

La(Ni<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> by neutron powder  
diffractionJulian R. Tolchard,<sup>a</sup> Marie-Laure Fontaine<sup>b</sup> and Tor  
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Lanthanum nickel niobium trioxide has been synthesized and its structure refined for the first time. It was found to be a member of the family of technologically important 'double perovskites', crystallizing in the monoclinic space group  $P2_1/n$ . The structure is characterized by a strong orthorhombic pseudosymmetry and a concurrent exhibition of both 1:1  $B$ -cation ordering and  $a^-a^-c^+$ -type tilting of the (Ni/Nb)O<sub>6</sub> structural units. Trivalent lanthanum resides on the perovskite  $A$  site, which is strongly distorted owing to the tilting of the (Ni/Nb)O<sub>6</sub> sublattice. Ordering of divalent nickel and pentavalent niobium on the  $B$  sublattice is described in terms of two twofold special positions ( $2c$  and  $2d$ ), with nickel taking almost complete occupancy of the  $2d$  site and the  $2c$  position being occupied by a statistical distribution of nickel and niobium.

## Comment

Complex perovskites of the general stoichiometry  $A(M'_{1-x}M''_x)O_3$  form a broad family of technologically and academically interesting materials. For convenience, the wider family can be split into the general compositions  $A^{2+}(M_{1/3}^{2+}M_{2/3}^{5+})O_3$ ,  $A^{3+}(M_{1/2}^{2+}M_{1/2}^{4+})O_3$  and  $A^{3+}(M_{2/3}^{2+}M_{1/3}^{5+})O_3$ , between which may exist regions of solid solubility. Although nominally all perovskite in structure, these may differ substantially in the exhibition of a number of structural modifications, most notably cation ordering and tilting of the  $MO_6$  octahedral units. Members of the family that show  $B$ -site ordering are of particular technological importance, finding widespread application in microwave electronics owing to their favourable dielectric loss or quality factors  $Q$  (Reaney & Iddles, 2006). For this reason, the  $A^{2+}(M_{1/3}^{2+}M_{2/3}^{5+})O_3$  and  $A^{3+}(M_{1/2}^{2+}M_{1/2}^{4+})O_3$  systems have attracted the greatest interest as they, respectively, correspond to stoichiometries ideal for 1:2 and 1:1 ordering of the  $B$  sublattice. It is generally the case that systems showing 1:2 ordering have the highest  $Q$  factors,

making such materials extremely attractive for telecommunications applications. Unfortunately, this form of ordering is relatively rare and extremely sensitive to composition. Even small deviations from the ideal 1:2  $B$ -cation ratio cause the breakdown of long-range ordering. The 1:1 rock-salt-type ordering is far more common and relatively insensitive to composition, and whilst these forms do not show the same magnitude of  $Q$  factor as the 1:2-ordered materials, their  $Q$  factors are still very high. In systems with low tolerance factors (Goldschmidt, 1926), such as La(Mg<sub>1/2</sub>Ti<sub>1/2</sub>)O<sub>3</sub> (Lee *et al.*, 2000; Salak *et al.*, 2008) and La(Mg<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> (Paik *et al.*, 1999, 2003), the tilting of the  $MO_6$  octahedra is linked to a negative temperature coefficient of resonant frequency  $\tau_f$ .

Except for La(Mg<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> and La(Mg<sub>2/3</sub>Ta<sub>1/3</sub>)O<sub>3</sub> (Kim & Woodward, 2007), the  $A^{3+}(M_{2/3}^{2+}M_{1/3}^{5+})O_3$  general composition has been very rarely investigated. The syntheses of several compounds of this type have been reported by both Blasse (1965) and Bazuev *et al.* (1986), with the latter reporting the structure of La(Ni<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> in a  $2^{1/2}a_c \times 2^{1/2}a_c \times 2a_c$  orthorhombic supercell of cubic perovskite with unit cell  $a_c$ . As for La(Mg<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub>, a 1:1 ordering of the  $B$  cations is suggested rather than the 2:1 form that the stoichiometry would suggest, but no further structural data were provided. In this communication, we present a detailed structural analysis of this compound.

A fitted neutron diffractogram of La(Ni<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> is presented in Fig. 1, and its refined structure is depicted in Fig. 2. La(Ni<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> is confirmed as an example of a  $B$ -site-ordered perovskite with concomitant  $a^-a^-c^+$ -type tilting of the  $MO_6$  octahedral units (Glazer, 1975). The refined unit-cell parameters are close to those described by Bazuev *et al.* (1986), and as with the isostructural La(Mg<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> (Choi *et al.*, 2000),  $\beta$  is close to 90° so the system can be regarded as pseudo-orthorhombic. A high degree of pseudosymmetry is normally observed in such systems, as the lowering of symmetry from orthorhombic to monoclinic does not arise from a distortion of the unit cell from orthogonality, but from the concurrent exhibition of both  $a^-a^-c^+$ -type octahedral tilting and cation ordering, which cannot be described in orthorhombic symmetry (Howard *et al.*, 2003).

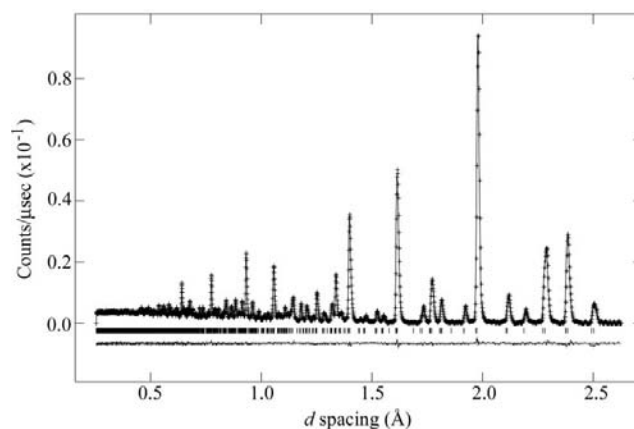
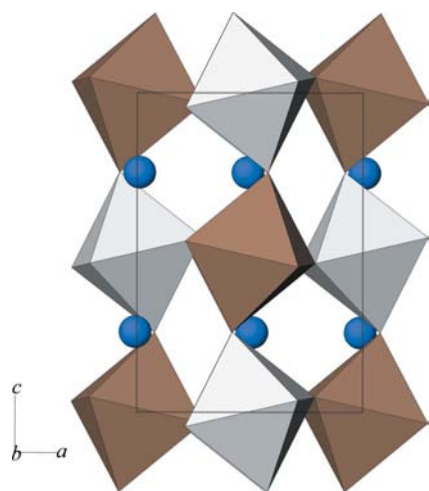


Figure 1

A fitted neutron powder diffractogram for La(Ni<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub>. The data shown are from the 91.3° bank.

As expected from the stoichiometry, lanthanum completely occupies the larger *A* site of the perovskite structure. A calculated tolerance factor of 0.94 for the compound (Goldschmidt, 1926) agrees well with the observed symmetry and  $MO_6$  tilting (Barnes *et al.*, 2006), indicating that lanthanum is too small to take the ideal 12-fold coordination in  $La(Ni_{2/3}Nb_{1/3})O_3$ . The position is thus distorted *via* the combination of  $MO_6$  tilting and an antiparallel shift of the lanthanum 4e position approximately along the [010] monoclinic direction. Such shifts often accompany  $MO_6$  octahedral tilting and allow a more favourable *A*-cation coordination environment, as *A*–O bond distances become shorter with increasing tilt angles (Woodward, 1997). Lanthanum in the title compound thus occupies a position with four of the 12 La–O bonds considerably shortened (Table 1). The average length of these La–O distances is 2.46 (7) Å, which agrees well with values found for isostructural materials, such as  $La(Mg_{2/3}Nb_{1/3})O_3$  (Choi *et al.*, 2000),  $Ca(Mg_{1/2}W_{1/2})O_3$  (Yang *et al.*, 2003) and  $La(Mg_{1/2}Ti_{1/2})O_3$  (Lee *et al.*, 2000).

The octahedrally coordinated *B*-cation position is split into two twofold sites (*2c* and *2d* of the  $P2_1/n$  space group), giving a 1:1 rock-salt-type ordering. Nickel takes ~90% occupancy of the *2d* position, with the stoichiometry then dictating mixed occupancy of the *2c* site. In this way, the difference in formal charges between the sites is maximized. As would be expected from the relative sizes of  $Ni^{2+}$  (0.69 Å) and  $Nb^{5+}$  (0.64 Å) (Shannon, 1976), the *2d* position is slightly larger than *2c* (Table 1), with average bond distances of 2.021 (9) and 2.038 (8) Å for *2c*–O and *2d*–O, respectively. Both octahedral positions show slight distortions due to the tilting phenomenon, with O–*2c*–O angles in the range 87.8 (2)–92.2 (2)° and O–*2d*–O angles in the range 88.1 (1)–91.9 (1)°. Given the similar sizes of  $Ni^{2+}$  and  $Nb^{5+}$  and similar *2c*- and *2d*-site environments, it can be concluded that the ordering is driven by electrostatic rather than steric considerations.



**Figure 2**  
The refined structure of  $La(Ni_{2/3}Nb_{1/3})O_3$  projected on to the (010) plane. La atoms are shown as spheres (the ordered *2c* and *2d* octahedrally coordinated cation sites, respectively, are shown in brown and grey in the electronic version of the paper).

**Experimental**

$La(Ni_{2/3}Nb_{1/3})O_3$  powder was synthesized *via* a polymeric route derived from the work of Pechini (1967). Stoichiometric quantities of reagent grade  $La(NO_3)_3 \cdot 6H_2O$ ,  $Ni(NO_3)_2 \cdot 6H_2O$  and  $NbCl_5$  were dissolved in deionized water. Citric acid and ethylene glycol were then added, and the solution was heated at 393 K for 5 h with constant stirring. In accordance with previous studies (Fontaine *et al.*, 2006), the cation/citric acid ratio was kept above 2 to obtain homogeneous sols. Burnout of organic components was performed in air at 673 K. The resulting grey powder was then fired in air at 1623 K for 2 h, with heating and cooling rates of 100 K h<sup>-1</sup>.

*Crystal data*

$LaNb_{0.33}Ni_{0.67}O_3$	<i>Z</i> = 4
<i>M<sub>r</sub></i> = 257.00	Neutron radiation
Monoclinic, $P2_1/n$	<i>T</i> = 295 K
<i>a</i> = 5.5823 (2) Å	Specimen shape: cylinder
<i>b</i> = 5.6194 (2) Å	Specimen prepared at 101.3 kPa
<i>c</i> = 7.9045 (3) Å	Specimen prepared at 1623 K
$\beta$ = 90.000 (9)°	Particle morphology: powder, grey
<i>V</i> = 247.96 (2) Å <sup>3</sup>	

*Data collection*

ISIS GEM diffractometer	Specimen mounted in transmission mode
Specimen mounting: packed powder	Scan method: time of flight

*Refinement*

<i>R<sub>p</sub></i> = 0.055	75 parameters
<i>R<sub>wp</sub></i> = 0.049	Preferred orientation correction: none
<i>S</i> = 1.26	
Profile function: convolution of the Ikeda–Carpenter and pseudo-Voigt functions	

**Table 1**

Selected geometric parameters (Å, °).

La1–O6	2.455 (5)	Ni3–O6	2.043 (4)
La1–O6 <sup>i</sup>	2.730 (4)	Ni3–O6 <sup>viii</sup>	2.043 (4)
La1–O6 <sup>ii</sup>	2.728 (5)	Ni3–O7 <sup>vi</sup>	2.043 (4)
La1–O6 <sup>iii</sup>	3.362 (5)	Ni3–O7 <sup>ii</sup>	2.043 (4)
La1–O7	2.636 (5)	Ni3–O8 <sup>vi</sup>	2.028 (8)
La1–O7 <sup>iv</sup>	2.422 (5)	Ni3–O8 <sup>ii</sup>	2.028 (8)
La1–O7 <sup>ii</sup>	3.396 (5)	Nb4–O6	2.009 (4)
La1–O7 <sup>v</sup>	2.835 (5)	Nb4–O6 <sup>ix</sup>	2.009 (4)
La1–O8 <sup>vi</sup>	3.1436 (13)	Nb4–O7	2.029 (4)
La1–O8	2.5597 (14)	Nb4–O7 <sup>ix</sup>	2.029 (4)
La1–O8 <sup>iv</sup>	3.1946 (21)	Nb4–O8 <sup>iv</sup>	2.024 (8)
La1–O8 <sup>vii</sup>	2.4196 (21)	Nb4–O8 <sup>x</sup>	2.024 (8)
O6–Ni3–O7 <sup>vi</sup>	89.99 (18)	O6–Nb4–O7	87.83 (18)
O6–Ni3–O7 <sup>ii</sup>	90.01 (18)	O6–Nb4–O7 <sup>ix</sup>	92.17 (18)
O6–Ni3–O8 <sup>vi</sup>	91.62 (10)	O6–Nb4–O8 <sup>iv</sup>	90.93 (9)
O6–Ni3–O8 <sup>ii</sup>	88.38 (10)	O6–Nb4–O8 <sup>xi</sup>	89.07 (9)
O6 <sup>viii</sup> –Ni3–O7 <sup>vi</sup>	90.01 (18)	O6 <sup>ix</sup> –Nb4–O7	92.17 (18)
O6 <sup>viii</sup> –Ni3–O7 <sup>ii</sup>	89.99 (18)	O6 <sup>ix</sup> –Nb4–O7 <sup>ix</sup>	87.83 (18)
O6 <sup>viii</sup> –Ni3–O8 <sup>vi</sup>	88.38 (10)	O6 <sup>ix</sup> –Nb4–O8 <sup>iv</sup>	89.07 (9)
O6 <sup>viii</sup> –Ni3–O8 <sup>ii</sup>	91.62 (10)	O6 <sup>ix</sup> –Nb4–O8 <sup>xi</sup>	90.93 (9)
O7 <sup>vi</sup> –Ni3–O8 <sup>vi</sup>	88.07 (11)	O7–Nb4–O8 <sup>iv</sup>	88.93 (10)
O7 <sup>vi</sup> –Ni3–O8 <sup>ii</sup>	91.93 (11)	O7–Nb4–O8 <sup>xi</sup>	91.07 (10)
O7 <sup>ii</sup> –Ni3–O8 <sup>vi</sup>	91.93 (11)	O7 <sup>ix</sup> –Nb4–O8 <sup>iv</sup>	91.07 (10)
O7 <sup>ii</sup> –Ni3–O8 <sup>ii</sup>	88.07 (11)	O7 <sup>ix</sup> –Nb4–O8 <sup>xi</sup>	88.93 (10)

Symmetry codes: (i)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iv)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (v)  $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (vi)  $x, y - 1, z$ ; (vii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (viii)  $-x + 1, -y, -z$ ; (ix)  $-x, -y + 1, -z$ ; (x)  $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (xi)  $x + \frac{1}{2}, -y + \frac{5}{2}, z + \frac{1}{2}$ .

X-ray powder diffraction data were collected in a  $2\theta$  range of 15–100° using a Siemens D5005 diffractometer equipped with a Cu  $K\alpha$  source and Si monochromator. Neutron powder diffractograms were collected using the GEM powder diffractometer at the ISIS facility, Rutherford Appleton Laboratory, England. Reflection positions were calculated using the *WinPLOTR* (Roisnel & Rodríguez-Carvajal, 2001) software package. Observed reflections from both X-ray and neutron data were combined and indexed using the *DICVOL* software (Boultif & Louër, 2004), with candidate space groups searched both manually and with the *Checkcell* software (Laugier & Bochu, 2001).

Good figures of merit were obtained for indexing of 47 observed reflections on an orthorhombic cell ( $M20 = 140$ ,  $F20 = 157$ ) corresponding to that of a  $2^{1/2}a_c \times 2^{1/2}a_c \times 2a_c$  perovskite supercell (where  $a_c$  is the cell edge of the cubic aristotype). Extinctions were found for  $h0l$ :  $h + l = 2n + 1$ ,  $h00$ :  $h = 2n + 1$ ,  $0k0$ :  $k = 2n + 1$  and  $00l$ :  $l = 2n + 1$ . We note here the importance of including both data sets in the indexing process, as an additional extinction was observed for  $0kl$ :  $k + l = 2n + 1$  in the X-ray data but not in the neutron data. The observed extinctions indicate  $Pmn2_1$  or  $Pmnm$  as orthorhombic symmetry choices, though the extinction for  $0k0$ :  $k = 2n + 1$  is not required for this assignment. Indexing on a monoclinic cell gave lower figures of merit ( $M20 = 25$ ,  $F20 = 31$ ), with extinctions at  $h0l$ :  $h + l = 2n + 1$  and  $0k0$ :  $k = 2n + 1$  indicating  $P2_1/n$  as a possible space group. From group theory considerations (Woodward, 1997), the assignment of  $Pmnm$  should correspond to a  $2a_c \times 2a_c \times 2a_c$  perovskite supercell, and our data unambiguously index as  $2^{1/2}a_c \times 2^{1/2}a_c \times 2a_c$ . Following the group theory work of Stokes *et al.* (2002), the assignment of  $Pmn2_1$  corresponds to a  $2^{1/2}a_c \times 2^{1/2}a_c \times 2a_c$  ferroelectric perovskite modification with possible  $A$ -site ordering. However, this is a very rarely reported perovskite form and is not expected given the composition of the material. Polymorphs with two distinct crystallographic  $A$  sites are expected to have two different  $A$  cations (Woodward, 1997). In general, double perovskites of the type  $A(M'_{1-x}M''_x)O_3$  crystallize in one of two forms: an orthorhombic polymorph (space group  $Pbnm$ ) with  $a^-a^-c^+$ -type octahedral tilting, and a monoclinic ( $P2_1/n$ ) polymorph, which additionally exhibits 1:1 rock-salt-type ordering of the  $B$ -sublattice cations. Both orthorhombic  $Pmn2_1$  and monoclinic  $P2_1/n$  polymorphs were tested *via* Rietveld refinement, and the former was found to be unstable to refinement, with a strong correlation between O-atom positions and between La-atom positions. Accordingly, the monoclinic form was assigned.

Rietveld refinement was performed using the *GSAS* software suite (Larson *et al.*, 2000). Data from banks 3–6 (positioned at 34.96, 63.62, 91.3 and 154.4°, respectively) were included in a multi-histogram refinement. Two peak profile parameters, zero shift and an eight-parameter Chebyshev-type background function, were included in the refinement in addition to lattice parameters, atomic coordinates and isotropic displacement parameters for all sites. Cation ordering on the  $B$  sublattice was included in the refinement, though with the

overall stoichiometry constrained to maintain the nominal  $\text{La}(\text{Ni}_{2/3}\text{Nb}_{1/3})\text{O}_3$  composition.

Program(s) used to solve structure: *WINPLOTR* (Roisnel & Rodríguez-Carvajal, 2001), *DICVOL* (Boultif & Louër, 2004) and *Checkcell* (Laugier & Bochu, 2001); program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 2000); molecular graphics: *ATOMS* (Dowty, 2002); software used to prepare material for publication: *GSAS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3004). Services for accessing these data are described at the back of the journal.

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