X-ray powder data and bond valence of $La_{0.65}Sr_{0.35}MnO_3$ after Rietveld refinement

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(Received 9 October 2001; accepted 4 April 2002)

Powder X-ray diffraction (XRD) data were collected for $La_{0.65}Sr_{0.35}MnO_3$ prepared through an alternative method from a stoichiometric mixture of Mn_2O_3, La_2O_3, and SrO_2, fired at 1300 °C for 16 h. XRD analysis using the Rietveld method was carried out and it was found that manganite has rhombohedral symmetry (space group $R\bar{3}c$). The lattice parameters are found to be **a**=5.5032 Å and **c**=13.3674 Å. The bond valence computation indicates that the initial inclusion of Sr occurs at higher temperature. © *2002 International Centre for Diffraction Data.* [DOI: 10.1154/1.1481522]

Key words: manganite, X-ray diffraction, Rietveld method, perovskite, bond valence

I. INTRODUCTION

Perovskite-type oxides ABO_3 having transition metals, whose valence in the B site is easily changeable, are interesting and important due to their properties, such as ferroelectricity, piezoelectricity, magnetic and nonlinear optical behavior (Glazer, 1972; Esaka *et al.*, 1996).

The discovery of the magnetoresistance effect in perovskite-type strontium-doped lanthanum manganite ($La_{1-x}Sr_xMnO_3$) has attracted renewed interest in understanding transport properties of these compounds (Asamitsu *et al.*, 1995, 1996) to use it in a wide range of applications like ethanol sensor (Obayashi *et al.*, 1976), field-sensing (Balcells *et al.*, 1976; Lecoeur *et al.*, 1997), electrodes of solid oxide fuel cells (Doshi *et al.*, 1994; Ohno *et al.*, 1983), among others. The substitution of La^{3+} ions by Sr^{2+} results in a transition from antiferromagnetic insulating state to a ferromagnetic metallic state with an $Mn^{3+}-Mn^{4+}$ mixed valence state responsible for the mobile charge carriers. In this article we present the powder diffraction data and the Rietveld and bond valence crystal structure analysis of $La_{0.65}Sr_{0.35}MnO_3$, which sample was obtained from an alternative method based on oxygen raising solid state oxidation reaction without oxygen atmosphere flux.

II. EXPERIMENT

Samples of $La_{0.65}Sr_{0.35}MnO_3$ were prepared through the standard ceramic procedure from stoichiometric mixtures of Mn_2O_3, La_2O_3, and SrO_2, fired at 1300 °C for 16 h with intermediate grinding. The lanthanum oxide was previously heated at 800 °C for 4 h to remove possible adsorbed carbon dioxide and water. The strontium peroxide, strategically used as an *in situ* oxidizing agent (Marques *et al.*, 2001), was weighed and mixed immediately before the thermal treatment to prevent its decomposition.

Powder X-ray data were collected using a SIEMENS D5000 diffractometer with copper radiation monocromatized by a graphite crystal. The diffractometer conditions were set at 40 kV and 30 mA. Other data collection conditions and results are summarized in Table I. The crystal structure was refined by the Rietveld method (Rietveld, 1969) using X-ray powder diffraction data and the Rietveld refinement program DBWS-9807A, which is an updated version of the program DBWS-9411 (Young *et al.*, 1995). The crystal structure of the strontium manganite was refined in the hexagonal setting with 6 unit formulas per unit cell. The initial crystal structure parameters were that given by Alonso (Alonso *et al.*, 1997). In the hexagonal setting, La and Sr are fixed at 6a site (0, 0, $\frac{1}{4}$) (symmetry 32), Mn is fixed at 6b (0, 0, 0) (symmetry –3) and O is at the 18e site (x, 0, $\frac{1}{4}$) (symmetry -2), with x being refined starting from the value 0.4561. Isotropic atom displacements for all atoms were refined alternating with the parameters for correction of the surface roughness. The La and Sr occupancies were refined and constrained to have their sum equal to 1.0.

The surface roughness correction was applied using the Suortti model below (S_R), with the fitting parameters p and q resulting from the refinement.

$$S_R = 1.0 - pe^{-q} + pe^{-q/\mathrm{sen}\,\theta}.$$

TABLE I. Data collection conditions and refinements results for $La_{0.65}Sr_{0.35}MnO_3$. W is the Wyckoff number. Space group: $R\bar{3}c$.

Sealed tube data: secondary graphite monochromatized Cu-$k\alpha$,
$20 \leqslant 2\theta \leqslant 100°$, $\Delta 2\theta = 0.02°$, $t = 5$ s, $Ik\alpha_2/Ik\alpha_1 = 0.5$,
divergence slit = 2 mm, receiving slit = 0.6 mm.
Analytical correction for surface roughness using the Suortti model.

W		X	Y	Z	Biso	Occ. factor
6	LA+3	0.000 00	0.000 00	0.250 00	0.23(2)	0.639(9)
6	SR+2	0.000 00	0.000 00	0.250 00	0.23(2)	0.361(9)
6	MN+3	0.000 00	0.000 00	0.000 00	0.07(4)	
18	O−1	0.541 5(8)	0.000 00	0.250 00	0.7(1)	

$a = 5.5032(1)$ $c = 13.3675(4)$ $V = 350.60(2)$ Å^3,
$\rho_x = 6.349$ g cm^{-3}
$p = 0.938$, $q = 0.024$
$R_p = 11.05$ $R_{wp} = 16.80$ $S = 1.32$ $R_B = 3.20$

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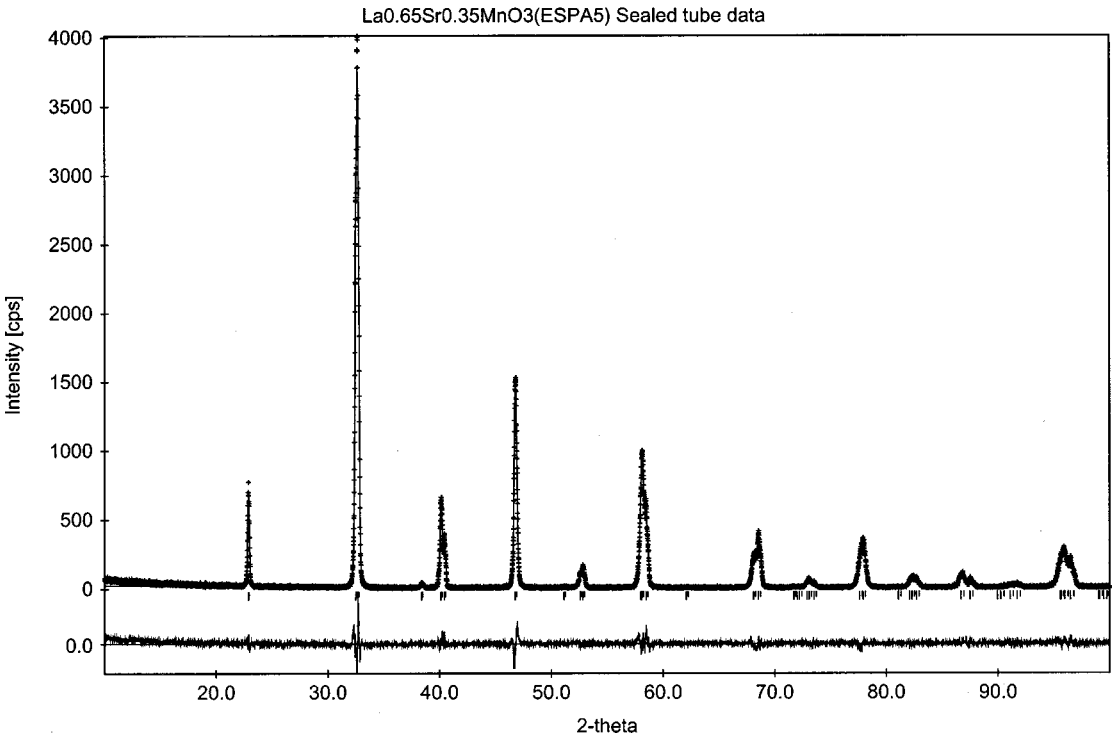

Figure 1. Rietveld plot for the $La_{0.67}Sr_{0.33}MnO_3$.

The background was fitted to a polynomial with six parameters being refined. The pseudo-Voigt function (Young and Wiles, 1982) was used to fit the peak profile and all the full width at half maximum and shape parameters being refined. The refinements were considered completed when all parameters shift were less than 10% of their respective standard deviations.

III. RESULTS AND DISCUSSION

Figure 1 shows the Rietveld plot at the end of the refinement and Table I also shows the refinement results. In the crystal structure of $La_{0.65}Sr_{0.35}MnO_3$, the lanthanum atom is coordinated by nine oxygen atoms. The Mn atom is coordinated by six oxygen atoms forming an irregular octahedra (trigonal anti-prism). Figure 2 shows the coordination polyhedra for the Mn and La/Sr, and a perspective view of the crystal structure of the lanthanum strontium manganite.

The interatomic distances are listed in Table II together with the interatomic distances for some rhombohedral lanthanum manganites found in the literature (VanRoosmalen *et al.*, 1994; Habekost *et al.*, 1994; Ferris *et al.*, 1995). The mean interatomic distance from La to all oxygen of the polyhedra is 2.68 Å in this work while it is around 2.62 Å for the other cases. According to Shannon (1976), for coordination number (CN) equal to 9, the Sr^{2+} and La^{3+} ionic radius are

TABLE II. Interatomic distances and bond valence for the manganite, calculated with the Rietveld refinements with conventional X-ray diffraction data.

		This work[a]	H1994[b]	VR1994[c]	F1995[d]
Unit cell	*a* (Å)	5.5032(1)	5.529	5.528	5.532
	c (Å)	13.3675(4)	13.363	13.327	13.337
	Volume (Å^3)	350.60(2)	353.78	352.69	353.47
6 bonds	La/Sr–O	2.746(4)	2.774	2.774	2.776
3 bonds	La/Sr–O	2.524(4)	2.303	2.303	2.305
6 bonds	Mn–O	1.954(4)	1.998	1.998	1.999
		Bond valence			
La/Sr site	Experimental	2.31	3.06	3.12	3.09
	Nominal[e]	2.36	2.79	2.85	2.84
Mn site	Experimental	3.48	3.15	3.00	2.97
	Nominal[e]	3.36	3.33	3.15	3.17

[a] $(La^{3+}_{0.639}Sr^{2+}_{0.361})(Mn^{3+}_{0.639}Mn^{4+}_{0.361})O_3$.
[b] Habekost *et al.* (1994). $La_{0.93}MnO_3$.
[c] Van Roosmalen *et al.* (1994). $La_{0.95}Mn_{0.95}O_3$.
[d] Ferris *et al.* (1995). $La_{0.945}Mn_{0.945}O_3$.
[e] Nominal weighted valence.

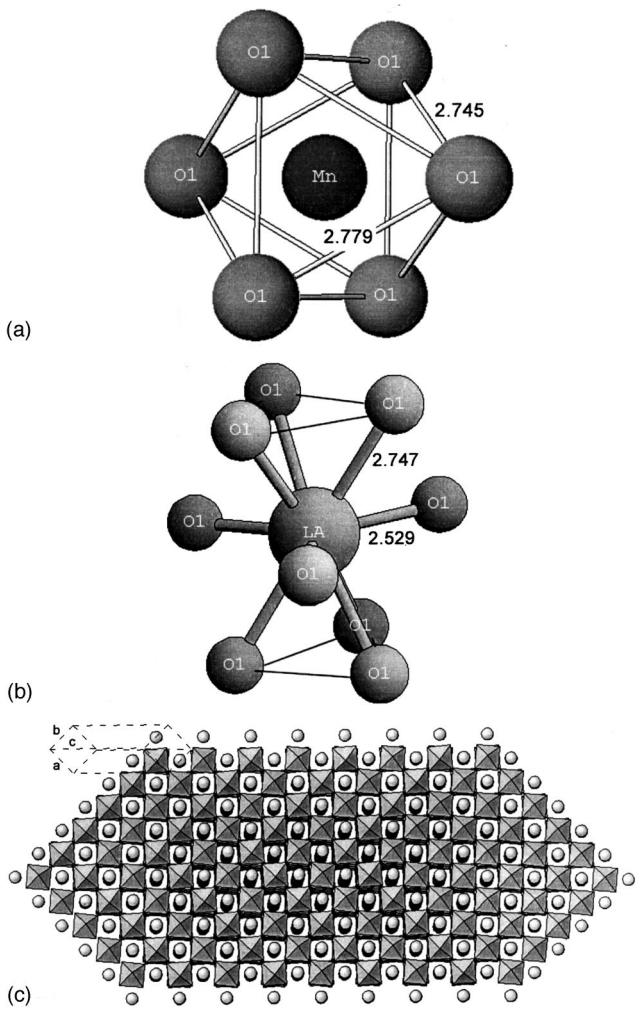

Figure 2. (a) Coordination polyhedras for Mn(CN=6), (b) for La(CN =9) with some interatomic distances, (c) perspective view of the lanthanum strontium manganite and the unit cell.

1.31 and 1.216 Å, respectively. That can explain the increase in the mean interatomic distance for La–O. The decrease in the Mn–O interatomic distance can be explained if the Mn valence changes from 3+ to 4+. The ionic radii for them are 0.645 and 0.530 Å, respectively. The ratio of Mn^{4+}/Mn^{3+} in the structure should be equal to the refined ratio of Sr^{2+}/La^{3+} to maintain the charge balance. Based upon these assumptions the unit formula is then $(La^{3+}_{0.64}Sr^{2+}_{0.36})(Mn^{3+}_{0.64}Mn^{4+}_{0.36})O_3$.

The bond valence (Brown and Altermatt, 1985) for La/Sr and Mn sites were then computed supposing the above-noted chemical unit formula. For comparison it was also calculated with literature data.

The atomic valence V_i of an atom i is defined as the sum of the bond valences v_{ij} of all the bonds from atom i to atoms j,

$$\sum_j v_{ij} = V_i .$$

The most commonly adopted empirical expression for the bond valence v_{ij} as a function of the interatomic distance d_{ij} is

$$v_{ij} = \exp[(r_0 - d_{ij})/B],$$

TABLE III. Intensity data after the Rietveld refinement for the lanthanum strontium manganite.

SG: $R\bar{3}c$, number 167		$Z=6$	$\rho_x=6.370$ g/cm^3		
λ Cu$K\alpha_1$ 1.5406 Å		$a=5.5032(1)$, $c=13.3675(4)$			
d	*hkl*	*I/Io*	*d*	*hkl*	*I/Io*
3.8788	012	182	1.2928	036	16
2.7361	104	999	1.2868	1010	8
2.3384	113	9	1.2253	128	91
2.2427	202	161	1.1703	226	20
2.2273	006	80	1.1217	404	25
1.9388	024	403	1.1137	0012	12
1.7315	116	37	1.0898	321	1
1.5848	214	258	1.0787	232	5
1.3673	208	96	1.0738	2110	6
1.3058	119	1			

where the parameter B is commonly taken to be an "universal" constant equal to 0.37 Å (Brown and Altermatt, 1985). Values of the reference distance r_0 are tabulated for various pairs of atoms (Brown and Altermatt, 1985).

The nominal valences were calculated considering the valence and fraction of each ion for each cation site. The results are also listed in Table II.

In this work it was observed that the bond valence for the La/Sr site is smaller than its nominal value, indicating that the bond strength between the oxygen and the La/Sr is weak and the cations are rattling at the La site. For the Mn atom, the bond valence is bigger than the nominal value indicating that the bond strength between the oxygen and Mn cations is strong. For all cases in the literature the La and Mn bond valence are, respectively, bigger and smaller than the corresponding nominal value. That suggests that the initial inclusion of Sr on the La site in the manganite is only possible at high temperatures. Once the inclusion process starts, the bond valence tends to decrease and new ions could go to the La site at temperatures progressively lower.

The intensity data after the Rietveld refinement are listed in Table III.

IV. CONCLUSIONS

The XRD pattern of single-phase polycrystalline $La_{0.65}Sr_{0.35}MnO_3$ has been obtained. The bond valence suggests that the initial inclusion of Sr on the La site in the manganite is possible only at high temperatures.

ACKNOWLEDGMENTS

The authors acknowledge FAPESP, CNPq, and Fundunesp for financial support.

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