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The perovskite system $La(Mg_{2/3}Nb_{1/3})O_3$ II. A neutron powder diffraction study

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Abstract

The crystal structure of the perovskite compound, lanthanum magnesium niobate [$La(Mg_{2/3}Nb_{1/3})O_3$ (LMN)] has been determined at 300 K by means of neutron powder diffraction. Subsequent Rietveld refinement indicates that the crystal structure has monoclinic $P2_1/n$ symmetry, which is relatively uncommon for oxide perovskites, ABO_3. An analysis of the structural data obtained reveals that this space group is uniquely capable of accommodating both BO_6-octahedral tilting and cationic ordering. Consideration is also given to the likelihood of further compositions adopting this symmetry, with some suggestions for future work on the pseudo-binary system $Pb(Mg_{1/3}Nb_{2/3})O_3$–$La(Mg_{2/3}Nb_{1/3})O_3$ (i.e. PMN–LMN or, equivalently, PLMN). © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

As reviewed in the accompanying paper,[1] previous speculations concerning the crystal structure of the perovskite compound lanthanum magnesium niobate [$La(Mg_{2/3}Nb_{1/3})O_3$ (LMN)] have considered it likely to exhibit rhombohedral symmetry, belonging to space group R3.[2] Whereas the arguments presented were based on the observed splitting of the (222) powder X-ray diffraction peak (referred to simple cubic axes), our work has revealed the presence of additional reflections in the X-ray diffraction pattern, which are incompatible with rhombohedral symmetry.[1] Thus the existence is suggested either of a perovskite phase of lower symmetry or of phases additional to the main perovskite phase. In order to resolve which of these alternatives applies, use is made here of the technique of neutron powder diffraction, since the observed Bragg peak intensities are much more sensitive to the positions of the oxygen ions in the crystal structure than is the case for X-ray scattering. It is precisely these anions which play a crucial rôle in determining the symmetry of the system.[3] Furthermore, through subsequent use of the Rietveld refinement method, the prospect is raised of deriving a full structural model of LMN, incorporating unit cell parameters and atomic coordinates. Information of this kind is essential for resolving key issues in the structural chemistry of perovskites, such as the relative contributions of octahedral tilting and cationic ordering in giving rise to 'superlattice reflections'.[4]

Apart from the importance of LMN as a chemical intermediate in the synthesis of $Pb_{1-x}La_x(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ (PLMN) solid solution ceramics,[5] it also has a structural significance, in that it corresponds to one end of the pseudo-binary system PMN-LMN. As recent work has shown that the compound at the other end, i.e. $Pb(Mg_{1/3}Nb_{2/3})O_3$, exhibits rhombohedral $R3m$ symmetry,[6] the sequence of structural phase transitions by which the symmetry changes from polar

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rhombohedral ultimately to the symmetry reported here, as x increases from 0 to 1, is worthy of further investigation, with work on this issue currently in progress.[7]

Although the occurrence of monoclinic symmetry in perovskites is comparatively uncommon, it has, for example, been reported for the system $La_{1-x}Sr_xMnO_{3+\delta}$ ($x \leqslant 0.01$) when synthesized at oxygen partial pressures less than 2×10^{-3} atm.[8]

2. Method

Single-phase LMN powders were prepared by an optimised two-step calcination method involving columbite-like $MgNb_2O_6$ intermediates.[1] Neutron powder diffraction (NPD) data were collected at the Swedish Research Reactor R2 in Studsvik, by means of a Huber two-circle diffractometer with an array of 35 ^3He detectors. The monochromator system used two parallel copper crystals in (220)-mode, giving rise to a wavelength of 1.470 Å. The neutron flux at the sample position was approximately 10^6 neutrons cm^{-2} s^{-1} Data were collected at 300 K from powdered samples of LMN (approximately 5 g) loaded into a vanadium container, with detector intensities statistically analysed and summed. Corrections for absorption effects were subsequently carried out in the Rietveld refinements, utilising the empirical value $\mu R = 0.0645$ cm^{-1} .The step-scan covered the 2θ range 4–140° with step-size 0.05°.

Diffraction datasets were refined by the Rietveld method using FULLPROF software,[9] with neutron scattering lengths as follows: La, 8.24; Mg, 5.38; Nb, 7.05; O, 5.81 fm. Diffraction peaks were quantified by a pseudo-Voigt function, with a peak asymmetry correction applied at angles below 35° 2θ. The background was described by a six parameter polynomial. Initial starting models were set up by assuming a random distribution of Mg and Nb atoms over the octahedral sites, with the occupancy factors constrained during the refinements to maintain electrical neutrality. Partly ordered distributions were also investigated by fixing oxygen positions and allowing just the scale factor, thermal parameters and Mg/Nb occupancy factors to vary. Oxygen occupancies were subsequently refined in order to check for deviations in stoichiometry. Each structural model was refined to convergence, with the best result selected on the basis of agreement factors and stability of the refinement.

3. Results

Rietveld refinements of the neutron diffraction data indicated a single phase with cationic and anionic stoichiometry close to the idealised formula of $La(Mg_{2/3}Nb_{1/3})O_3$ (Fig. 1). Initial attempts to refine a structural model in space group R3, as suggested by earlier work[2], met with little success. The best agreement between calculated and experimental diffraction patterns could be

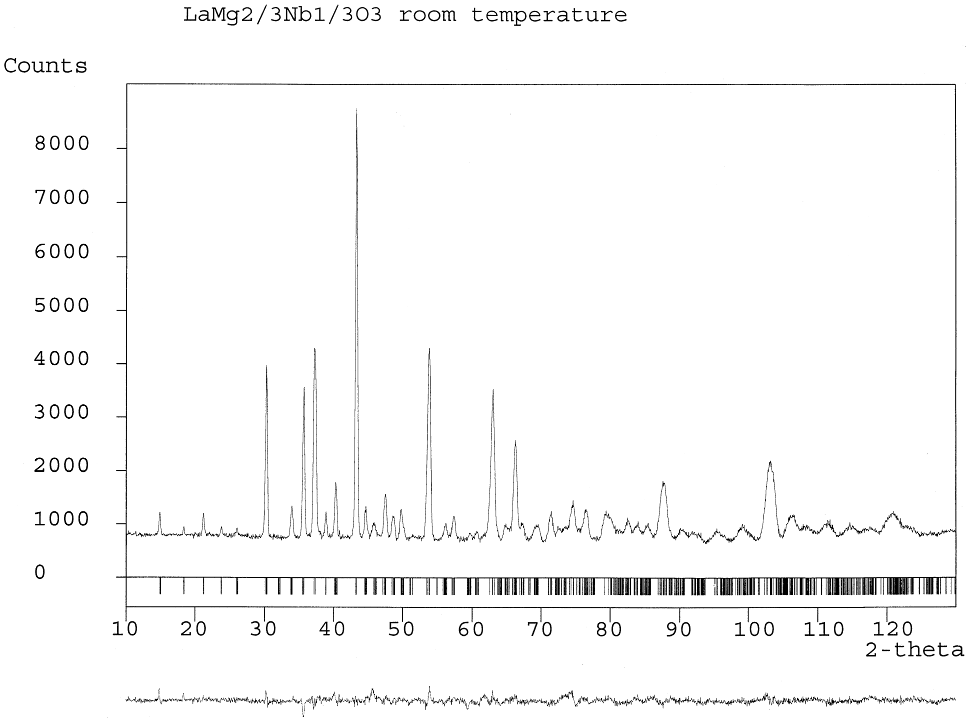

Fig. 1. Rietveld profile-fitting for LMN at 300 K.

obtained for monoclinic symmetry in s.g. $P2_1/n$. The final agreement factors obtained in the refinement were $R_p=3.56$, $R_{wp}=4.69$, $R_{exp}=3.19$, $R_B=4.81$. Closest agreement was obtained by assigning Mg to 2*a* and 2*b* sites and Nb to 2*c* sites, together with random occupancy of the 2*d* sites by both Nb and Mg atoms (Table 1). Refined oxygen occupancies were found to be within 1% of expected values. Thus the sample investigated here is highly crystalline and very close to the intended stoichiometry.

A grasp of the structural essentials may be gained from Fig. 2, where the tilting of the MgO_6 and NbO_6 octahedra is readily apparent, together with the distribution of Mg and Nb ions over B sites.

4. Discussion

A rapid quantitative appraisal of the features of the structural solution may be carried out by calculating the volumes of the LaO_{12} and MgO_6/NbO_6 cation coordination polyhedra, as quoted in the column headed V_c in Table 1. Since the mean ratio of the LaO_{12} to MgO_6/NbO_6 volumes (i.e. V_A/V_B) is equal to 4.625, and a polyhedral ratio of this order of magnitude is more frequently associated with the widely occurring *Pnma* symmetry,[3] it follows that the observed $P2_1/n$ symmetry is necessarily connected with the different structural requirements of the Mg^{2+} and Nb^{5+} ions. Since the corresponding six-fold-coordinated ionic radii for these ions are 72 and 64 pm, respectively, there will be a natural tendency for Mg^{2+} ions to occupy larger octahedral sites than Nb^{5+} ions. Under $P2_1/n$ symmetry, there is flexibility in the volumes of the individual BO_6 octahedra, thereby permitting a variety of different cation ordering patterns over B-sites.

Strong support for the proposed structure is given by the calculated polyhedral volumes of the BO_6 octahedra. Since Mg^{2+} ions have larger radii than their Nb^{5+} counterparts, it is reasonable that the two sites occupied solely by Mg have the largest volumes, i.e. Mg(1) and Mg(2), with volumes 12.09 and 11.26 Å^3, respectively. Similarly, it is appropriate that the smallest BO_6-volume corresponds to the only site which is solely occupied by Nb^{5+} ions, i.e. Nb(1), for which $V_C=10.89$ Å^3. The 2*d* sites, which are occupied on average by (0.68 Mg, 0.32 Nb) have intermediate BO_6-volumes of 11.01 Å^3, as would be expected.

It is also to be noted that the two symmetry-independent lanthanum sites, i.e. La(1) and La(2) have AO_{12} polyhedral volumes which differ from each other. As is often the case in perovskites,[3] the larger LaO_{12} polyhedron is associated with a greater off-centre displacement, d_A, of the La ion: $d_A=0.321$ Å for the La(1) ion compared to a value of 0.165 Å for the La(2) ion.

A more fundamental understanding of *how* monoclinic $P2_1/n$ symmetry is able to accommodate cations with widely differing size requirements may be gained by use of the method which has been proposed for the global parameterization of perovskites.[3] According to this, there are 28 structural degrees of freedom (dof) for a unit cell with this symmetry. Four are associated with variable unit cell parameters (*a, b, c, β*), with 24 associated with the coordinates of the ions in the unit cell. The breakdown of these is given in Table 1, in the column headed N_f. Since the *x, y* and *z* coordinates of both lanthanum ions can be fixed independently, each ion is associated with three dof. By comparison, all the magnesium and niobium ions are located at special positions, for which *x, y* and *z* are fixed. Hence, $N_f=0$ for these ions. Of particular significance is the presence of six symmetry-independent oxygen ions in the unit

Table 1
Unit cell parameters, symmetry and atomic coordinates of $La(Mg_{2/3}Nb_{1/3})O_3$ at 300 K[a]

Atom	Occupancy factor	Point symmetry	*x*	*y*	*z*	B (pm)	V_C / Å^3	N_f
La(1)	0.94 (1)	4*e*	0.2353 (9)	0.258 (1)	0.2827 (7)	143 (10)	54.54	3
La(2)	0.98 (1)	4*e*	0.2358 (7)	0.255 (1)	0.7584 (8)	79 (8)	50.10	3
Mg(1)	0.94 (3)	2*a*	0	0	0	84 (11)	12.09	0
Mg(2)	1.00 (4)	2*b*	0	0	1/2	34 (13)	11.26	0
Nb(1)	1.01 (4)	2*c*	1/2	0	1/2	48 (12)	10.89	0
Mg(3)	0.68 (2)	2*d*	1/2	0	0	27 (11)	11.01	0
Nb(2)	0.32 (2)	2*d*	1/2	0	0	27 (11)	11.01	0
O(1)	1	4*e*	0.262 (1)	−0.0293 (9)	−0.0516 (9)	62 (8)		3
O(2)	1	4*e*	0.758 (1)	0.4585 (9)	0.0485 (9)	78 (8)		3
O(3)	1	4*e*	0.0400 (8)	0.255 (1)	0.0390 (8)	89 (9)		3
O(4)	1	4*e*	0.475 (1)	0.251 (1)	−0.058 (1)	44 (12)		3
O(5)	1	4*e*	0.0068 (9)	−0.045 (1)	0.2548 (8)	148 (13)		3
O(6)	1	4*e*	0.459 (1)	0.049 (1)	0.2505 (8)	24 (10)		3

[a] Cell parameters: $a=796.55$ (9) pm; $b=794.83$ (5) pm; $c=797.35$ (8) pm; $\beta=90.534$ (4)°; space group $P2_1$/n (no. 14); mean V_A/V_B ratio = 4.625.

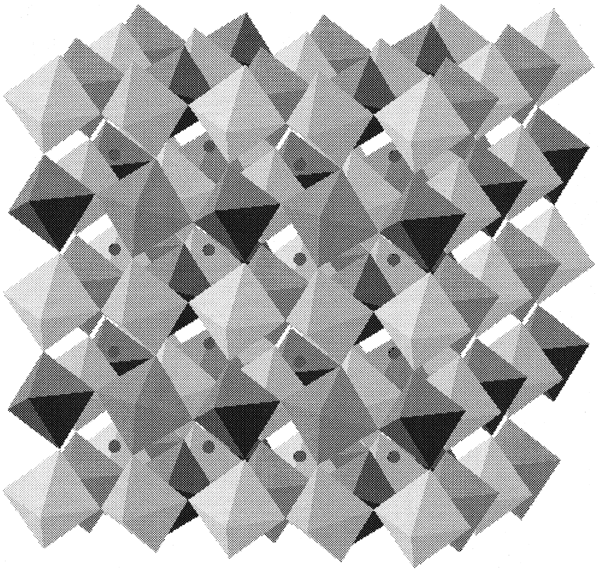

Fig. 2. The proposed structural model of LMN, indicating octahedral tilting and the ordering of Mg2+ and Nb2+ ions over B sites [grey-shading key, in order of increasing brightness: 1, Mg(2) (darkest); 2, Mg(3)/Nb(2); 3, Nb(1); 4, Mg(1) (brightest)].

cell, in general positions. Thus there are three dof for each oxygen ion, making a total of 18 dof which are associated with oxygen ion positions alone. This situation is to be contrasted with the symmetry restrictions governing oxygen ion positions in the more common space group *Pnma*, where there are just five dof connected with oxygen ion coordinates.[3] This difference gives direct insight into the ability of $P2_1/n$ symmetry to accommodate different cation types by adapting the dimensions and orientations of the oxygen octahedra.

An appreciation of the relevance of these considerations to the LMN system may be gained by considering, as described earlier,[3] the octahedral stalk-lengths, s, (i.e. distances between opposite octahedral vertices) and their corresponding angles of tilt, θ, with respect to unit cell axes $\underset{\sim}{a}$, $\underset{\sim}{b}$ and $\underset{\sim}{c}$. These values are summarised in Table 2. Since the angles of intersection of the three stalks of a given octahedron do not deviate significantly from 90°, the octahedral volume, V_B may be approximated by $s_x s_y s_z/6$. Thus, the ability of s_x, s_y and s_z to take on different values for the four symmetry-independent octahedra in space group $P2_1/n$ permits the ordering of ions of differing radii over the B-sites.

Although 24 s_i and θ_i values are quoted in Table 2, a consideration of Fig. 2, together with use of arguments invoked earlier,[3] reveals that there are nine constraints of two general forms:

$$(s_z \sin\theta_z)_{\mathrm{Mg(1)}} = (s_z \sin\theta_z)_{\mathrm{Mg(2)}}$$
$$\text{(plus five similar relationships)} \qquad (1)$$

Table 2
Volumes of BO_6 octahedra, V_B, together with octahedral stalk-lengths s_x, s_y, s_z and corresponding tilt-angles θ_x, θ_y, θ_z[a]

B cation	V_B (Å^3)	s_x (Å)	s_y (Å)	s_z (Å)	θ_x (°)	θ_y (°)	θ_z ($^=$)
Mg(1)	12.09	4.287	4.149	4.126	12.74	12.33	10.10
Mg(2)	11.26	4.227	4.084	3.978	13.92	14.23	10.48
Nb(1)	10.89	3.994	3.994	4.101	14.74	12.82	14.35
Mg(3)/Nb(2)	11.01	3.900	4.114	4.127	14.03	14.12	14.26

[a] s_x represents the length of the octahedral stalk which is oriented most closely with the x-axis direction, with θ_x the angle between this stalk and the x-axis. Comparable meanings may be inferred for the parameters s_y, s_z, θ_y and θ_z.

$$(s_z \cos\theta_z)_{\mathrm{Mg(1)}} + (s_z \cos\theta_z)_{\mathrm{Mg(2)}}$$
$$= (s_z \cos\theta_z)_{\mathrm{Nb(1)}} + (s_z \cos\theta_z)_{\mathrm{Mg(3)/Nb(2)}}$$
$$\text{(plus two similar relationships)} \qquad (2)$$

Eq. (1) convey the periodicity of the structure, with two sets of oppositely tilted octahedra along each axial direction. By comparison, Eq. (2) are concerned with the requirement that the octahedral chains in a given direction, *x, y* or *z* are identical in length. Thus there are 24−9 = 15 dof associated with the s_i and θ_i parameters. This situation is to be contrasted with the more common space group *Pnma*, where there are just five dof. connected with s_i and θ_i parameters. Of the remaining thirteen dof in $P2_1/n$ symmetry, six relate to A-ion coordinates, one to the monoclinic angle β (which fixes the unit cell axes in absolute Cartesian space) and the other six to the orientations of the planes formed by the chains of octahedral stalks, as described earlier.[3]

Finally, it is appropriate to speculate whether monoclinic $P2_1/n$ symmetry is likely to recur for other perovskite compositions of relevance to applications. In essence, this space group provides the flexibility to accommodate both octahedral tilting and cationic ordering. In the particular case of LMN, it may be argued that the degree of ordering is at the maximum extent which is consistent with the stoichiometry and the requirement of full site occupancies. As the B-ion composition of the asymmetric unit, i.e. $4(\mathrm{Mg}_{2/3}\mathrm{Nb}_{1/3}) = \mathrm{Mg}_{2.667}\mathrm{Nb}_{1.333}$ does not permit total ordering of Mg and Nb ions over the four B sites, there is no means by which disorder on one of the B sites (in this case, the *2d* sites) can be avoided.

For other perovskite compositions, it is conceivable that $P2_1/n$ symmetry would offer the potential of complete cationic ordering. One such possibility would be the system $\mathrm{La(Mg_{3/4}W_{1/4})O_3}$, where the significant differences in ionic radii between $\mathrm{Mg^{2+}}$ and $\mathrm{W^{6+}}$ would lead to a strong driving force towards ordering. The existence of two symmetry-independent A-ion sites in the asymmetric unit would also make $P2_1/n$ symmetry a strong candidate for hypothetical mixed A-ion systems such as $(La_{1/2}Bi_{1/2})(Mg_{3/4}W_{1/4})O_3$.

Since our initial work on the pseudo-binary system PMN–LMN, i.e. $Pb_{1-x}La_x(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$ has indicated significant potential for developing a deeper understanding of phase transitions between perovskite phases with differing octahedral tilt geometries, and how these influence dielectric properties,[5,7] it would be interesting to probe the width of the stability field of the structure with $P2_1/n$ symmetry. Since we have already found[7] that this system exhibits a disordered structure with *Pnma* symmetry for $x=0.75$, a cross-over from monoclinic to orthorhombic symmetry is implied in the range $0.75 < x < 1$. Since the differences in B-ion radii suggest that there would still be a strong driving force towards ordering at $x=0.75$, it is likely that the progressive introduction of larger Pb^{2+} ions on to the A-sites destabilises the $P2_1/n$ phase in favour of the *Pnma* alternative.

5. Conclusion

Neutron diffraction studies have provided evidence for monoclinic $P2_1/n$ symmetry in lanthanum magnesium niobate at 300 K. This centrosymmetric space group, which is relatively uncommon for perovskite structures, is capable of accommodating both BO_6 octahedral tilting and ordering of ions over A and B sites. Work is currenly in progress concerning the sintering characteristics and dielectric properties of this compound.[9]

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