Phase transition behaviour in the *A*-site deficient perovskite oxide La$_{1/3}$NbO$_3$

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Abstract

The crystal structure of the layered perovskite La$_{1/3}$NbO$_3$ has been studied between room temperature and 500 °C using synchrotron X-ray powder diffraction methods. The structure shows ordering of the La cations at all temperatures. At room temperature La$_{1/3}$NbO$_3$ is orthorhombic with the NbO$_6$ octahedra showing out-of-phase tilting about the *a*-axis. This tilting diminishes as the temperature increases, so that above 200 °C the structure is tetragonal. The transition to the tetragonal structure is found to be continuous and analysis of the spontaneous strains shows it to be tricritical in nature.
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Keywords: Perovskite oxide; Phase transition

1. Introduction

Non-stoichiometric perovskite-type oxides are of considerable interest for use in solid-state electrochemical cells, either as ion conductors for example in solid oxide fuel cells or as electrodes in Li ion insertion reactions [1]. The perovskite structure, written as ABO$_3$ is based on a motif of corner sharing BO$_6$ octahedra. The ideal or aristotype cubic structure places strict bonding requirements on the two cations and most perovskites actually adopt a distorted variant of the ideal structure. By far the most common distortion is displacement of the oxygen anions associated with tilting of the BO$_6$ octahedra [2,3]. Another commonly observed structural variant is where cation and/or anion vacancies occur. The title compound La$_{1/3}$NbO$_3$ falls into this latter class of compounds and two-thirds of the available *A*-type cation sites are vacant. The non-stoichiometry and tilting

are not mutually exclusive and there are examples where both distortions are present [3].

La$_{1/3}$NbO$_3$ has been studied for a number of years as a possible candidate for use in Li-ion batteries [4–6]. The crystal structure of La$_{1/3}$NbO$_3$ was first described by Iyer and Smith [7] who demonstrated that the La ions ordered into alternate (001) planes so doubling the crystallographic *c*-parameter. This has led to the description of the structure of La$_{1/3}$NbO$_3$ in the tetragonal space group *P*4/*mmm*, despite the observation that the cell is actually orthorhombic [7,8]. This situation is very similar to that described for La$_{2/3}$TiO$_3$ where it has been established that the orthorhombic distortion is a consequence of out-of-phase tilting of the TiO$_6$ octahedra perpendicular to the *c*-axis [9]. The appropriate space group for such a combination of cation–vacancy ordering and tilting is *Cmmm* [9,10].

Using XAFS Nakayama et al. [11] postulated that the lowering of symmetry in La$_{1/3}$NbO$_3$ was due to octahedral tilting and they concluded that such tilting is sensitive to the extent of electrochemically inserted Li.

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These workers postulated that the tilting could be controlled by the electrochemical reaction. It may be concluded that the suitability of $La_{1/3}NbO_3$ for use in Li insertion electrodes will be dependent on the precise structure of the material.

The aim of the present work was to establish if the orthorhombic distortion observed in $La_{1/3}NbO_3$ is a consequence of tilting of the NbO_6 octahedra in an analogous manner to that seen in $La_{2/3}TiO_3$ and to establish if such tilting can be removed by heating of the sample.

2. Experimental

A polycrystalline sample of $La_{1/3}NbO_3$ was prepared by standard high-temperature ceramic methods. A stoichiometric mixture of La_2O_3 and Nb_2O_5 was thoroughly ground in an agate mortar with ethanol and heated in air in an alumina crucible at $800\,°C$ for 1 day and then at $1300\,°C$ for 2 days with intermediate regrindings. The reaction was monitored using X-ray diffraction data recorded at room temperature using a Shimadzu D6000 diffractometer (Cu $K\alpha$ radiation, Bragg Brentano plate geometry).

High-energy synchrotron X-ray powder diffraction data were obtained at BL-02B2 SPring-8, Hyogo Japan [12]. For these measurements the sample was housed in a 0.2 mm diameter glass capillary and the wavelength, $0.38937\,\text{Å}$, was calibrated using a CeO_2 standard. Variable temperature synchrotron X-ray powder diffraction measurements were performed on the large Debye–Scherrer diffractometer at BL-20B, The Australian National Beamline Facility (ANBF), at the Photon Factory, Tsukuba Japan [13]. The finely ground sample was contained in a 0.3 mm diameter quartz capillary. The X-ray wavelength used during the measurements was $0.80953(1)\,\text{Å}$ as calibrated using a Si NIST-640b standard. Data were collected at angles of up to $2\theta = 60°$ using two Fuji Image Plates as detector. Temperature control was achieved using a custom built furnace and the temperature was held to within $\pm2°$ of the set point during the measurements. The diffraction measurements were carried out at increasing temperatures, with steps of $5°$ in the vicinity of the transition temperature. The structures were refined by the Rietveld method using the program RIETICA [14], and a pseudo-Voigt profile shape function was assumed. The background was estimated by interpolation between up to 40 user-defined points.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction pattern of $La_{1/3}NbO_3$ recorded using 32 keV X-rays at SPring-8.

This pattern shows a number of strong X-point reflections, indexed as $h\,k\,\frac{1}{2}$ based on the parent $Pm\bar{3}m$ cubic cell, as a result of the layered ordering of cations and vacancies on the perovskite A-site, Fig. 2. Although the pattern did not show distinct splitting of any reflections indicative of orthorhombic symmetry it does contain a number of weak R-point reflections arising from out-of-phase tilting of the NbO_6 octahedra. Such tilting causes an expansion of the cell. Diffraction patterns recorded at longer wavelengths (0.8 Å) on the ANBF diffractometer at the Photon Factory showed characteristic splitting of the (cubic $Pm\bar{3}m$) 200 type reflection demonstrating the structure to be orthorhombic, Fig. 3. Following the arguments presented by Howard and Zhang the most likely structure is in the orthorhombic space group $Cmmm$ [9,10].

The structure was refined in $Cmmm$ using the high-energy data and the details of the structural refinement are listed in Table 1. These results are similar to those of Dilanian et al. [15]. Refinements where the La was allowed to occupy both sites invariably showed that all the La occupied the $4g$ site. Similar results were obtained when 0.8 Å ANBF data were used in the refinement. The displacement of the Nb atoms results alternating long, $2.072(1)\,\text{Å}$ and short $1.901(1)\,\text{Å}$ Nb–O bonds along the c-axis with the average Nb–O distance, $1.975\,\text{Å}$ being typical of Nb(V) oxides. The structural refinements indicated the magnitude of the tilting of the NbO_6 octahedra at room temperature $\approx 4.4°$, comparable with that seen in $La_{2/3}TiO_3$, $\approx 4.7°$ [9]. We note that the superlattice reflections arising from the tilts are very weak in the diffraction patterns, due to the much stronger scattering power of Nb and La.

Heating the sample results in a progressive reduction in the magnitude of the orthorhombic splitting and at $200\,°C$ the structure appears to be tetragonal. The
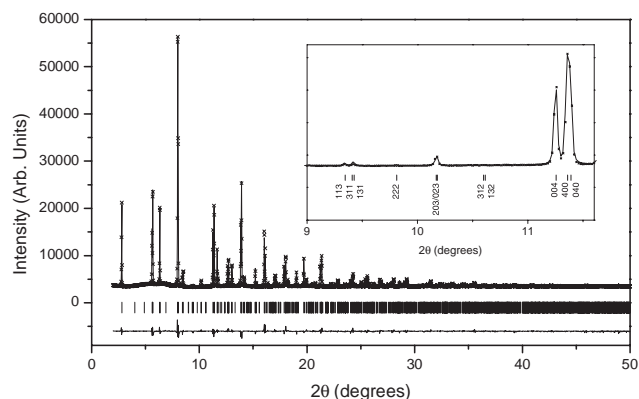

Fig. 1. The observed, calculated and difference diffraction profiles for $La_{1/3}NbO_3$ at room temperature collected using X-rays of wavelength 0.38937 Å. The inset shows details of some diagnostic reflections—the appearance of the 113/311/131 multiplet is indicative of doubling of the cell due to tilting of the octahedra and the broadening of the 400/040 reflection is indicative of the orthorhombic distortion.
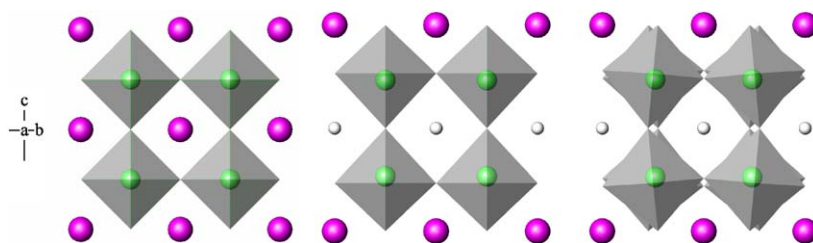
Fig. 2. Representations of (a) the cubic perovskite structure, (b) the high-temperature tetragonal structure and (c) the room temperature orthorhombic structure. In (b) and (c) the smallest spheres represent the position of the unoccupied *A*-type sites. Such sites are, of course, occupied in the cubic perovskite structure. This figure highlights the movement of the Nb cation as a result of the cation:vacancy ordering and the tilting of the octahedra in the orthorhombic structure.
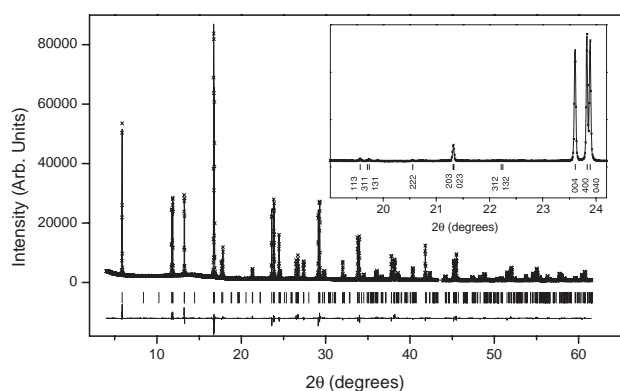

Fig. 3. The observed, calculated and difference diffraction profiles for $La_{1/3}NbO_3$ at room temperature collected using X-rays of wavelength 0.80953 Å. At this wavelength the splitting of the 400/040 reflection indicative of the orthorhombic distortion is evident.

Fig. 4. Temperature dependence of the lattice parameters for $La_{1/3}NbO_3$ from the Rietveld structural refinements of synchrotron X-ray powder diffraction data collected at the ANBF. The dashed vertical line shows the apparent transition temperature. The solid line is the best fit to the scaled tetragonal *a*-parameter, extrapolated into the orthorhombic phase.

Table 1
Refined, lattice and positional parameters for $La_{1/3}NbO_3$ in both the orthorhombic (RT) and tetragonal (500 °C) phases

Atom	Site	x	y	z
RT $a = 7.8562(2)$ $b = 7.8361(2)$ $c = 7.9298(2)$ Å R_p 3.83 R_{wp} 3.81%				
La1	4g	0.2516(3)	0	0
La2	4h	0.250[a]	0	$\frac{1}{2}$
Nb	8n	0	0.2616(1)	0.263(3)
O1	4i	0	0.2736(4)	0
O2	4j	0	0.2253(9)	$\frac{1}{2}$
O3	4k	0	0	0.2190(10)
O4	4l	0	$\frac{1}{2}$	0.2577(9)
O5	8m	$\frac{1}{4}$	$\frac{1}{4}$	0.2341(5)
$T = 500$ °C $a = 3.92446(5)$ $c = 7.9461(1)$ Å R_p 7.51 R_{wp} 7.54%				
La1	1c	$\frac{1}{2}$	$\frac{1}{2}$	0
La2	1d	$\frac{1}{2}$ [a]	$\frac{1}{2}$	$\frac{1}{2}$
Nb	2g	0	0	0.2168(1)
O1	1a	0	0	0
O2	1b	0	0	$\frac{1}{2}$
O3	4i	0	$\frac{1}{2}$	0.2340(7)

[a]Refinements showed that no La occupied this site. In the orthorhombic structure the *x* parameter for the 4h site is variable.
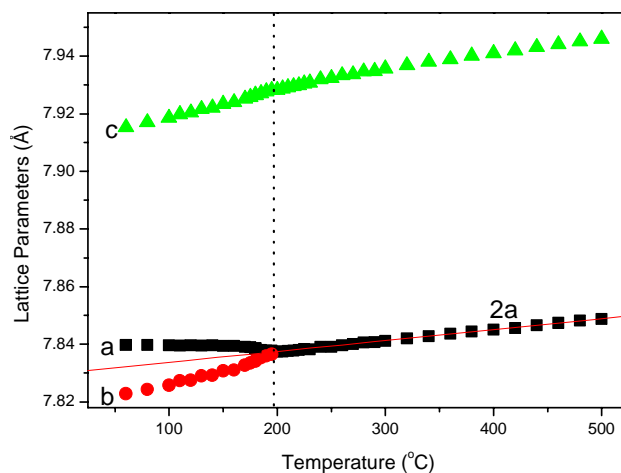
temperature dependence of the lattice parameters indicates that the orthorhombic to tetragonal transition is continuous, Fig. 4. This figure illustrates that the rate of increase in *a* is approximately equal to the rate of decrease in *b*. The nature of the transition can be established by examination of the temperature dependence of an appropriate order parameter [16]. The order parameter may be estimated from either the spontaneous strains or the magnitude of the octahedral tilts. The temperature dependence of the latter can be fitted to an expression of the type $A(T-T_c)^n$, where *n* is either $\frac{1}{2}$ or $\frac{1}{4}$. These correspond to a second order and tricritical phase transition, respectively. That these cannot be distinguished is a consequence of the uncertainty in the determination of the internal coordinates, and hence tilt angle, in the orthorhombic structure using X-ray diffraction methods. The lattice parameters are much
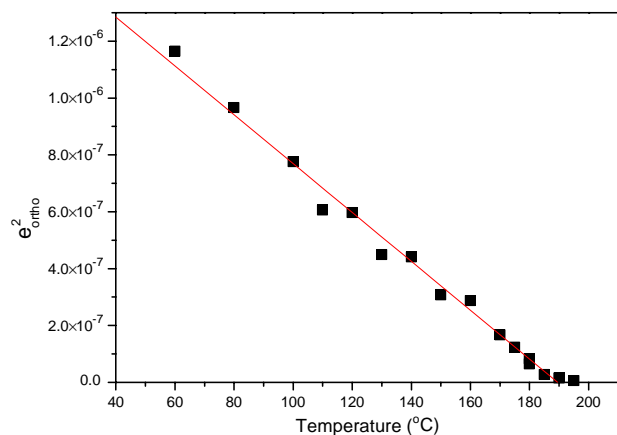
Fig. 5. Temperature dependence of the square of the orthorhombic strain for $La_{1/3}NbO_3$. The solid line is a linear fit to the data.

Fig. 6. Temperature dependence of the volumes for $La_{1/3}NbO_3$. The dashed line is the fit to the volumes observed in the tetragonal phase extrapolated into the orthorhombic phase showing the reduction in volume in the latter.

better determined and in this circumstance the spontaneous strains are a better indicator of the transition [16].

The most readily estimated strain is the orthorhombic strain given by $e_{ortho} = (a - b)/(a + b)$. This strain has a symmetry different from that of the order parameter, Q, so we expect e_{ortho} to be proportional to Q^2 [16,17]. A plot of the temperature dependence of the square of the orthorhombic strain is linear (Fig. 5), that is Q^4 is linearly dependent on temperature, showing the transition to be tricritical in nature. The critical temperature is estimated to be 190 °C which is in reasonable agreement with that estimated from the fit to the tilt angle, 195 °C. The volume strain e_V is estimated from the difference in the observed volume for the orthorhombic phase and that obtained by extrapolation from volumes for the high temperature tetragonal phase. As evident in Fig. 6 the volume of the orthorhombic phase is smaller than that estimated by extrapolation. The square of the volume strain also shows a linear dependence on temperature as predicated for a tricritical phase transition.

The bond valence sum (BVS) of the Nb site is typical [18] of Nb(V) in both structures, being 5.09 at room temperature and 5.05 at 500 °C. The effective valence for the La on the $4g$ site is higher than that of the $4h$ site 2.51 vs 2.09 and a similar difference is observed at high temperatures. This difference in the local bonding of the two sites is consistent with the exclusive occupation by the La of the orthorhombic $4g$ or tetragonal $1c$ sites, any La that occupied the $4h$ or $1d$ sites would be severely under bonded. It is reasonable to predict from the BVS calculations that any Li incorporated into the structure would preferentially occupy the $4h/1d$ sites. Studies to confirm this would be useful.

In conclusion, we have confirmed that $La_{1/3}NbO_3$ has an orthorhombic structure at room temperature as a consequence of both cation–vacancy ordering and tilting
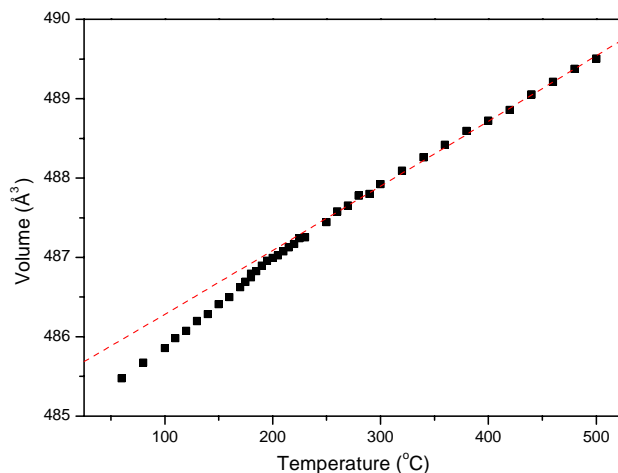
of the NbO_6 octahedra. We find that heating reduces the latter and the $La_{1/3}NbO_3$ undergoes a continuous tricritical transition, as monitored by the spontaneous strain, to a tetragonal structure near 195 °C. The ordering of the La in the orthorhombic $4g$ sites is consistent with BVS calculations.

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