

Crystal Structure of the Mixed Oxides $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ ($0 \leq z \leq 1$)

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The crystal structure and nonstoichiometry of several compositions in the system $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ ($0 \leq z \leq 1$) have been investigated by powder X-ray diffraction (PXD), powder neutron diffraction (PND), thermogravimetry (TG), including full reduction in hydrogen, and chromatometric titration. The system formed solid solutions over the entire compositional range ($0 \leq z \leq 1$) crystallizing in the rhombohedral structure (space group $R\bar{3}c$). The lattice constant increased with increasing Mn content z . The cation stoichiometry (occupancy) was calculated from refinement of PXD data, and oxygen positions and occupancies were calculated from PND data. These results confer with the TG and chemical analysis of oxygen content in that the Co-rich compositions exhibit oxygen deficiency (oxygen vacancies), while the Mn-rich compositions exhibit oxygen excess in the form of metal vacancies. © 1999 Academic Press

Key Words: perovskite, mixed oxides; structure; nonstoichiometry; lanthanum manganite; lanthanum cobaltate; powder X-ray diffraction (PXD); powder neutron diffraction (PND).

1. INTRODUCTION

Several useful properties of perovskite-type oxides $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$, such as electrical conductivity, catalytic activity, and electron emission, are the result of their oxygen nonstoichiometry and electron structure. The high temperature properties have been extensively studied due to the materials' potential use as electrodes in fuel cells and other electrochemical devices and as mixed conducting, oxygen permeable membranes for gas separation.

Partial replacement of lanthanum by strontium leads to increased electronic disorder and to changes in the oxidation state of the $3d$ transition metal and in the oxygen nonstoichiometry. The Sr-doped cobaltate $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3\pm y}$ tends to show large oxygen deficiency (high oxygen vacancy concentration) (1–4). The Sr-doped manganate

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3\pm y}$, on the other hand, shows a smaller tendency to oxygen deficiency and may even show oxygen excess at near-atmospheric oxygen activities (5–10).

Despite the interest, a relatively limited number of studies on the properties of the mixed $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ system have been reported, covering phase transitions, thermal expansion, oxygen transport, and conductivity (11–16). The crystal structure and magnetic properties of the mixed oxides $\text{LaCo}_{1-z}\text{Mn}_z\text{O}_3$ (without Sr doping) have been investigated (17, 18). It was shown (18) that the $\text{LaCo}_{1-z}\text{Mn}_z\text{O}_3$ system has two regions of solid solution with the rhombohedral structure (space group $R\bar{3}c$) from LaCoO_{3-y} ($z = 0$) to $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ ($z = 0.3$) and the orthorhombic structure (space group $Pnma$) from $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ ($z = 0.5$) to LaMnO_{3+y} .

In the present work the crystal and defect structures of the mixed $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ ($0 \leq z \leq 1$) system have been studied by powder X-ray diffraction (PXD), powder neutron diffraction (PND), and high temperature thermogravimetry (TG). The present article presents the XRD and PND structure studies, while the nonstoichiometry and defect chemistry obtained from the gravimetric data will be presented elsewhere. These papers form the continuation of work published previously (4, 9, 18).

2. MATERIALS AND METHODS

The specimens in the series $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ ($0 \leq z \leq 1$) were prepared using standard ceramic processing with two-stage firing in air at 1170 and 1270 K for 12 h each. All the samples were identified by X-ray powder diffraction as single phases.

Prior to structural analysis the samples were equilibrated in air at 770 K and quickly cooled to room temperature. The crystal structures of these samples were refined from PXD and PND data taken at room temperature.

PXD patterns were obtained using the DRON-3 diffractometer with $\text{CuK}\alpha$ radiation in the angle range $20^\circ < 2\theta < 100^\circ$ with 0.05° steps.

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PND experiments were carried out by use of the neutron diffractometer at the IVV-2M reactor in a setup with a 10-detector registration system. It was equipped with a pyrolytic graphite crystal of 40' mosaicity (002) and a germanium crystal of 17' mosaicity as a double monochromator. To achieve optional resolution at large scattering angles, where the density of Bragg peaks becomes high, the monochromator Ge scattering angle was selected to be close to 90°. The neutron wavelength of 1.515 Å was calibrated from refinements of a PND diffraction pattern of a standard Al_2O_3 sample. The horizontal and vertical collimation between reactor, monochromators, sample, and detectors gives a resolution $d/d = 0.2\%$. The samples were wrapped in a thin Al foil, which is invisible to neutrons, and the PND patterns were collected from 9° to 110° in steps of 0.1°.

The absolute oxygen contents of samples were found by two procedures, namely by complete thermogravimetric reduction in a hydrogen flux and by chromatometric titration.

3. RESULTS AND DISCUSSION

3.1. PXD Investigation

In our previous investigation (18) it was shown that lanthanum cobaltate-manganates (without Sr) have two regions of solid solution with the rhombohedral structure (space group $R\bar{3}c$) from $\text{LaCoO}_{3\pm y}$ to $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_{3\pm y}$ and the orthorhombic structure (space group $Pnma$) from $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_{3\pm y}$ to manganate $\text{LaMnO}_{3\pm y}$. In contrast, 30% Sr-doped lanthanum cobaltate-manganates form uninterrupted solid solutions $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ ($0 \leq z \leq 1$) which all crystallize in the rhombohedral structure. Typical PXD patterns obtained at room temperature are shown in Fig. 1. The refinement programs Fullprof and DBWS-9411 were used to refine the structure within the rhombohedral symmetry (space group $R\bar{3}c$) in the following manner.

Initially it was supposed that the occupancies of oxygen and metal ions equal the ideal values. The amplitude of dispersion of X-rays by oxygen is small, and therefore the oxygen nonstoichiometry was set to remain at the ideal value of 3. Debye-Waller factors were taken equal to zero, and the occupancies of the cations (lanthanum, strontium and 3d-metals) were refined, yielding synthesized diffractograms which confer well with the experimental ones.

The results of the refinement are given in Table 1. They show that the lattice constants increase with increasing manganese contents z . Furthermore, they indicate that Sr-doped lanthanum cobaltates and solid solutions with partial replacement of cobalt by manganese ($z = 0, 0.25$, and 0.50) exhibit full occupancies in the metal sublattices, i.e., the La + Sr and Mn + Co occupancies both equal unity. However, in samples with high manganese contents ($z = 0.75$ and $z = 1.00$) a metal deficiency develops. According to the

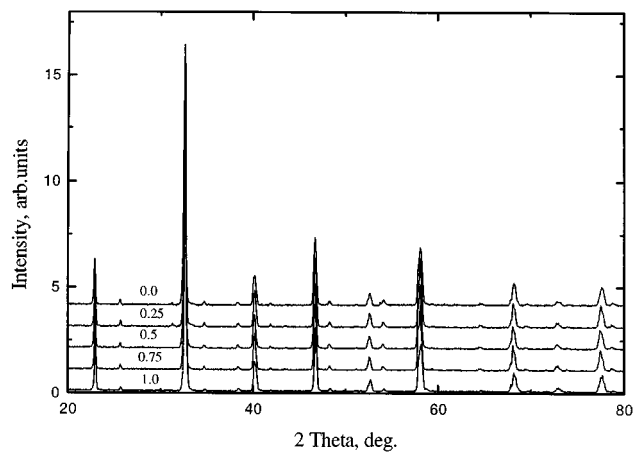


FIG. 1. PXD patterns of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ for $z = 0, 0.25, 0.5, 0.75$, and 1.0 obtained at room temperature on samples quenched after annealing at 770 K in air.

refinement the $z = 0.75$ sample has a concentration of vacancies in the lanthanum sublattice equal to 0.05, while the $z = 1.00$ sample has vacancies in both the La + Sr and the Mn sublattices, amounting to concentrations of 0.03 and 0.02, respectively.

3.2. PND Investigation

The oxygen positions and occupancies have been refined based on the PND results. The lattice parameters and the atomic coordinates determined from the PXD refinement were used as starting values for the Rietveld refinement of the PND data. The amplitude of dispersion of neutron radiation of the 3d metals ($b = b_{\text{Co}} + b_{\text{Mn}}$) was taken to be close to zero (because $b_{\text{Mn}} = -0.373, b_{\text{Co}} = 0.253$). The

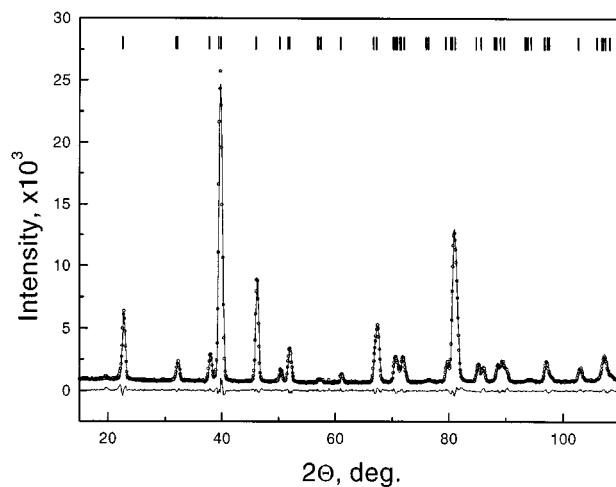


FIG. 2. Neutron diffraction pattern $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3-y}$ quenched after annealing at 770 K in air, typical of Co-rich samples.

TABLE 1
Structure Parameters from X-ray Diffraction Data of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$

| Parameter | $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ $z = 0.00$ | $z = 0.25$ | $z = 0.50$ | $z = 0.75$ | $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3,}$ $z = 1.00$ |
|-----------------------|--|------------|------------|------------|---|
| $a = b$ (Å) | 5.4406(2) | 5.4473(3) | 5.4657(3) | 5.4845(3) | 5.5023(2) |
| c (Å) | 13.1950(8) | 13.2136(8) | 13.2504(1) | 13.3004(8) | 13.3486(7) |
| V (Å ³) | 338.25(4) | 339.57(3) | 342.81(4) | 346.45(4) | 349.99(3) |
| c/a | 2.425 | 2.426 | 2.424 | 2.425 | 2.426 |
| n , La | 0.70(2) | 0.70(2) | 0.70(2) | 0.67(2) | 0.68(1) |
| n , Sr | 0.30(2) | 0.30(2) | 0.30(2) | 0.28(2) | 0.29(2) |
| $[V_{\text{La}}^x]$ | 0.00(2) | 0.00(2) | 0.00(2) | 0.05(2) | 0.03(2) |
| n , Co | 1.00(1) | 0.75(2) | 0.50(2) | 0.25(2) | — |
| n , Mn | — | 0.25(2) | 0.50(2) | 0.75(2) | 0.98(2) |
| $[V_{\text{Mn}}^x]$ | 0.00(2) | 0.00(2) | 0.00(2) | 0.00(2) | 0.02(2) |
| x , O | 0.450(2) | 0.452(2) | 0.455(2) | 0.450(2) | 0.454(2) |
| R_p | 6.51 | 9.61 | 8.02 | 8.72 | 8.09 |
| R_{wp} | 9.32 | 12.15 | 9.53 | 10.75 | 10.78 |
| R_b | 8.52 | 8.93 | 7.25 | 6.62 | 4.39 |
| R_f | 6.51 | 6.56 | 6.61 | 5.43 | 3.17 |

Note. Space group $R\bar{3}c$. The atomic positions are La/Sr 6a [0, 0, 0.25]; Co/Mn 6b [0, 0, 0]; O 18e [x , 0, 0.25]. Occupancies (n) are expressed in terms of atoms per formula unit. x , O represents the first, variable, coordinate for the oxygen. R_p , R_{wp} , R_b , and R_f are the conventional factors showing the quality of the agreement between observed and calculated data.

occupancies of the La + Sr and Co + Mn sublattices were set to unity, while the occupancies of the oxygen atoms were refined. Figure 2 shows a typical example of such refinements of the PND data. In general the difference curves show that the experimental and theoretical diffractograms fit each other reasonably well. Substantial deviation was observed only for the end composition $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3+y}$ ($z = 1.0$), notably at small angles of dispersion (see Fig. 3).

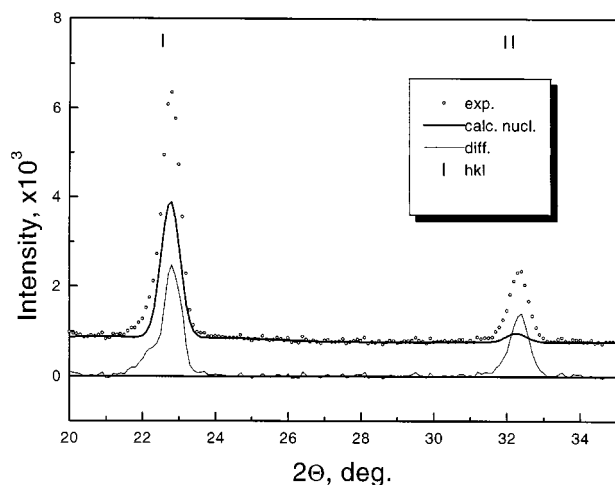


FIG. 3. Small angle fragment of the neutron diffraction pattern of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{MnO}_{3+y}$ compared with a simulated pattern based only on dispersion of neutrons by nuclei.

This is attributed to magnetic ordering of this phase at room temperature ($T_C = 370$ K). For the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3+y}$ we therefore took the ferro-magnetic ordering into account and then obtained a reasonable correlation also in this case (see Fig. 4).

The parameters refined from the PND data are given in Table 2. The results indicate that Sr doped lanthanum cobaltate $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-y}$ contains oxygen vacancies corresponding to $3 - y = 2.96 \pm 0.02$ and that the mixed

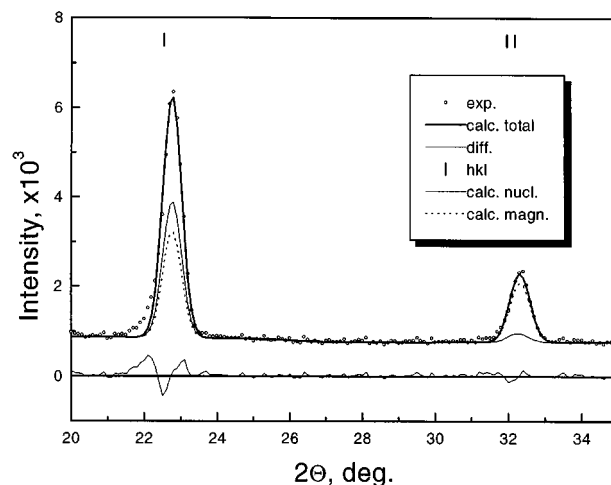


FIG. 4. Small angle fragment of the neutron diffraction pattern of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3+y}$ with ferromagnetic order of the $3d$ ions taken into account in the fitted pattern.

TABLE 2
Structural Parameters from Neutron Diffraction Data of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$

| Parameter | $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ $z = 0.00$ | $z = 0.25$ | $z = 0.50$ | $z = 0.75$ | $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, $z = 1.00$ |
|----------------------------|--|-------------|-------------|-------------|--|
| $a = b$ (Å) | 5.4352(3) | 5.4432(5) | 5.4583(5) | 5.4833(5) | 5.4967(5) |
| c (Å) | 13.1831(11) | 13.2100(15) | 13.2462(18) | 13.2917(19) | 13.3321(11) |
| V (Å ³) | 337.27(4) | 338.95(6) | 341.77(7) | 346.09(6) | 348.84(5) |
| c/a | 2.426 | 2.427 | 2.427 | 2.424 | 2.425 |
| B (Å ⁻²) | 0.27(5) | 0.41(7) | 0.25(5) | 0.29(7) | 0.51(4) |
| n , La | 0.70(1) | 0.70(1) | 0.70(2) | 0.69(1) | 0.700(5) |
| n , Sr | 0.30(1) | 0.30(1) | 0.30(2) | 0.29(1) | 0.300(5) |
| $[V_{\text{La}}^x]$ | 0.00(1) | 0.00(1) | 0.00(1) | 0.02(1) | 0.00(1) |
| B (Å ⁻²) | 0.1(1) | 0.41(7) | 0.25(5) | 0.29(7) | 0.11(9) |
| n , Co | 1.00(1) | 0.75(1) | 0.50(1) | 0.25(2) | — |
| n , Mn | — | 0.25(1) | 0.50(1) | 0.75(2) | 0.98(2) |
| $[V_{\text{Mn}}^x]$ | 0.00(1) | 0.00(1) | 0.00(1) | 0.00(1) | 0.02(2) |
| x , O | 0.4628(2) | 0.4620(3) | 0.4600(3) | 0.4577(3) | 0.4582(3) |
| B (Å ⁻²) | 0.52(2) | 0.65(2) | 0.71(5) | 0.78(6) | 0.79(4) |
| n , O | 2.970 | 2.98(3) | 2.99(2) | 3.00(2) | 3.00(2) |
| $[V_{\text{O}}^x]$ | 0.03(2) | 0.02(3) | 0.01(2) | 0.00(2) | 0.00(2) |
| R_p | 4.52 | 5.90 | 6.35 | 5.83 | 3.68 |
| R_{wp} | 5.96 | 8.10 | 8.57 | 8.32 | 5.15 |
| R_b | 3.65 | 5.15 | 4.73 | 4.03 | 2.60 |
| R_f | 2.92 | 4.15 | 4.79 | 3.35 | 2.02 |
| $\mu(\text{Mn})$, μ_B | — | — | — | — | 2.4 (± 0.1) |
| R_M | — | — | — | — | 4.19 |

Note. Atom positions and notations as in Table 1 where applicable. B represents isotropic temperature parameters for the atom. $\mu(\text{Mn})$, μ_B represents the ferromagnetic moment and R_M the quality factor of the fit of this parameter.

oxide $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.75}\text{Mn}_{0.25}\text{O}_{3\pm y}$ is close to stoichiometric ($3 \pm y = 2.99 \pm 0.02$) with respect to oxygen.

When the occupancy of oxygen in the Sr doped manganate $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3+y}$ was set to unity, the refinement

gave a metal deficiency (metal vacancies) in agreement with the results of the PXD data refinement.

The atomic distances and tolerance factors ($t = d_{\text{Ln-O}}/d_{\text{Co-O}}\sqrt{2}$) as a function of composition are shown in

TABLE 3
Interatomic Distances and Tolerance Factor t as a Function of the Mn Concentration of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ Calculated Using PND-Based Data from Table 2

| Parameter | $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ $z = 0.00$ | $z = 0.25$ | $z = 0.50$ | $z = 0.75$ | $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, $z = 1.00$ |
|------------------------|--|------------|------------|------------|--|
| (La-La) $\times 6$ (Å) | 3.8308(2) | 3.8371(3) | 3.8477(3) | 3.8639(3) | 3.8741(2) |
| (La-Co) $\times 2$ (Å) | 3.2958(3) | 3.3025(4) | 3.3115(4) | 3.3229(4) | 3.3330(3) |
| $\times 6$ (Å) | 3.3248(2) | 3.3299(3) | 3.3391(3) | 3.3540(3) | 3.3624(3) |
| (La-O) $\times 3$ (Å) | 2.515(1) | 2.515(2) | 2.511(2) | 2.510(2) | 2.519(2) |
| (La-O) $\times 6$ (Å) | 2.7074(2) | 2.7128(3) | 2.7211(3) | 2.7326(3) | 2.7401(2) |
| (La-O) $\times 3$ (Å) | 2.920(1) | 2.928(2) | 2.947(2) | 2.974(2) | 2.978(2) |
| (Co-O) $\times 6$ (Å) | 1.9260(1) | 1.9297(2) | 1.9362(3) | 1.9458(2) | 1.9506(2) |
| (O-O) $\times 4$ (Å) | 2.7074(8) | 2.716(1) | 2.721(1) | 2.733(1) | 2.740(1) |
| (O-O) $\times 4$ (Å) | 2.7401(8) | 2.745(1) | 2.755(1) | 2.771(1) | 2.777(1) |
| (O-O) $\times 2$ (Å) | 3.555(1) | 3.556(2) | 3.551(2) | 3.550(2) | 3.563(2) |
| (O-O) $\times 2$ (Å) | 3.8520(2) | 3.8594(4) | 3.8724(4) | 3.8916(4) | 3.9012(3) |
| t | 0.995 | 0.995 | 0.995 | 0.996 | 0.996 |

TABLE 4
Oxygen Nonstoichiometry y at 770 K in Air as a Result of Chromatometric Titration and TG Analysis of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$

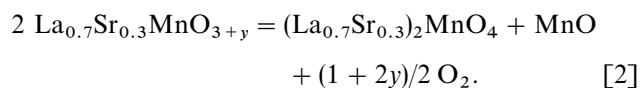
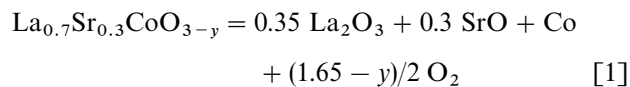
| Composition (z) of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-z}\text{Co}_z\text{O}_{3\pm y}$ | Concentration of $[\text{Me}^{+4}]$ | $\pm y$ (chrom. titr.) for 770 K, air | $\pm y(\text{TG})$ for 770 K, air |
|--|-------------------------------------|---------------------------------------|-----------------------------------|
| $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-y}$ | 0.234 ± 0.001 | -0.033 ± 0.0005 | -0.030 ± 0.001 |
| $z = 0.1$ | 0.273 ± 0.001 | -0.013 ± 0.0005 | — |
| $z = 0.3$ | 0.287 ± 0.001 | -0.006 ± 0.0005 | — |
| $z = 0.5$ | 0.293 ± 0.001 | -0.003 ± 0.0005 | — |
| $z = 0.7$ | 0.299 ± 0.001 | -0.0002 ± 0.0005 | — |
| $z = 0.9$ | 0.331 ± 0.001 | $+0.015 \pm 0.0005$ | — |
| $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3+y}$ | 0.361 ± 0.001 | $+0.030 \pm 0.0005$ | $+0.051 \pm 0.002$ |

Note. $[\text{Me}^{+4}]$ is the fraction of +4 metal ions ($\text{Me}^{+4} = \text{Mn}^{+4} + \text{Co}^{+4}$).

Table 3. The tolerance factors are close to a unity for all samples, indicating that the rhombohedral structure is stable.

3.3. Oxygen Nonstoichiometry

The absolute values of the oxygen nonstoichiometry were determined by full reduction by hydrogen in the thermobalance, and from these reference points the TG analyses yielded the stoichiometry also under other conditions. The phase composition of the reduced samples was identified only for the two $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ samples with end compositions $z = 0$ and $z = 1$:



We could not determine the phase composition of the reduction products of the intermediate compositions ($0 < z < 1$). Therefore, the absolute values of the oxygen nonstoichiometry (y) for the whole series $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ ($0 \leq z \leq 1$) were calculated from chromatometric titration of samples equilibrated in air at 770 K and quenched to room temperature. The results of these investigations are listed in Table 4 and shown in Fig. 5. The oxygen nonstoichiometry of the samples $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ under near-atmospheric oxygen partial pressures at 770 K changes from negative values for the cobalt-rich compositions to positive for the manganese-rich, the transformation taking place around $z = 0.7$.

In broad terms there is thus agreement between the results of the refinements of the PXD and PND data and the chemical analyses of the oxygen content. The details of the oxygen nonstoichiometry as a function of oxygen activity, temperature and manganese content, as well as the interpretation in terms of point defect models and thermodynamic parameters will be reported elsewhere (19).

4. CONCLUSIONS

Mixed Sr-doped lanthanum cobaltate-manganates $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ form solid solutions over the entire compositional range ($0 \leq z \leq 1$) and crystallize in the rhombohedral distorted pseudocubic perovskite structure. The lattice constants increase with manganese content z . All methods employed (PXD, PND, and chemical analyses by TG and chromatometric titration) show that the compounds at 770 K in air exhibit oxygen deficiency (oxygen vacancies) for z up to around 0.7 and oxygen excess in the form of metal vacancies for z above approximately 0.7.

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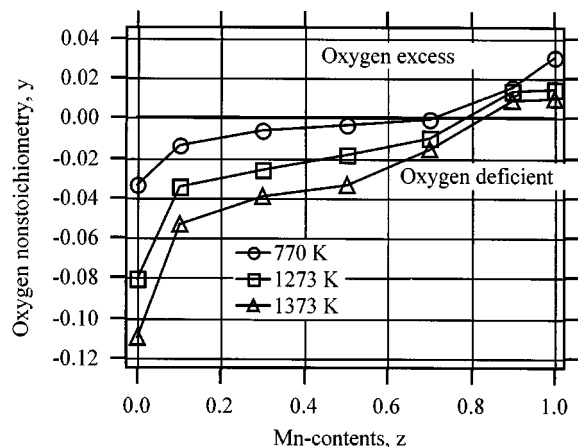


FIG. 5. The absolute values of oxygen nonstoichiometry for samples $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-z}\text{Mn}_z\text{O}_{3\pm y}$ equilibrated in air as a function of composition (z) at different temperatures.

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