation of the "interstitial" anion sites exclusively by fluoride ions has been observed widely in other topochemically fluorinated n = 2 Ruddlesden–Popper oxide phases.^{17–20} The composition of the fluorinated phase requires fluoride ions to have been exchanged with oxide ions of the "parent" oxide phase.

The data in Table 3 show that the BVS of the "apical" X(1) site is the lowest of the remaining anion sites, suggesting that it is occupied by a 3:1 mixture of F^-/O^{2-} to make up the overall $YSr_2Mn_2O_{5.5}F_{3.5}$ stoichiometry. Similarly, preferential substitution of fluoride for oxide at the apical anion site has been observed in other topochemically fluorinated phases such as $Sr_3(Fe_{0.5}Ru_{0.5})_2O_{5.5}F_{3.5}$ and $La_3Ni_2O_{5.5}F_{3.5}$ are given in Table S6, with selected bond lengths and angles in Table S2 and a plot of



Figure 2. Structures of YSr₂Mn₂O₇ and YSr₂Mn₂O_{5.5}F_{3.5}.

the observed and calculated data shown in Figure S3. A representation of the structure of $YSr_2Mn_2O_{5.5}F_{3.5}$ is shown in Figure 2.

Magnetism. Zero-field-cooled and field-cooled magnetization data collected from $YSr_{0.5}Ca_{1.5}Mn_2O_7$ in an applied field of 100 Oe, shown in Figure 3, are qualitatively very similar to



Figure 3. Zero-field-cooled and field-cooled magnetization data collected from $YSr_2Mn_2O_7$ and $YSr_{0.5}Ca_{1.5}Mn_2O_7$ in an applied field of 100 Oe.

the analogous data collected from $YSr_2Mn_2O_7$, also shown in Figure 3. The latter phase has been characterized as a spin-glass,²⁵ suggesting that $YSr_{0.5}Ca_{1.5}Mn_2O_7$ is also a spin-glass with a slightly elevated freezing temperature compared to $YSr_2Mn_2O_7$.

DISCUSSION

Phase Separation in YSr_{2-x}**Ca**_x**Mn**₂**O**₇. The phase separation observed upon calcium doping of YSr₂Mn₂O₇ is analogous to that reported for other $\text{RESr}_2\text{Mn}_2\text{O}_7$ (RE = Y, Ln) n = 2 Ruddlesden–Popper phases.^{26–28} Previous studies

focused on $RESr_2Mn_2O_7$ phases observed that it was generally only possible to prepare single-phase samples for compositions containing small RE^{3+} cations (Tb–Er and Y) and that systems containing large RE^{3+} cations (La–Gd) split into two-phase mixtures.

This difference in behavior between the large and small Acation systems has been attributed to the differing degrees of cation order that these phases exhibit. Compositions containing small RE cations (Tb–Er and Y) order to place Sr^{2+} on the 12coordinate A-sites, and a 1:1 mixture of Sr^{2+} and RE^{3+} on the 9coordinate A-sites in the framework. As the size of RE^{3+} increases, the degree of A-cation order diminishes, and this is associated with samples separating into two or more different *n* = 2 Ruddlesden–Popper phases. The decline in the degree of A-cation order can be attributed to the reduction in the size difference between Sr^{2+} and RE^{3+} as the size of RE^{3+} increases.

The results of the calcium-for-strontium cation exchange of YSr₂Mn₂O₇ reported here support the association between the degree of A-cation order and single-phase/multiphase behavior. Low levels of calcium substitution (25-50%) lead to separation into two phases that appear to have similar compositions but different degrees of A-cation order. In addition, the two observed phases become more dissimilar as the concentration of calcium increases (Table 1). This behavior can be rationalized by observing that partial substitution of Sr²⁺ by Ca^{2+} makes the average size of the AE^{2+} ($AE^{2+} = Ca^{2+}$, Sr^{2+}) cations smaller, and therefore more similar to the size of Y³⁺, disrupting the A-cation order of the host phase and leading to multiphase behavior. Thus, the phase separation observed for $YSr_{2-x}Ca_xMn_2O_7$ (0.25 < x < 1) compositions can be seen as analogous to that observed for the RESr₂Mn₂O₇ phases because both are associated with the loss of A-cation order as the difference in the average radii of the RE³⁺ and AE²⁺ cations decreases.

Structural Influence of Calcium Doping. It is surprising at first sight that replacing of 50% of Sr^{2+} with Ca^{2+} leads to only a modest increase in the magnitude of the cooperative distortions of the $YSr_{2-x}Ca_xMn_2O_7$ framework, increasing the MnO_6 rotation angle from 3.52° at x = 0 to 7.12° in the majority phase at x = 1 (Figure 4) but leading to no change in structural symmetry, despite the fact that the structural tolerance factor, calculated using ionic radii,³⁵ changes from t= 0.98 for $YSr_2Mn_2O_7$ to t = 0.95 for $YSrCaMn_2O_7$.

This modest structural response to cation substitution can be rationalized by observing that the majority of the substituted calcium cations reside on the 9-coordinate A-sites in the lattice. In contrast to the 12-coordinate A-cation sites, the A-O bond lengths of the 9-coordinate A-cation sites can be contracted, to accommodate a decline in the average A-cation radius, by simply contracting the rock-salt layers of the Ruddlesden-Popper framework along the z-axis. Such a contraction brings the perovskite blocks closer together without deforming the MnO₆ octahedra or requiring them to cooperatively rotate, leading to the observed contraction in the *c*-lattice parameters upon calcium substitution (Table 1), but only a modest change to the tilting distortion of the Mn–O framework. Thus, it is not until the cation-substitution level exceeds 50%, and a significant concentration of Ca2+ resides on the 12-coordinate A-cation site, that a large increase in the magnitude of the MnO₆ tilts, and a change in lattice symmetry, is observed.

Crystal Structure of YSr_{0.5}**Ca**_{1.5}**Mn**₂**O**₇**.** As shown in Figure 4, when 75% of the strontium is replaced by calcium, the system changes symmetry to adopt an $a^{-}b^{-}c^{-}/b^{-}a^{-}c^{-}$ -distorted



Figure 4. Structures of $YSr_{2-x}Ca_xMn_2O_7$ phases highlighting how the A-cation distribution and the collective tilting and twisting of the MnO_6 octahedra change with the calcium content. Octahedral rotation angles were determined via O-O-O-O torsion angles, as described in the Supporting Information.

lattice, in space group $P2_1/n11$. To the best of our knowledge, this is the first report of an n = 2 Ruddlesden–Popper phase adopting this distortion pattern. Typically, as the tolerance factor of a $P4_2/mnm$ a⁻b⁰c⁰/b⁰a⁻c⁰-distorted n = 2 Ruddlesden-Popper phase is reduced, the arrangement of titled octahedra changes to an Amam $a^{-}a^{-}c^{0}/a^{-}a^{-}c^{0}$ distortion in which a rotation is added around the y-axis with the same magnitude as the x-axis, as observed during the cation substitution of LnAE₂Fe₂O₇ phases.¹⁶ In contrast, the lattice distortion observed for YSr_{0.5}Ca_{1.5}Mn₂O₇ maintains the large $a^{-}b^{0}c^{0}/b^{0}a^{-}c^{0}$ distortion component observed for $YSr_{2-x}Ca_xMn_2O_7 x < 1$ and adds small $a^0b^-c^0/b^-a^0c^0$ and $a^{0}b^{0}c^{-}/b^{0}a^{0}c^{-}$ components such that the average rotation angles are $8.74(12)^{\circ}$, $1.72(14)^{\circ}$, and $0.89(25)^{\circ}$ for a, b, and c, respectively. In terms of an irreducible representation (irrep) description, the octahedral tilting in the $P4_2/mnm a b^0 c^0/$ $b^0 a^- c^0$ structures (symmetry D_{4h}^{14}) is described by a distortion mode that transforms as $X_3^{-}(a;a)$. Upon lowering of the symmetry to $P2_1/n11$ (C_{2h}^{-5}), this $X_3^{-}(a;a)$ mode becomes an $X_{3}^{-}(a;b)$ mode, leading to a change to an $a^{-}b^{-}c^{0}/b^{-}a^{-}c^{0}$ distortion, which, upon the addition of an X₁⁻ distortion mode, becomes an $a^{-}b^{-}c^{-}/b^{-}a^{-}c^{-}$ distortion.

The reason for $YSr_{0.5}Ca_{1.5}Mn_2O_7$ adopting this unusual distortion pattern is not immediately clear. However, it should be noted that, despite the extensive cation substitution, the phase retains a high level of cation order such that the average radii of the cations on the 9- and 12-coordinate A-sites remain significantly different. It seems likely that this unusual feature is responsible for the novel octahedral tilting arrangement, although the microscopic mechanism by which it stabilizes this distortion is unclear.

Fluorination of YSr₂Mn₂O₇. In common with a number of other n = 2 Ruddlesden–Popper phases, topochemical fluorination of YSr₂Mn₂O₇ proceeds via a mixture of anion insertion and anion exchange to yield YSr₂Mn₂O_{5.5}F_{3.5} μ , in

which fluoride ions have been inserted into tetrahedral coordination sites in the rock-salt layers of the framework and also exchanged with "apical" oxide ions in the perovskite sheets.

An unusual feature of this chemical transformation is that, unlike many analogous fluorination reactions, it is not accompanied by a change in crystallographic symmetry. Specifically, fluorination of $YSr_2Mn_2O_7$ does not induce a cooperative twist of the $Mn(O/F)_6$ units around the *z*-axis, a structural deformation that is observed in a number of analogous fluorination reactions.^{17–20}

The tendency for fluorination to induce a "*z*-twist" to the perovskite framework of n = 2 Ruddlesden–Popper oxide phases can be rationalized by observing that insertion of fluoride ions into the rock-salt layers of the structure leads to a contraction of these blocks as the inserted fluoride ions pull the A-cations closer together. This contraction acts to constrict the *ab*-plane of the perovskite sheets, as indicated by a contraction of the *a*- and *b*-lattice parameters.^{17,18,20} In response, the BO₆ octahedra cooperatively rotate around the *z*-axis to relive the bond strain induced by this *ab*-plane compression.

When the structures of $YSr_2Mn_2O_7$ and $YSr_2Mn_2O_{5.5}F_{3.5}$ are compared, it can be seen that a similar contraction has occurred, with the area of the *ab*-plane declining from 29.20(1) to 28.37(1) Å² upon fluorination. However, this contraction does not induce a *z*-twist into the perovskite framework because concomitant oxidation of $Mn^{3.5+}$ to $Mn^{3.75+}$, which occurs upon fluorination, leads to a contraction in the average Mn-O bond length, so the bond strain induced by the *ab*plane contraction is much reduced and can be relieved by enhancing the *x*-twist of the parent oxide phase. This mechanism of strain relief is particularly effective for $YSr_2Mn_2O_{5.5}F_{3.5}$ because there is a large change in the $\langle Mn O \rangle$ bond length upon oxidation (6CN radii: Mn^{3+} , 0.645 Å; Mn^{4+} , 0.530 Å),³⁵ compared to other elements, for example, ruthenium (6CN radii: Ru⁴⁺, 0.620 Å; Ru⁵⁺, 0.565 Å),³⁵ which is present in many of the other oxide–fluoride systems previously studied. Thus, fluorination of $YSr_2Mn_2O_7$ to $YSr_2Mn_2O_{5.5}F_{3.5}$ leads to only a modest change in the tilting distortion of the perovskite network, with the rotation of the MnX_6 units around the *x*-axis increasing from $3.52(3)^\circ$ to $4.58(13)^\circ$, without a change in the crystallographic symmetry (Figure 2).

CONCLUSION

The cation-ordered structure of $YSr_2Mn_2O_7$ incorporating an $a^-b^0c^0/b^0a^-c^0$ distortion is very robust to cation substitution and anion insertion. In order to modify the distortion mode of the structure by calcium-for-strontium exchange, 75% of the strontium must be exchanged to drive a change in the crystallographic symmetry. Principally, this is because the small Ca^{2+} cations are substituted preferentially onto the 9-coordinate A-site in the structure, which has only a small influence on the collective tilting distortions of the perovskite layers. Thus, it could be argued that the A-cation order of the phase "protects" the $a^-b^0c^0/b^0a^-c^0$ -distorted lattice from modification by cation exchange, which further suggests that, in general, it will be hard to utilize cation doping of cation-ordered n = 2 Ruddlesden—Popper phases to induce noncentrosymmetric lattice distortions.

 $YSr_2Mn_2O_7$ also undergoes only minimal structural deformation upon fluorine insertion because of the large contraction of the $\langle Mn-O \rangle$ bond lengths, which compensates for the lattice contraction that occurs when fluoride ions are intercalated into the rock-salt layers of the structure. These two effects mean that the Y-Sr-Ca-Mn-O-F system retains $a^-b^0c^0/b^0a^-c^0$ -distorted perovskite blocks over a wide range of composition.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01525.

Structural parameters, selected bond lengths and observed and calculated data from the structural refinements of YSrCaMn₂O₇, YSr_{0.5}Ca_{1.5}Mn₂O₇, and YSr₂Mn₂O_{3.5}F_{5.5}, and a description of the method used for determining octahedral rotation angles from O–O–O–O–O torsion angles (PDF)

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Notes

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