Acta Chemica Scandinavica, 1994: 48: 377–381
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Neutron and X-Ray Powder Diffraction Studies of Lanthanum Manganite, a Nonstoichiometric Perovskite

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Habekost, S., Norby, P., Jørgensen, J. E. and Lebech B., 1994. Neutron and X-Ray Powder Diffraction Studies of Lanthanum Manganite, a Nonstoichiometric Perovskite. – Acta Chem. Scand. 48: 377–381 © Acta Chemica Scandinavica 1994.

The defect structure of a hexagonal perovskite-type lanthanum manganite was studied using Rietveld refinement of powder diffraction data. The nominal composition of the sample was $La_{0.85}Mn_{1.00}O_{3\pm\delta}$. The structure was refined using simultaneous refinement of two sets of neutron diffraction data and one set of X-ray diffraction data in order to combine the advantages of using different types of radiation and different wavelengths. A precise determination of the occupancies of La and Mn is difficult owing to a very strong correlation between occupancies and temperature factors. These difficulties are discussed based on a series of models using various constraints on the temperature factors. It is concluded that the manganese and oxygen sublattice in the lanthanum manganite is fully occupied, whereas vacancies are present in the lanthanum sublattice.

In recent years undoped and doped nonstoichiometric lanthanum manganites (doped with e.g. Sr and Ca) have been investigated with great interest, especially because these compounds are potential cathode materials for solid oxide fuel cells (SOFC).[1–6] At present the oxygen stoichiometry and oxygen-ion diffusion in lanthanum manganites is being studied. Knowledge of the defect structure of these materials is very important in order to understand the physical properties.

Lanthanum manganites have distorted perovskite-type structures.[7–15] Tofield and Scott[7,8] studied the defect structure of an oxidized sample of hexagonal lanthanum manganite using powder neutron diffraction. A defect structure was proposed from refinement using 19 reflections in the powder diagram.

Recently van Roosmalen *et al.*[15] studied the defect chemistry of $LaMnO_{3\pm\delta}$, and they propose a new defect model to describe the oxygen deficiency in those perovskite-type oxides.

Lanthanum manganites with manganese in excess or lanthanum in deficit are also interesting, as the defect structure of these materials influences the electrocatalytic properties of the materials.

In the present work a sample of microcrystalline lanthanum-deficient lanthanum manganite, with nominal composition $La_{1.00}Mn_{1.18}O_{3.27\pm\delta}$, was synthesized. Powder diffractograms were obtained by both X-ray and neutron diffraction. The structure of the sample was refined by the Rietveld method, using simultaneous refinement of X-ray and neutron powder data, thereby combining the advantages of both experimental techniques. Oxygen has a large scattering factor for neutrons, and the neutron scattering length for Mn is negative. In order to determine reliable occupancies using structure refinement it is important to consider the significant correlation between temperature factors and occupancies. It was our hope that by using simultaneous refinement of X-ray and neutron diffraction data, it would be possible to reduce the effect of this correlation.

Experimental

Preparation of the compound. The compound was made by a modified Pechini method.[17] The water content of the starting chemicals $La(NO_3)_3 \cdot 6H_2O$ (Ventron, pure) and $Mn(NO_3)_2 \cdot 2.25\ H_2O$ (Riedel-de Haën, pure) was determined by thermogravimetry on a SETARAM TG/DTA 92 thermobalance. The sample was made by dissolving quantitative amounts of the nitrates in a mixture of ethylene glycol and citric acid. The molar ratios between the metal nitrates and the citric acid were approximately 1 to 10.

In this synthesis 7.447 g of $La(NO_3)_3 \cdot 6H_2O$ (0.017 mol), 5.0202 g $Mn(NO_3)_2 \cdot 2.25H_2O$ (0.02 mol),

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40 g citric acid (0.208 mol) and 50 g ethylene glycol (0.58 mol) were used.

The solvent in excess was removed by heating and the remaining black-brownish resin was calcined at 700°C for 36 h in order to remove the organic components. Sintering for 24 h at 1100°C in air gave the final product. The material was obtained as a black powder with good crystallinity.

The lattice constants were determined from an X-ray diffractogram recorded on a Siemens D5000 powder diffractometer with Cu$K\alpha_1$ radiation and a primary Ge monochromator. All lines (except four weak lines which could be attributed to Mn_3O_4) could be indexed based on a hexagonal cell with $a = 5.5248(2)$ and $c = 13.3539(5)$ Å. The program CELLKANT[18] was used in refining the unit-cell parameters from observed d-spacings.

Diffraction studies. Several sets of powder diffraction data at room temperature were collected for structure refinement. Two powder neutron diffraction data sets of the sample were measured using the multi-detector powder diffractometer at Risø National Laboratory.[19] For one set of data (Fig. 1, histogram 1) the 711 reflection from the Ge monochromator crystal was used for producing a monochromatic neutron beam of wavelength 1.1125 Å. Another set of powder data (Fig. 1, histogram 2) was collected at $\lambda = 2.3969$ Å using the Ge(311) reflection. The directions of the incident and scattered beams were defined by Soller collimators of angular divergence 10 minutes of arc. The powder was placed in a 9 mm cylindrical vanadium container. The two sets of powder data were measured in the 2θ range 6.00–111.78° and 15.00–120.78° (max. $\sin\theta/\lambda = 0.744$), respectively, in steps of 0.053° in 2θ. The calculated number of reflections in these ranges are 238 and 16, respectively.

X-Ray powder data (Fig. 1, histogram 3) were collected on an automated Phillips PW1049/10 diffractometer.[20] The data were collected from 15 to 110° in 2θ (max. $\sin\theta/\lambda = 0.547$, calculated number of reflections 104) in Bragg–Brentano geometry using a 1° divergence slit and a step size of 0.02°. Cu$K\alpha_1$ radiation was selected by a curved Ge(111) monochromator mounted in the diffracted beam.

The four weak lines not belonging to the hexagonal phase, which were observed in the X-ray diffraction pattern, were identified as Mn_3O_4. In the neutron diffraction patterns used for the refinements weak reflections from Mn_3O_4 were visible too.

The Rietveld structure analysis[21] was performed using the program GSAS.[22] The following neutron scattering lengths were used in the calculations: $b(\mathrm{La}) = 8.27$, $b(\mathrm{Mn}) = -3.73$ and $b(\mathrm{O}) = 5.81$ fm.

The lanthanum, manganese(III) and manganese(IV) contents in the sample were determined by chemical analysis. The oxygen content was then calculated from these determinations. Details of the procedure for the chemical analyses will be published later.[23]

Results and discussion

It was evident from the indexing of the powder pattern obtained at the Siemens D5000 powder diffractometer that the investigated sample had hexagonal distorted perovskite-type structure. According to the work of Tofield and Scott,[7] the hexagonal distortion is due to rotation of the MnO_6 octahedra about the trigonal $< 1\ 1\ 1 >$ axis of the cubic perovskite unit cell. Furthermore, the MnO_6 polyhedron deviates slightly from a perfect octahedron (see Table 2 later).

The crystal structure was refined in space group R-3c using the hexagonal setting. The choice of spacegroup was based upon the work of Tofield and Scott.[7] Cell parameters from the unit-cell refinement with CELLKANT together with atomic parameters derived from Ref. 7 were used as starting parameters in the refinement. In the hexagonal setting La is in site 6a (0,0,1/4), Mn in site 6b (0,0,0) and O in site 18e (x,0,1/4). The transformed atomic parameters for oxygen (from Ref. 7) give $x = 0.4476$.

Using powder diffraction to determine small deviations in stoichiometry is a challenge, and care must be taken in the interpretation of the results. It is therefore necessary to obtain powder diffraction data of good quality. In this structure refinement we used on X-ray data set and furthermore two neutron data sets obtained at two different wavelengths. The data set at the long wavelength gives good resolution of the diffraction peaks, but limits the $\sin\theta/\lambda$ range. Using the short wavelength, information is obtained to higher $\sin\theta/\lambda$-values, which is essential in order to determine reliable temperature factors. It is also important to have a well defined background. If the background is wrongly determined at high 2θ-values, the observed intensities will be affected, resulting in an erroneous evaluation of the temperature factors.

The two neutron powder diffractograms and the X-ray powder diffractogram were refined simultaneously using the GSAS-program. In the refinement the instrumental parameters for each data set are refined separately, while the structural parameters are refined using the information from all data sets. The instrumental parameters refined for each powder dataset were zero-point correction, profile parameters (four parameters in the refinement of the Gaussian profile used in the two neutron data set while the pseudo-Voigt profile used in the X-ray data set demanded refinement of 7 parameters), background parameters and scale factors. The refined structural parameters were unit-cell parameters, the x-coordinate for oxygen, occupancies for lanthanum and manganese, and isotropic temperature factors for all atoms. The occupancy for oxygen (N_O was fixed at 3.0 during the refinements.

The nonstoichiometry in the structure may be caused by vacancies at the metal and oxygen in positions and/or by interstitial oxygen.

According to the considerations in the work of Tofield and Scott[7] the nonstoichiometry could be due to oxygen

at interstitial positions. There were only two interstitial positions possible in the structure: Site (0, 0, 1/8) and site (1/3, 1/6, 1/6), both in the hexagonal description. A refinement with oxygen situated on these two positions gave

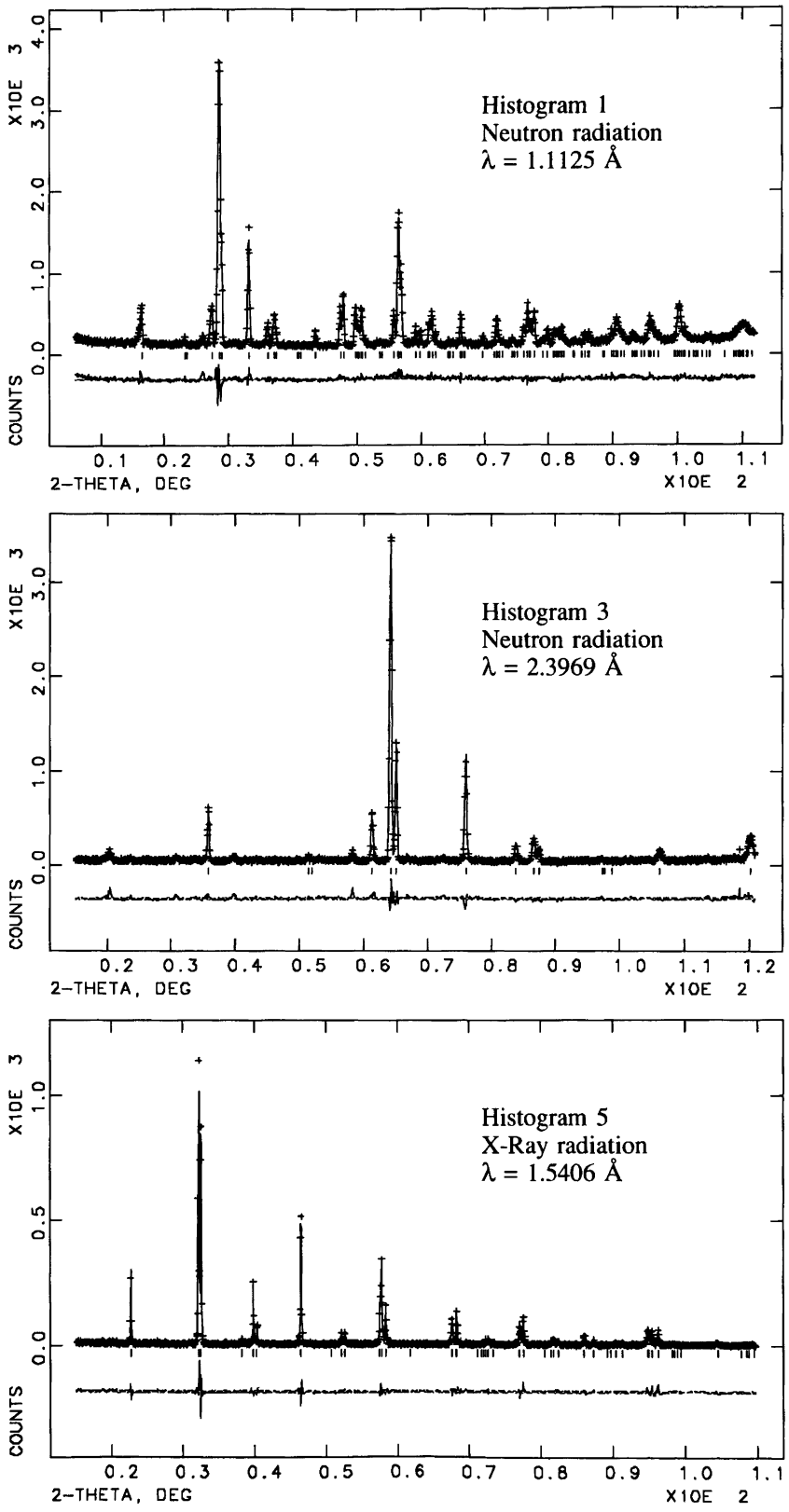

Fig. 1. Observed (++++), calculated (-----) and difference powder diffraction profiles of the initial refinement.

Table 1. Crystallographic parameters of $LaMnO_{3\pm\delta}$.[a]

Parameters	Model 1, $U_{La}=0.4\ U_{Mn}$	Model 2, $U_{La}=U_{Mn}$	Model 3, $U_{La}=2\ U_{Mn}$	Unconstrained refinement
N_{La}	0.897(5)	0.918(6)	0.929(6)	0.937(6)
N_{Mn}	1.033(8)	1.020(7)	1.004(7)	0.975(8)
N_o	3.0	3.0	3.0	3.0
Formula[b]	$La_{0.87}Mn_{1.00}O_{2.90}$	$La_{0.90}Mn_{1.00}O_{2.94}$	$La_{0.93}Mn_{1.00}O_{2.99}$	$La_{0.96}Mn_{1.00}O_{3.08}$
100 U_{iso}, La	0.38(2)	0.72(3)	0.90(4)	1.08(5)
100 U_{iso}, Mn	0.96(5)	0.72(3)	0.45(2)	0.01(7)
100 U_{iso}, O	1.38(4)	1.36(4)	1.34(4)	1.34(4)
$wR_{p,\ hist.1}$[d]	0.105	0.104	0.103	0.103
$wR_{P,\ hist.3}$[d]	0.170	0.170	0.171	0.171
$wR_{P,\ hist.5}$[d]	0.314	0.309	0.306	0.304
$wR_{P,\ tot}$[c]	0.159	0.157	0.157	0.156
$R_{P,\ hist.1}$[c]	0.081	0.080	0.080	0.080
$R_{P,\ hist.3}$[c]	0.123	0.123	0.124	0.124
$R_{P,\ hist.5}$[c]	0.214	0.210	0.208	0.207
$R_{P,\ tot}$[f]	0.106	0.105	0.105	0.105
$D_{dw,\ hist.1}$[f]	0.896	0.918	0.923	0.923
$D_{dw,\ hist.3}$[f]	0.925	0.925	0.924	0.921
$D_{dw,\ hist.5}$[f]	1.396	1.434	1.454	1.468
d_{dw}[f]	1.124	1.145	1.152	1.155
χ_{red}[e]	2.004	1.963	1.945	1.936

[a] Data from model 3: $a=5.5289(2)$, $c=13.3628(6)$ Å, $V=353.76(4)$ Å^3. $x(O)=0.4506(2)$. Temperature factors are given in Å^2. [b] Normalized to $N_{Mn}=1.00$.

[c] $R_p = \dfrac{\Sigma\,|I_o - I_c|}{\Sigma\,I_o}$ [d] $wR_p = \left(\dfrac{\Sigma\,w(I_o - I_c)^2}{\Sigma\,[wI_o^2]}\right)^{1/2}$ [e] $\chi^2 = \dfrac{\Sigma\,w(I_o - I_c)^2}{(N_{obs} - N_{var})}$

For a description of the Durbin–Watson factor, D_{dw}, see Ref. 25.

occupancies of 0.006(5) and −0.003(4), respectively, showing that no interstitial oxygen is present. This conclusion is in agreement with the findings of Tofield and Scott.[7]

An initial refinement using the three data sets was made with no constraints on the temperature factors. The temperature factor of Mn refined to an unacceptably low value (Table 1), indicating a high correlation between occupancies and temperature factors.

After the initial refinements three models were tested in which different constraints were put on the temperature factors.

The constraint between the temperature factors of lanthanum and manganese in Model 1 was $U_{La}=0.4\ U_{Mn}$. This constraint was suggested after considering the relationship between the atomic mean-square displacement $<u^2>$ and the atomic mass in the Debye approximation.[24] In the Debye approximation the magnitude of the mean-square atomic displacement $<u^2>$ is inversely proportional to the mass of the atom. The ratio between the atomic weight of La and Mn is 138.91/54.938 = 2.528, suggesting that $<u^2_{La}>$ is constrained to be equal to $0.4<u^2_{Mn}>$. This calculation does not take into account effects from interactions due to coordination in the crystal structure. As the lanthanum manganite perovskite may be seen as a fairly rigid framework built from MnO_6 octahedra, with lanthanum more softly coordinated to oxygen, the thermal displacement parameters will be effected by this structural construction.

In Models 2 and 3 the constraints on the temperature factors were based upon a search on earlier structure determinations of different ABO_3 perovskites in which the ratio between the masses of the A and B metal ions were comparable with the ratio between the masses of La and Mn. The literature search showed that most of the ratios between the temperature factors of the A and B ions were supposed/estimated to be between 1:1 and 2:1. In Model 2 the ratio between the temperature factors of La and Mn was therefore constrained to 1:1 while this ratio in Model 3 was constrained to be 2:1.

Table 2. Distances (in Å) and angles (in °) in the $LaMnO_{3\pm\delta}$ structure for Model 3.

Mn-O(×6)	1.9652(2)	La-O(×6)	2.7536(2)
La-Mn(×6)	3.3808(2)	La-O(×3)	2.491(1)
La-Mn(×2)	3.3407(2)	La-O(×3)	3.038(1)
∠O-Mn-O(×6)	88.947(5)	∠O-La-O(×6)	61.232(6)
∠O-Mn-O(×6)	91.053(5)	∠O-La-O(×3)	113.05(3)
∠O-Mn-O(×3)	180	∠O-La-O(×6)	84.31(3)
∠Mn-O-Mn	164.02(7)	∠O-La-O(×3)	168.61(5)
∠O-La-O(×3)	126.21(3)	∠O-La-O(×6)	123.48(2)
∠O-La-O(×6)	63.10(2)	∠O-La-O(×3)	120

In Table 1 the crystallographic parameters of both the initial refinement and the refinement of the three models are shown, while the refined distances and angles are shown in Table 2. The final Rietveld plot of the initial refinement is shown in Fig. 1.

The results in Table 1 show a clear correlation between the calculated occupancy and the temperature factor of lanthanum. Similarly the calculated occupancy of manganese decreases with the decreasing temperature factor. This is in agreement with the expected correlation between occupancies and temperature factors. By the chemical analyses the total content of manganese is determined. It is not possible by these chemical analyses to distinguish between the manganese belonging to the lanthanum manganite and the manganese belonging to the Mn_3O_4 impurity in the sample. By a quantitative analysis by X-ray diffraction on a Siemens D5000 powder diffractometer the amount of Mn_3O_4 was estimated as 2 wt% in the sample. The result of the chemical analyses gave the composition $La_{0.88}Mn_{1.00}O_{2.91}$, normalized after the content of manganese. When taking into account an amount of 2 wt% Mn_3O_4 in the sample, a recalculation of the results of the chemical analyses gives a composition of the lanthanum manganite of $La_{0.94}Mn_{1.00}O_{3.01}$.

Judged by the temperature factors and the chemical composition of the sample, we believe that the most probable results are given by Model 3, which gave the composition $La_{0.93}Mn_{1.00}O_{2.99}$. However, it should be remarked that Models 1, 2 and 3 all show that the Mn sublattice is fully occupied and vacancies are present in the La sublattice.

With both the X-ray data set and the two neutron data sets included in the structure refinement, the progress of the refinement is improved as compared to refinements of the individual diagrams. However, a high correlation between the occupancies and the temperature factors is still observed. We would expect that neutron data sets obtained with better counting statistics would give more realistic temperature factors.

Acknowledgment. We thank *Statens Teknisk Videnskabelige Forskningsråd* in Denmark for making these investigations possible by offering S. H. a grant for her Ph.D. work. Research assistant I. G. Krogh Andersen is thanked for the chemical analyses of the sample. The Albani Brewery Foundation, Odense, Denmark, is thanked for their donations to the Siemens D5000 powder diffractometer.

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Received August 2, 1993.