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Synthesis and structural characterization of $\text{La}_x \text{Sr}_{1-x} \text{MnO}_{2.6+\delta}$ (0.1 < x < 0.4) compounds displaying compressed octahedral coordination of $\text{Mn}^{(4-5x)+\frac{1}{24}}$

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ABSTRACT

La_xSr_{1-x}MnO_{2.6+δ} (x = 0.1-0.4) compounds have been obtained by low-temperature annealing of stoichiometric materials in hydrogen. La_{0.1}Sr_{0.9}MnO_{2.6+δ} ($\delta = 0.15$) and La_{0.3}Sr_{0.7}MnO_{2.6}, tetragonal (*P*4/*m*), and La_{0.2}Sr_{0.8}MnO_{2.6}, pseudo-tetragonal monoclinic (*P*2/*m*), structures are isostructural with oxygen-vacancy-ordered Sr₅Mn₅O₁₃ ($a = b \approx \sqrt{5}a_p$, $c \approx a_p$). La_{0.4}Sr_{0.6}MnO_{2.6} shows cubic perovskite structure with disordered oxygen vacancies. In the vacancy-ordered (La_xSr_{1-x})₅Mn₅O₁₃ phases four out of five Mn cations are Mn³⁺ and show a typical Jahn-Teller elongated pyramidal coordination while the fifth one Mn^{(4-5x)+}, in octahedral environment, shows decreasing formal charge from Mn⁴⁺ (x = 0) to Mn^{2.5+} x = 0.3. This unusual selective doping of the octahedral site produces structural strain due to increasing size of the Mn^{(4-5x)+} and, in the case of (La_{0.2}Sr_{0.8})₅Mn₅O₁₃, the unusual compressed octahedral arrangement of oxygen atoms around it. The coordination geometry implies that either the $d_{x^2-y^2}$ orbital is occupied, which would be a rare example of inverted occupancy of e_g orbitals in manganites, or that disordered Mn³⁺ apically elongated MnO₆ octahedra are present with normal electronic configuration $d_{1_{2g}}^3 d_{x^2-y^2}^2 d_{2g}^2$, and the observed bond distances are the average of the long and intermediate in-plane Mn–O bonds. Several structural features favor the second case.

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1. Introduction

Oxygen-vacancy ordering in perovskites has been a topic of intense research for decades [1]. Vacancy ordering phenomena have been important to understanding conducting, magnetic and superconducting properties of technologically important materials such as solid oxide fuel cell (SOFC) cathodes and hightemperature superconducting cuprates. The large amount of information accumulated for Cu-containing perovskites, although serving as a guide for the possible orderings, could not be directly applied to other 3d transition metal elements due to the differences in the electronic structures and cation sizes that determine the bonding and coordination preferences. Recently, we

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have been studying mixed electronic and ionic conductivity in the lightly La-substituted La_xSr_{1-x}MnO_y system, which exhibits complex vacancy-ordered phases [2-4]. The formation of these phases poses a difficulty for the development of practical devices due to deleterious decreases of electrical and ionic conductivity resulting from charge ordering. Knowledge of the structure and stability of vacancy-ordered phases is of critical importance for future advances in SOFC cathodes [5]. Several phases have been described for the La_xSr_{1-x}MnO_y system with vacancy ordering arrangements dictated by the coordination preferences and the ratios of the Mn²⁺, Mn³⁺ and Mn⁴⁺ ions [2–8]. Among them, the brownmillerite-type structure [9] observed in La_xSr_{1-x}MnO_{2.5} (x = 0.6, 0.75 and 0.8) [8] contains tetrahedral Mn²⁺ and octahedral Mn²⁺/Mn³⁺ coordinated cations that differ from the $Ca_2Mn_2O_5$ structure type [10] observed in $La_xSr_{1-x}MnO_{2.5}$ for x = 0 and 0.1 [2–4] where only pyramids of Mn³⁺ or Mn²⁺/Mn³⁺ are observed. At higher oxygen contents, structures closely related to the brownmillerite have been described for the La-rich compositions La₈Mn₈O₂₃ (LaMnO_{2.875}) and La₄Mn₄O₁₁ (LaMnO_{2.75}) [7]. For the Sr-rich compositions the following structures related to Ca₂Mn₂O₅ have been observed: Sr₅Mn₅O₁₃ (SrMnO_{2.6}), Sr₇Mn₇O₁₉ $(SrMnO_{2.714})$ [3], $(La_{0.1}Sr_{0.9})_2Mn_2O_{5.1}$ $(La_{0.1}Sr_{0.9}MnO_{2.55})$, $(La_{0.2})_3MnO_{2.55}$ $Sr_{0.8})_5Mn_5O_{13} \quad (La_{0.2}Sr_{0.8}MnO_{2.6}) \quad and \quad (La_{0.3}Sr_{0.7})_5Mn_5O_{13.25}$

^{\pm} Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/ ecid/Internet/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-419750 for (La_{0.3}Sr_{0.9})₅Mn₅O_{13.77}, CSD-419751 for (La_{0.2}Sr_{0.8})₅Mn₅O_{13.77}, CSD-419752 for (La_{0.3}Sr_{0.9})₅Mn₅O_{13.77}, CSD-419753 for (La_{0.3}Sr_{0.9})₅Mn₅O_{13.77}, CSD-419753 for (La_{0.3}Sr_{0.9})₅Mn₅O_{13.77}, CSD-419754 for (La_{0.3}Sr_{0.9})₅Mn₅O_{13.77}, CSD-419755 for (La_{0.4}Sr_{0.9})₅Mn₅O_{13.77}, CSD-419754 for (La_{0.3}Sr_{0.9})₅Mn₅O_{13.77}, CSD-419755 for (La_{0.4}Sr_{0.9})₅Mn₅O_{13.77}, CSD-419755 for (La_{0.4}Sr_{0.9})₅Mn₅O_{1.9}, CSD-419755 for (La_{0.4}Sr_{0.9})₅

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(La_{0.3}Sr_{0.7}MnO_{2.65}) [2]. In particular, oxygen-vacancy-ordered SrMnO_y (y = 2.5, 2.6 and 2.714) were found to form the Sr_{4+n}Mn⁴₄+Mn⁴₇O_{10+3n} homologous series of compounds [3,11] exhibiting very interesting orbital ordering features as a result of the charge separation of Mn³⁺ and Mn⁴⁺ in pyramids and octahedra, respectively.

We have been systematically studying the structure and properties of oxygen-vacancy-ordered arrangements for La_xSr_{1-x} MnO_y compounds in the range $0 \le x \le 0.5$ and $2.5 \le y \le 3$. Neutron powder diffraction was used as the structural characterization technique as it provides accurate atomic coordinates and allows precise determination of the subtle structural distortions associated with the vacancy ordering. In this paper we describe the preparation and structures of the $La_xSr_{1-x}MnO_{2.6}$ ($0.1 \le x \le 0.4$) compounds closely related to the $Sr_5Mn_4^{3+}Mn_{4+}O_{13}$ (SrMnO_{2.6}), displaying apparent compressed octahedral coordination geometry around $Mn^{(4-5x)+}$ and a compositional order-disorder phase transition as a function of La substitution.

2. Experimental

Sample preparation and thermogravimetric analysis: Synthesis of the La_xSr_{1-x}MnO_y (y = 2.6, x = 0.1-0.4) samples was achieved by using three-step solid state reaction of appropriate amounts of MnO₂, La₂O₃ and SrCO₃ (all >99.99% purity). The oxygendeficient perovskites were prepared in the first step using low

partial pressure of oxygen at \sim 1400 °C since the synthesis of the Sr-rich compositions in air is complicated by the relatively small size of Mn⁴⁺ cation with respect to Sr²⁺ and La³⁺ which results in formation of hexagonal 4 layer phase [12]. In the second step, the oxygen-deficient materials were annealed in air between 400 and 500 °C to achieve stoichiometric oxygen content. This procedure has been previously applied for preparation of $La_{x}Sr_{1-x}MnO_{3}$ materials (0 < x < 0.5) [13] and was used in this work to obtain starting materials for the preparation of oxygen-deficient phases. The annealing conditions for preparation of vacancy-ordered compounds were established from thermogravimetric measurements (Cahn TG171). Fig. 1 shows the reduction of stoichiometric $La_xSr_{1-x}MnO_3$ samples (x = 0.1–0.4) using 48% H₂ in Ar gas flow (60 sccm) with very slow heating rate of 0.1° /min. The samples, consisting of a crushed pellet of material with initial weights between 0.85 (x = 0.4) and 0.90 (x = 0.1)g, show weight loss starting at ~200 °C which proceeds monotonically until decomposition above 600 °C. The curves show slope changes that could be associated with the formation of stable phases displaying particular oxygen contents at certain temperatures. The most significant slope changes observed near $y \approx 2.6$ at 350–450 °C are associated with a stable equilibrium of the O_{2.6} phases for samples with x = 0.2, 0.3 and 0.4. The La_{0.1}Sr_{0.9}MnO_v (x = 0.1) sample differs from others through a less visible slope change that occurs over a broad range of oxygen contents with a slightly more pronounced change at $y \approx 2.55$ corresponding to an average Mn³⁺ content and vacancy-ordered La_{0.1}Sr_{0.9}MnO_{2.55} phase, in accord



Fig. 1. Reduction of $La_xSr_{1-x}MnO_3$, x = 0.1 (left) to x = 0.4 (right) samples in 48% H₂/Ar flow (60 sccm) with $0.1^{\circ}/min$ heating rate.

with previous observations [2,4]. Based on the TGA data the $La_xSr_{1-x}MnO_{2.6}$ samples with $x \neq 0.1$ were prepared in the third step of synthesis as follow. Approximately 1.5 g of oxygen stoichiometric samples with x = 0.2, 0.3 and 0.4 were annealed in flowing H₂ in a tube furnace at 300, 360 and 365 °C, respectively, during two 20h annealing periods. The oxygen content of these samples was determined with a precision of 0.01 atoms per formula unit from the mass change observed after re-oxidation of \sim 250 mg of the reduced material in air at 500 °C for 12 h that yielded the stoichiometric $La_xSr_{1-x}MnO_3$ compounds. The oxygen contents of reduced compounds was found y = 2.59(1), 2.61(1) and 2.62(1) for x = 0.2, 0.3 and 0.4, respectively. The absence of a plateau at y = 2.6 for x = 0.1 prevented us from preparation of a stoichiometric sample La_{0.1}Sr_{0.9}MnO_{2.6}. The sample obtained from firing La_{0.1}Sr_{0.9}MnO₃ in Ar at 1350 °C with an oxygen content y = 2.74(1) showed similar structural arrangement to x = 0.2 and 0.3 samples, therefore it was used for the structural characterization of the series. The phase purity of all samples after every synthesis step was checked by conventional X-ray powder diffraction using a Rigaku D-MAX diffractometer.

Topotactic reduction at low temperatures usually leads to samples characterized by presence of structural inhomogeneities and small crystalline domains. X-ray data for x = 0.2 and 0.3 samples showed significant broadening of superstructure peaks originating from the oxygen-vacancy ordering. This suggested presence of small coherently scattering domains of the anion sublattice within the grains (note that the cation sub-lattice is almost unchanged with respect to the cubic perovskite precursor apart from small shifts around vacant sites). Since previous results showed that La_{0.2}Sr_{0.8}MnO_{2.6} with fixed oxygen content undergoes a reversible vacancy order-disorder transition at \sim 700 °C [4] we have attempted to improve the crystallinity of the samples by annealing. A portion of the La_{0.2}Sr_{0.8}MnO_{2.59} sample (#1) was annealed in pure Ar (\sim 0.1 ppm O₂) at 800 °C for 2 h and slowly cooled to 500 °C, to give sample (#2), to allow oxygen-vacancy reordering into larger domains. Another attempt was made to prepare a La_{0,2}Sr_{0,8}MnO_{2,6} sample away from the equilibrium conditions by a controlled reduction of La_{0.2}Sr_{0.8}MnO₃ in 1%H₂/Ar at 1300 °C to y = 2.6 on the thermobalance, followed by slow cooling to room temperature in pure Ar to give sample (#3). Although this last sample showed slightly narrower peaks, none of these attempts improve crystallinity significantly, indicating that the small coherent oxygen-vacancy-ordered regions appear to be intrinsic to the structure in accord with structural features that will be discussed in the following paragraphs.

Neutron powder diffraction data collection and analysis: Samples of $La_xSr_{1-x}MnO_{2.6}$ with x = 0.1, 0.2 (#1, #2 and #3), 0.3 and 0.4 were analyzed by neutron time-of-flight powder diffraction at Argonne's Intense Pulsed Neutron Source (SEPD (Special Environment Powder Diffractometer)) and (GPPD (General Purpose Powder Diffractometer)) stations [14]. Different instruments were used to obtain high-intensity high-resolution (GPPD) or high d-spacing range (SEPD) data to perform the structural characterization of the samples. The data was analyzed by the Rietveld Method using the GSAS/EXPGUI [15,16] suite of programs. Highresolution GPPD data was collected for the x = 0.2 (#1 and #3), the x = 0.3 and x = 0.4 samples in order to provide better description of the monoclinic distortion of La_{0.2}Sr_{0.8}MnO_{2.6}, rule out the presence of a similar distortion in La_{0.3}Sr_{0.7}MnO_{2.6}, and rule-out distortions from cubic symmetry in La_{0.4}Sr_{0.6}MnO_{2.6}. High d-spacing SEPD data was collected for the x = 0.1 (previously identified as tetragonal [4]) and x = 0.2 (#2) samples. Two data banks (1 and 5 for GPPD data and 1 and 3 for SEPD data) were simultaneously fit to access the highest d-spacing reflections available ($d_{max} = 4.5$ and 9Å for GPPD Bank 5 and SEPD Bank 3, respectively). Background, absorption, and geometrical corrections were refined for each data bank. The broadening of superstructure peaks observed for x = 0.1, 0.2 and 0.3 samples was successfully modeled using the Stephens formulation [17] implemented in profile function 4 in GSAS. In all cases, the symmetry-allowed coordinates and independent isotropic displacement parameters were refined for each La/Sr and O site and one global thermal parameter was refined for all Mn atoms to avoid unphysical values. Anisotropic displacement parameters were refined for O atoms in La_{0.1}Sr_{0.9}MnO_{2.6+δ}, La_{0.3}Sr_{0.7}MnO_{2.6} and La_{0.4}Sr_{0.6}MnO_{2.6} but not in La_{0.2}Sr_{0.8}MnO_{2.6} where correlations of parameters in the pseudo-tetragonal cell lead to non-positive definite ellipsoids. Site occupation factor (S.O.F.) of partially occupied oxygen vacant sites was refined for $La_{0.1}Sr_{0.9}MnO_{2.6+\delta}$ where significant occupation was expected and for La_{0.4}Sr_{0.6}MnO_{2.6} where the structure was cubic. For the rest of the compositions the oxygen contents were fixed at 2.6, in accordance with TGA data. La/Sr occupation was refined on various sites but no clear indication of ordering was obtained, therefore, a fully disordered model was adopted for all the structures. Initial refinements of oxygen's anisotropic displacement parameter in the vacancy-disordered La_{0.4}Sr_{0.6}MnO_{2.6} cubic phase (space group Pm3m) showed a huge anisotropy between the directions along and perpendicular to the Mn-O bond. This suggested that the O1 atom was displaced from the 3d Wyckoff site (0.5, 0, 0) in the plane normal to the Mn–O bond. The atom was placed at 12 h site (0.5, ε , 0), allowing ε , the S.O.F and the anisotropic displacement parameters to refine. The refined value of ε converged to 0.061(4) corresponding to a shift of 0.24(1)Å from the ideal position. This significant deviation of the O atom from its ideal position is an indication of the possible shortrange ordering of vacancies that do not extend far enough in the crystallites to produce long-range order necessary for the observation of a non-cubic diffraction pattern. Fig. 2(a-d) shows the fitted patterns and Table 1 lists final refined parameters and residuals. In the case of $x = 0.2 \text{ La}_{0.2}\text{Sr}_{0.8}\text{MnO}_{2.6}$, the results for the sample (#3), obtained from reduction at 1300 °C (1% H₂/Ar) and slow cooling in Ar on TGA, are presented. Details of fitted patterns demonstrating splitting of cubic 221/300 and 220 peaks are shown in Fig. 3(a-d). The larger degree of structural distortion observed for monoclinic P2/m La_{0.2}Sr_{0.8}MnO_{2.6} sample is clearly visible in Fig. 3(b). Additionally the existence of local ordering in x = 0.3 sample is also visible in Fig. 3(d) in a subtle background increase around d = 1.29 Å among other features described above. Fig. 4 shows the final structural models for La_{0.2}Sr_{0.8}MnO_{2.6} (very similar to x = 0.1 and 0.3 compounds) and La_{0.4}Sr_{0.6}MnO_{2.6} compounds, and Table 2 lists selected bond distances for the four compounds.

3. Discussion

The stabilization of vacancy-ordered perovskite phases ABO_{2.6} (ABO_{3- δ} with $\delta = 0.4$ or A₅B₅O₁₃) was initially shown for the cuprates BaLa₄Cu₅O_{13+ δ} [18], La₅Cu₅O_{13+ δ} [19], Nd₅Cu₅O_{13+ δ} [20] and recently for manganites Sr₅Mn₅O₁₃ [3] and (La_{0.2}Sr_{0.8})₅ Mn₅O₁₃ [2,4]. In BaLa₄Cu₅O_{13+ δ}, the Ba and La are ordered on different crystallographic sites; no such ordering was observed for other compounds. The oxygen-vacancy-ordered compounds La_xSr_{1-x}MnO_{2.6} (or (La_xSr_{1-x})₅Mn₅O₁₃) with *x* = 0.1–0.3 show the same vacancy ordering arrangement (see Fig. 4) that produces four square-base pyramidal and one octahedral Mn cations per unit cell. BaLa₄Cu₅O₁₃ and Sr₅Mn₅O₁₃ display tetragonal symmetry, space group P4/*m*, with $a \approx \sqrt{5}a_P$ and $c \approx a_P$ also observed for (La_{0.1}Sr_{0.9})₅Mn₅O_{13+ δ} and (La_{0.3}Sr_{0.7})₅Mn₅O_{13+ δ}. The compounds La₅Cu₅O_{13+ δ} and Nd₅Cu₅O_{13+ δ} have monoclinic symmetry, space group P2/*m*, with pseudo-tetragonal axes $a \approx b \approx \sqrt{5}a_P$, $c \approx a_P$ and



Fig. 2. Rietveld fit of neutron diffraction data for (a) tetragonal P4/m (La_{0.1}Sr_{0.9})₅Mn₅O_{13,75}, (b) monoclinic P2/m (La_{0.2}Sr_{0.8})₅Mn₅O₁₃, (c) tetragonal P4/m (La_{0.3}Sr_{0.7})₅Mn₅O₁₃ and (d) cubic Pm3m La_{0.4}Sr_{0.6}/MnO_{2.6}. Observed intensities and peak positions are marked with +and | symbols, respectively. The curve through the experimental points is the fit while the curve in the bottom is the difference between observed and calculated intensities. Insets show high d-spacing data normalized by the incident neutron spectrum to enhance the visibility of small superstructure peaks.

 $\gamma \approx 90^{\circ}$ observed in $(La_{0.2}Sr_{0.8})_5Mn_5O_{13}$ [2] (confirmed in this work, as shown in Table 1).

Although the vacancy ordering arrangement is the same for the three (x = 0.1, 0.2 and 0.3) compounds, and also similar to Sr₅Mn₅O₁₃ (x = 0, shown in the first column of Table 2), the reduction of average Mn charge and concomitant increase of the ionic size of Mn with increasing x have significant effect on structural features that will be described in the following discussion.

The Sr₅Mn₅O₁₃ compound (x = 0) shows charge separation of Mn³⁺ cations in pyramids and Mn⁴⁺ cations in octahedra (as can be seen in Fig. 4). Additionally, electronic orbital ordering is present for Mn³⁺ where half-occupied d_{z^2} orbitals are aligned along the apical direction of the pyramids showing characteristic bond distances and angles pattern which are also observed in Sr₂Mn₂O₅ [3,21] and Ca₂Mn₂O₅ manganites [10] and in cuprates [18–20]. This orbital ordering is present for all vacancy-ordered compounds ($x \neq 0.4$), even for La_{0.1}Sr_{0.9}MnO_{2.6+ δ}, containing significant amounts of oxygen in the nominally vacant sites. The characteristic separation of pyramidal Mn–O bond lengths into three groups is observed: elongated apical, intermediate equator-

ial and short equatorial Mn–O bonds with average values of 2.02, 1.93 and 1.86 Å, respectively, similar to observed in Sr₂Mn₂O₅ and Sr₅Mn₅O₁₃. The long and short Mn–O bonds for two adjacent pyramids correspond to the O atoms that connect their apical and equatorial positions, respectively. This Mn–O bond pattern indicates that the half-occupied d_{z^2} orbital points towards the apical direction of the pyramids and the $d_{x^2-y^2}$ orbital remains empty for the d^4 Mn³⁺ cation that shows the electronic configuration $d_{t_{zg}}^3 d_{z^2}^1$. Fig. 5 shows in detail the coordination polyhedra around Mn1 and Mn2/3 sites for x = 0.2 compound.

The average charge 4-x-2y of Mn in these compounds as a function of x and y is shown in the last row of Table 2. As x increases from 0 to 0.4 the average charge decreases from 3.2+ to 2.8+. However, the constancy of the dimensions of Mn³⁺ pyramids indicates that the extra electrons provided by the La doping are not evenly distributed over both Mn sites, but are added only to the octahedral Mn sites. A similar observation is made for the x = 0.1 sample for which excess oxygen seems to dope charge only to the octahedral Mn sites. Considering that four out of five Mn ions in the structure are pyramidal coordinated and remain 3+, the charge of the octahedral Mnⁿ⁺ is changing with substitution x

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Table 1Structural parameters for $La_xSr_{1-x}MnO_{2.6+\delta}$ samples..

| | | <i>x</i> = 0.1 | <i>x</i> = 0.2 | <i>x</i> = 0.3 | <i>x</i> = 0.4 |
|--------------------|--|---|---|---|--|
| Oxygen Content (y) | Reoxidation Refinement ^a Space Group a (Å) b (Å) c (Å) γ (°) V (Å ³) | 2.74(1) 2.749(2) P4/m (#83) 8.6123(1) 3.84084(4) 284.8814) | 2.59(1) 2.6 P2/m (#10) 8.6983(1) 8.6736(1) 3.82324(3) 90.267(3) 288.444(6) | 2.61(1) 2.6 P4/m (#83) 8.6921(1) 3.85213(7) 291.041(6) | 2.62(1) 2.601(6) Pm3m (#221) 3.8917(5) 58.94(1) |
| La/Sr1 | Wyckoff $U_{iso}~(\times 100~\textrm{\AA}^2)$ | 1d 0.99(5) | 1h 0.71(5) | 1d 0.74(12) | 1b 2.22(7) |
| La/Sr2 | Wyckoff x Y $U_{iso}($ \times 100 Å ² $)$ | 4k 0.1121(2) 0.7128(2) 0.68(1) | 2n 0.1164(4) 0.7184(3) 0.10(2) | 4k 0.1137(3) 0.7193(3) 1.17(6) | |
| La/Sr3 | Wyckoff x y $U_{iso}(\times 100 \text{ Å}^2)$ | | 2n 0.2822(3) 0.1165(4) 0.87(4) | | |
| Mn1 | $\begin{array}{l} Wyckoff \\ U_{iso}{}^a\!(\times 100 \mathring{A}^2) \end{array}$ | 1a 0.59(2) | 1a 0.33(3) | 1a 0.85(5) | 1a 1.28(6) |
| Mn2 | Wyckoff x y | 4j 0.1986(4) 0.4024(4) | 2m 0.1993(7) 0.4020(7) | 4j 0.2001(5) 0.4100(6) | |
| Mn3 | Wyckoff x y | | 2m 0.5879(7) 0.1958(7) | | |
| 01 | | 1b 1.79(6) 2.22(6) 0.70(5) -1.75(7) | 1b 1.21(8) | 1b 2.83(25) 2.93(29) 1.07(15) -1.21(20) | 12h ^b 0.061(4) 1.34(12) 5.6(8) 2.8(4) 0.2167 |
| 02 | $ \begin{array}{l} Wyckoff \\ x \\ y \\ U_{11/iso}(\times 100 \ \text{\AA}^2) \\ U_{22}(\times 100 \ \text{\AA}^2) \\ U_{33}(\times 100 \ \text{\AA}^2) \\ U_{12}(\times 100 \ \text{\AA}^2) \end{array} $ | 4k 0.1806(2) 0.4074(4) 0.94(6) 3.23(6) 1.65(6) 0.82(9) | 2n 0.1641(4) 0.4157(5) 1.09(6) | 4k 0.1766(4) 0.4157(6) 1.15(22) 4.52(24) 4.53(23) 2.22(20) | |
| 03 | $ \begin{array}{l} Wyckoff \\ x \\ y \\ U_{11/iso}(\times 100 \ \text{\AA}^2) \\ U_{22}(\times 100 \ \text{\AA}^2) \\ U_{33}(\times 100 \ \text{\AA}^2) \\ U_{12}(\times 100 \ \text{\AA}^2) \end{array} $ | 4j 0.0813(2) 0.2100(3) 3.69(9) 1.07(6) 0.76(5) -1.19(8) | 2n 0.5814(5) 0.1745(4) 1.05(6) | 4j 0.0802(4) 0.2226(4) 4.30(26) 3.39(23) 0.54(16) -0.90(18) | |
| 04 | $ \begin{array}{l} Wyckoff \\ x \\ y \\ U_{11/iso}(\ \times \ 100 \ \mathring{A}^2) \\ U_{33}(\ \times \ 100 \ \mathring{A}^2) \end{array} $ | 4j 0.4003(3) 0.2904(3) 1.73(10) 0.60(15) | 2m 0.0769(4) 0.2192(5) 1.06(6) | 4j 0.4010(5) 0.3010(7) 3.9(4) 1.0(5) | |
| 05 | Wyckoff x y $U_{iso}(\times 100 \text{ Å}^2)$ | | 2m 0.2269(4) 0.9262(4) 0.80(5) | | |

| Table 1 (continued) | | | | | | | |
|---------------------|--|--------------------------|---|----------------|----------------|--|--|
| | | <i>x</i> = 0.1 | <i>x</i> = 0.2 | <i>x</i> = 0.3 | <i>x</i> = 0.4 | | |
| | | | | | | | |
| 06 | Wyckoff x y $U_{iso}(\times 100 \text{\AA}^2)$ | | 2m 0.3979(5) 0.2943(5) 1.00(5) | | | | |
| 07 | | | 2m 0.7142(5) 0.4003(5) 1.38(6) | | | | |
| O_{δ} | $\begin{array}{l} Wyckoff \\ U_{iso}(\times100~{\mbox{\AA}}^2) \\ S.O.F \end{array}$ | 2e 2.6(2) 0.373(6) | | | | | |
| R _p (%) | Bank 1 Bank 3/5 | 4.35 4.74 | 3.96 5.68 | 4.87 4.71 | 5.66 6.40 | | |
| R _{wp} (%) | Bank 1 Bank 3/5 | 6.10 6.54 | 5.20 7.54 | 6.64 6.78 | 7.34 8.67 | | |
| χ ² | | 3.800 | 1.446 | 2.461 | 1.361 | | |

^a Isotropic displacement parameters of all Mn in the same structure were constrained to be equal to avoid unphysical values.

^b O atom was refined displaced from the ideal 3d (0, 1/2, 0) position at 12 h one (see text).



Fig. 3. Details of the neutron diffraction patterns near cubic 221/300 (left) and 220 (right) peaks highlighting splitting in the 1.26–1.39 Å d-spacing range for (a) tetragonal P4/m (La_{0.1}Sr_{0.9})₅Mn₅O_{13.75}, (b) monoclinic P2/m (La_{0.2}Sr_{0.8})₅Mn₅O₁₃, (c) tetragonal P4/m (La_{0.3}Sr_{0.7})₅Mn₅O₁₃ and (d) cubic Pm3m La_{0.4}Sr_{0.6}MnO_{2.6}. Normalization by one on the vertical axis represents 250 counts/µs. Colors and symbols are as in Fig. 2.

as n = 4-5x. This implies that the octahedral Mn⁴⁺ cation in Sr₅Mn₅O₁₃ (x = 0) changes to Mn^{3.5+} in (La_{0.1}Sr_{0.9})₅Mn₅O₁₃ (x = 0.1, in the absence of extra oxygen), to Mn³⁺ in (La_{0.2}Sr_{0.8})₅ Mn₅O₁₃ (x = 0.2), to Mn^{2.5+} in (La_{0.3}Sr_{0.7})₅Mn₅O₁₃ (x = 0.3) and to Mn²⁺ in a hypothetical long-range vacancy-ordered structure for La_{0.4}Sr_{0.6}MnO_{2.6} (x = 0.4). Charge reduction of the octahedral Mn1 site causes its significant size increase that has to be accommodated within geometrical constraints imposed by the constant

geometry of Mn^{3+} pyramids. Apical Mn1–O bond distance of the octahedral Mn site shows only a slight increase with increasing *x* from 1.905 Å (x = 0) to 1.926 Å (x = 0.3) (see Table 2). The fixed size of the pyramids in the x = 0-0.3 compounds imposes constraints on Mn1–O1 bond distance. The charges of the octahedral Mn as derived from the Mn–O bond distances and bond valence sum (BVS) parameters (calculated using the program VALENCE [22]) are shown in Table 2. The Mn⁴⁺ cation



Fig. 4. Structure of (a) monoclinic P2/m (La_{0.2}Sr_{0.8})₅Mn₅O₁₃ and (b) cubic Pm3m La_{0.4}Sr_{0.6}MnO_{2.6} obtained from Rietveld fits of neutron diffraction data. La³⁺/Sr²⁺ cations and O²⁻ anions are represented as big dark-grey and small red spheres, respectively. All symmetry permitted positions for O²⁻ anions around Mn atom are shown for La_{0.4}Sr_{0.6}MnO_{2.6} to emphasize the positional disorder described in text.

in Sr₅Mn₅O₁₃, with d^3 electronic configuration, shows almost undistorted octahedral coordination [3] as expected for three *d* electrons occupying the lower energy t_{2g} orbitals while both e_g orbitals pointing towards the O atoms are empty. The octahedral coordinated d^4 Mn³⁺ cation in (La_{0.2}Sr_{0.8})₅Mn₅O₁₃ has an additional electron that could either occupy one of the half-filled t_{2g} orbitals to give low-spin Mn³⁺ or occupy one of the empty e_g orbitals to give a high-spin electronic configuration. Trivalent Mn in low-spin state, to the best of our knowledge not observed in perovskite oxides to date, should produce shorter average Mn–O bonds than the high-spin, resulting in larger BVS values. This is not the case as the BVS values shown in Table 2 are identical for both octahedral and pyramidal Mn^{3+} . Since Mn in pyramids is high-spin [3,10,21], the octahedral Mn^{3+} appears to also assume high-spin electronic configuration. Therefore, the extra electron should be placed in one of the empty e_g orbitals and the octahedra should show Jahn-Teller distortion to reduce the energy of the otherwise degenerate half-occupied e_g levels.

The observed Mn³⁺–O bond distances are atypical, however, for a high-spin state normally observed for Mn³⁺. Four long (2 × 2.012 and 2 × 2.078 Å) and two short (2 × 1.912 Å) Mn–O bonds define a compressed MnO₆ octahedron.

Two possible explanations can be proposed for this finding that we will describe in the following. One possibility is that the observed bond distances appear as a consequence of the occupation of the $d_{x^2-v^2}$ orbital instead of the usually occupied d_{z^2} that would be empty in this case. The electronic configuration of Mn³⁺ in (La_{0.2}Sr_{0.8})₅Mn₅O₁₃ would then be $d_{t_{2g}}^3 d_{x^2-y^2}^1 d_{z^2}^0$ for the octahedra in contrast to the pyramids which show $d_{t_{2g}}^3 d_{x^2-y^2}^0 d_{z^2}^1$ configuration. Fig. 6a shows the proposed electronic configuration and octahedral distortion derived from it. A similar compressed Mn³⁺ octahedron has been proposed for the La_{1.2}Sr_{0.8}MnO_{4.27} [23] compound using conventional X-rays. However, a disordered apical position was found in that compound, which could imply that the actual Mn-O apical bond distances extracted from the Rietveld refinement are reduced with respect to the real ones by the averaging of several oxygen atom positions. The apically compressed octahedral coordination of Mn³⁺ in (La_{0.2}Sr_{0.8})₅ Mn₅O₁₃ with electronic configuration $d_{t_{2g}}^3 d_{x^2-y^2}^1 d_{z^2}^0$ would be, to the best of our knowledge, the first experimental observation of such a state for transition metal perovskites [24]. The second explanation could be that the observed bond distances do not originate form a single arrangement of oxygen around the octahedral Mn³⁺ but from the superposition of two different orientations of a typical elongated MnO₆ octahedra as is observed in LaMnO₃ [25] with the long and intermediate Mn-O bonds (2.178 and 1.968 Å, respectively) oriented in either x or y direction in the x-y plane and the short one (1.907 Å) always in the z direction. In such a case, both kinds of octahedral Mn^{3+} in $(La_{0.2}Sr_{0.8})_5Mn_5O_{13}$ would show a $d_{l_{2g}}^3d_{x^2-y^2}^0d_{z^2}^1$ electronic configuration and averaging of short and $\log Mn - O$ bonds in the x - yplane would explain the observed bond distances. Fig. 6b shows how, by overlapping two elongated octahedra rotated 90° with respect to each other in the x-y plane, the average compressed octahedra could be obtained with Mn-O bond distances approximately equal to those observed in (La_{0.2}Sr_{0.8})₅Mn₅O₁₃. Such elongated octahedra oriented in-plane would frustrate orbital arrangement and the bond lengths of two out of four adjacent pyramids. This may be a reason for a presence of two different pyramids in the refined x = 0.2 structure. However, since the long axis of JT-octahedron cannot be placed along the *c*-axis due to the size mismatch, this frustration may be also a good reason for the electron to occupy the x^2-y^2 orbital, which fits perfectly in-plane with an empty and short z^2 orbital along *c*-axis as proposed in first scenario. More high-resolution NPD data, structural local probes, as well as theoretical input are necessary to clarify this issue.

The second scenario is consistent with the breaking of the fourfold symmetry producing a monoclinic unit cell. The presence of disordered elongated octahedra lying in the x-y plane would break the local tetragonal symmetry of the system. On the contrary, if Mn^{3+} showed $d_{1_{2g}}^3 d_{x^2-y^2}^1 d_{2^2}^{20}$ electronic configuration, there would be no a-priori need to break it as the Mn^{3+} cation would still have an electronic configuration compatible with the 4-fold symmetry of the site. Moreover, the presence of disorder is consistent with the observation of small and anisotropic scattering domains that produce broadening of superstructure peaks. Finally, the observation of slightly different values of the

| | x = 0 [3] | <i>x</i> = 0.1 | <i>x</i> = 0.2 | | <i>x</i> = 0.3 | <i>x</i> = 0.4 |
|-----------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------|--------------------------------------|
| Octahedral | | | | | | |
| Mn1-O _{ap} | $1.9051(1) \times 2$ | 1.92042(2) × 2 | 1.91162(2) × 2 | | 1.92606(3) × 2 | 1.9603×5.2 |
| Mn1–O _{eg} | 1.930(4) × 4 | 1.939(3) × 4 | $2.012(4) \times 2$ | | $2.057(4) \times 4$ | |
| Mn1-O _{eq} | | | $2.078(4) \times 2$ | | | |
| BVS | 3.8 (Mn ⁴⁺) | 3.7 (Mn ⁴⁺) | 3.2 (Mn ³⁺) | | 3.06 (Mn ³⁺) | 2.9 (Mn ³⁺) ^a |
| | | | | | | |
| Pyramidal | | | Mn2 | Mn3 | | |
| Mn2/3-O _{an} | 2.058(4) | 1.987(4) | 1.968(8) | 2.082(8) | 1.987(5) | |
| $Mn2/3-O_{eq}$ | $1.9212(5) \times 2$ | $1.9272(3) \times 2$ | $1.9397(12) \times 2$ | $1.9213(7) \times 2$ | $1.9374(6) \times 2$ | |
| $Mn2/3-O_{eq}$ | 1.938(5) | 1.942(4) | 1.906(7) | 1.932(7) | 1.934(7) | |
| $Mn2/3-O_{eq}$ | 1.846(4) | 1.874(4) | 1.869(8) | 1.863(7) | 1.862(7) | |
| Mn2–O _δ | | 1.906(3) | | | | |
| BVS | 3.2 (Mn ³⁺) | 3.2(3+)/3.8(4+) | 3.2 (Mn ³⁺) | 3.1 (Mn ³⁺) | 3.2 (Mn ³⁺) | |
| Avg. Mn valence | 3.20+ | 3.38+ | 3.00+ | | 2.90+ | 2.80+ |

Selected bond distances (Å) bond valence sums and average observed Mn valence for $La_xSr_{1-x}MnO_{2.6+\delta}$ (x = 0–0.4) compounds.

^a Coordination index 5 was assumed for this calculation.



Fig. 5. Coordination polyhedra around Mn atoms for $(La_{0.2}Sr_{0.8})_5Mn_5O_{13}$. Color scheme is as in Fig. 4. Relevant bond distances are given (Å).

monoclinic angle with different thermal treatments of the sample could also be explained by the fact that different degrees of disorder of the elongated octahedra would produce slightly different average structures.

In a previous report based on lower resolution data [4], we have modeled the structure of $(La_{0.2}Sr_{0.8})_5Mn_5O_{13}$ between 500 and 700 °C using a tetragonal P4₂/m space group where ordering of elongated octahedra alternating along between the *x* and *y* directions is possible. Such a model gave a poor fit to the higher resolution room temperature data, confirming the absence of long-range ordering in the direction of the apical elongation of Mn³⁺ octahedra in the *x*–*y* plane.

Similar compressed Mn–O octahedral coordination is observed for the x = 0.3 compound $(La_{0.3}Sr_{0.7})_5Mn_5O_{13}$ where 50% of the Mn1 site is occupied by $d^5 Mn^{2+}$ cations. Since the Mn1 site is, on average, even larger than in $(La_{0.2}Sr_{0.8})_5Mn_5O_{13}$ we still assign a high-spin electronic configuration to both Mn^{2+} and Mn^{3+} cations (low-spin configuration of Mn^{2+} is even less favored than for Mn^{3+} due to the large exchange energy loss). The BVS for Mn1 cation using Mn^{3+} parameters for the calculation supports this picture; BVS decreases from 3.2 in x = 0.2 to 3.06 in x = 0.3 indicating reduction of the average charge of Mn1 site with x. The non-Jahn-Teller high-spin Mn²⁺–O bond lengths (with both e_g orbitals half-filled) do not conform to the required short Mn1–O distance. Average Mn²⁺–O bond distances for (La_{0.3}Sr_{0.7})₅Mn₅O₁₃ are at least 0.1 Å longer than the average bond observed in (La_{0.2}Sr_{0.8})₅Mn₅O₁₃, therefore huge chemical pressure, alleviated only by the presence of disordered Mn³⁺ and Mn²⁺ octahedra, is present in this compound as extracted from the high value of the calculated BVS for the Mn1 site. The diffraction data still shows significant superstructure-peaks broadening but an overall tetragonal symmetry is observed. No indication for the presence of superstructures arising from coherent orientations of the Mn³⁺ octahedra has been found in the analyzed data.

The concentration of Mn^{3+} elongated octahedra may explain the change in symmetry from P4/m for x = 0.1 to P2/m (x = 0.2) and back to P4/m for x = 0.3. For both x = 0.1 and 0.3 the Mn^{3+} coexist with an equal number of isotropic Mn^{4+} or Mn^{2+} cations, respectively. These cations form regular octahedra conforming to the 4/m symmetry, therefore, the local distortion caused by the Mn^{3+} anisotropic octahedron is diluted in the network. For x = 0.2, only the elongated Mn^{3+} octahedra with the long axis lying in the x-y plane in a disordered manner are present. The relative orientation of these octahedra in different structural domains does not perfectly average into a tetragonal structure; i.e., the 2/m symmetry of the octahedral sites persists in the average structure with the degree of distortion depending on the sample preparation conditions.

The oxygen-vacancy ordering and orbital ordering of Mn^{3+} pyramids is finally destabilized with respect to the formation of an oxygen-vacancy disordered cubic phase in $La_{0.4}Sr_{0.6}MnO_{2.6}$ for which only Mn^{2+} would be found in hypothetical long-range oxygen-vacancy-ordered ($La_{0.4}Sr_{0.6})_5Mn_5O_{13}$ compound. This vacancy-disordered phase shows, however, clear signs of local ordering in domains smaller than the neutron sampling volume as confirmed by the observation of displacement of O anions from the ideal crystallographic position for the cubic perovskite phase and the increased background in regions of the diffraction patterns where superstructure peaks are present for the other compounds, as discussed before.

4. Conclusions

The oxygen-vacancy-ordered phases $(La_xSr_{1-x})_5Mn_5O_{13}$ (x = 0.1-0.3) and vacancy-disordered $La_{0.4}Sr_{0.6}MnO_{2.6}$ have

Table 2



Fig. 6. Two possible explanations for the observed Mn–O bonds in the octahedral Mn³⁺ cation in $(La_{0.2}Sr_{0.8})_5Mn_5O_{13}$: (a) the electronic configuration of the d^4 Mn³⁺ cation is $d_{t_{2g}}^3 d_{g^{2-}y^2}^1 d_{g^2}^2$ making O atoms in the plane move further away from the cation while the apical Mn–O bond is unchanged respect to x = 0 and 0.1 compounds; (b) the observed octahedron is the averaging of two apically elongated Mn³⁺ octahedra with the long and intermediate bonds in the x-y plane and a short one in the z direction.

been prepared and their structures characterized by neutron timeof-flight powder diffraction. The vacancy-ordered phases show common structural features with the previously studied compound $Sr_5Mn_5O_{13}$ (x = 0), that contains in its structure four orbital-ordered Mn³⁺ pyramids and one octahedral Mn cation that changes its charge from Mn^{4+} in x = 0 through Mn^{3+} in x = 0.2 to $Mn^{2.5+}$ in x = 0.3. The change from non-Jahn-Teller Mn^{4+} to Jahn-Teller Mn³⁺ requires distortions of the octahedral coordination constrained by the fixed geometry of the Mn^{3+} pyramids in the z direction that results in observation of compressed Mn³⁺ octahedra. This geometry can be interpreted in two ways: (1) the electronic configuration of Mn in the octahedral site is a novel $d_{t_{2g}}^3 d_{x^2-y^2}^1 d_{z^2}^0$ as compared to the typical $d_{t_{2g}}^3 d_{x^2-y^2}^0 d_{z^2}^1$ for Mn³⁺ in pyramidal sites or (2) the disordered Mn³⁺ apically elongated octahedra are present with normal electronic configuration $d_{t_{2\sigma}}^3 d_{x^2-y^2}^0 d_{z^2}^1$, and the observed bond distances are the average of the long and intermediate in-plane Mn-O bonds typical for the elongated MnO₆ octahedra. Several structural features favor the second case, however, further high-resolution diffraction and local probes should be used to unambiguously confirm that. The decrease in charge and increase in size of the octahedral Mn site produced by La substitution finally destabilizes the vacancyordered structure producing a vacancy-disorder phase for x = 0.4that shows clear signs of short-range vacancy ordering through the displacement of oxygen atoms from the ideal site in the cubic perovskite structure.

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