

# Crystal structure of $Ln_{1/3}NbO_3$ ( $Ln = Nd, Pr$ ) and phase transition in $Nd_{1/3}NbO_3$

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## Abstract

The crystal structure of the *A*-site deficient perovskite  $Ln_{1/3}NbO_3$  ( $Ln = Nd, Pr$ ) at room temperature has been determined, for the first time, as orthorhombic in space group *Cmmm* using high-resolution neutron powder diffraction. Pertinent features are the alternation of unoccupied layers of *A*-sites and layers partly occupied by *Ln* cations, as well as out-of-phase tilting of the  $NbO_6$  octahedra around an axis perpendicular to the direction of the cation/vacancy ordering. The phase transition behaviour of  $Nd_{1/3}NbO_3$  has also been studied in situ. This compound undergoes a continuous phase transition at around 650 °C to a tetragonal structure in space group *P4/mmm* due to the disappearance of the octahedral tilting. The analysis of spontaneous strains shows that this phase transition is tricritical in nature. © 2007 Elsevier Inc. All rights reserved.

**Keywords:** Perovskites; Crystal structures; Octahedral tilting; Cation/vacancy ordering; Phase transition; Neutron powder diffraction

## 1. Introduction

There has been a great deal of interest in the *A*-site deficient perovskites such as  $Ln_{1/3}NbO_3$  ( $Ln = La, Ce, Pr, Nd$ ), due to the promising potential of these materials as host crystals for  $Li^+$ -ion intercalation [1,2] as well as their interesting electrical properties [3–5]. The crystal structure of the  $Ln_{1/3}NbO_3$  ( $Ln = La, Ce, Pr, Nd$ ) compounds was first reported by Iyer and Smith 40 years ago [6]. Although their Guinier patterns showed small orthorhombic splitting, the structures of  $Ln_{1/3}NbO_3$  ( $Ln = La, Ce, Pr, Nd$ ) were all refined as tetragonal in space group *P4/mmm* on a  $1 \times 1 \times 2$  cell (referred to the edge of the cubic perovskite aristotype). The doubling of the *c*-parameter was a result of *A*-site cation/vacancy ordering onto alternate (001) planes. Later Abakumov et al. reported that the symmetry for  $Ln_{1/3}NbO_3$  ( $Ln = La, Ce, Nd$ ) was orthorhombic in space

group *Pmmm* (also on a  $1 \times 1 \times 2$  cell) [4], whereas Bridges et al. determined the structure of  $Ce_{1/3}NbO_3$  as monoclinic in *P2/m* [7]. More recently a different space group of *Cmmm* (on a  $2 \times 2 \times 2$  cell) was proposed for  $La_{1/3}NbO_3$  [8–10]. This was supported by Howard and Zhang using group theoretical analysis [11]. They concluded that the correct structural model for  $La_{1/3}NbO_3$  is orthorhombic in *Cmmm* — the same as for  $La_{2/3}TiO_3$ , and identified the orthorhombic distortion as a consequence of the cation/vacancy ordering combined with out-of-phase octahedral tilting around an axis perpendicular to the ordering direction. It was also suggested by these authors, based on literature data, that the same structure may be adopted by all  $Ln_{2/3}TiO_3$ ,  $Ln_{1/3}NbO_3$  and  $Ln_{1/3}TaO_3$  ( $Ln = La, Ce, Pr, Nd$ ) compounds (e.g., they demonstrated that the reported monoclinic structure of  $Ce_{1/3}NbO_3$  in *P2/m* [7] could be described equally well using the orthorhombic model in *Cmmm*). However, a recent study of  $Nd_{0.7}Ti_{0.9}Al_{0.1}O_3$  (believed to be isostructural to  $Nd_{2/3}TiO_3$ ) revealed its room temperature structure as monoclinic in space

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group  $C2/m$  on a  $2 \times 2 \times 2$  cell; the lower symmetry was attributed to the smaller ionic radius<sup>1</sup> of  $\text{Nd}^{3+}$  (1.27 Å) than  $\text{La}^{3+}$  (1.36 Å) [13]. This monoclinic structure is characterised by  $A$ -site cation/vacancy ordering along the  $c$ -axis and out-of-phase  $\text{TiO}_6$  octahedral tilting independently around  $c$ - and  $a$ -axis (these being parallel and perpendicular to the ordering direction, respectively).

The main aim of the present study is to examine the structure of  $\text{Ln}_{1/3}\text{NbO}_3$  ( $\text{Ln} = \text{Nd}$  and  $\text{Pr}$ ) at room temperature, to establish whether the smaller (than  $\text{La}$ )  $A$ -site cation also results in lower symmetry than that for  $\text{La}_{1/3}\text{NbO}_3$ . Temperature dependent studies were also carried out to determine whether heating removes octahedral tilting as observed for  $\text{La}_{1/3}\text{NbO}_3$ .

## 2. Experimental

The polycrystalline samples of  $\text{Nd}_{1/3}\text{NbO}_3$  and  $\text{Pr}_{1/3}\text{NbO}_3$  were prepared by standard high-temperature ceramic methods.  $\text{Nd}_2\text{O}_3$  (99.9% in purity, Aldrich) and  $\text{Pr}_6\text{O}_{11}$  (99.9%, Aldrich) starting powders were first preheated at 1000 °C overnight, and then mixed with  $\text{Nb}_2\text{O}_5$  (99.9%, Aldrich) in an agate mortar under acetone. The mixtures were subsequently placed in alumina crucibles and heated at temperatures of 800 °C for 20 h and 1300 °C for 50 h with intermediate grinding. The sample purity was confirmed by powder X-ray diffraction measurements using a Shimadzu D-6000 diffractometer with  $\text{CuK}\alpha$  radiation.

Time-of-flight powder neutron diffraction data were recorded using the high-resolution powder diffractometer, HRPD, at the ISIS neutron facility, Rutherford Appleton Laboratories, UK [14]. The powdered samples of  $\text{Nd}_{1/3}\text{NbO}_3$  and  $\text{Pr}_{1/3}\text{NbO}_3$  were loaded into thin-walled 11 mm diameter vanadium sample cans, which were then suspended from the standard ISIS candlesticks for room temperature measurements. Temperature dependent studies were also carried out for  $\text{Nd}_{1/3}\text{NbO}_3$ , from 100 to 750 °C. For these measurements, the vanadium sample can was mounted in an ISIS designed furnace. This furnace employs a cylindrical vanadium element and operates under high vacuum (pressure  $< 10^{-4}$  mbar). The thermometry is based on type-K (chromel-alumel) thermocouples positioned in contact with the sample can at about 20 mm above the beam centre. During data collection in furnace, the temperature fluctuation is approximately  $\pm 0.5$  °C. The diffraction patterns were recorded over the time-of-flight range 30–130 ms in both back-scattering and 90° detector banks, corresponding to  $d$ -spacings from 0.6 to 2.6 Å (at a resolution  $\Delta d/d \sim 4 \times 10^{-4}$ ) and from 0.9 to 3.7 Å ( $\Delta d/d \sim 2 \times 10^{-3}$ ), respectively. The patterns were normalised to the incident beam spectrum as recorded in the upstream monitor, and corrected for detector efficiency according to prior calibration with a vanadium scan. Patterns were recorded to a total incident proton beam of at least 70  $\mu\text{A h}$

at room temperature, corresponding to approximately 2.2 h of data collection, to allow precise structure determination. The high-temperature patterns were recorded to a total incident proton beam of about 8  $\mu\text{A h}$ , corresponding to roughly 15 min of data collection, sufficient to give a good determination of lattice parameters and reasonable estimates of internal co-ordinates. The temperature intervals were typically 20 °C, but varied from 10 to 50 °C. In order to allow for thermal equilibration of the sample, data collection was delayed for a period of at least 5 min (depending on the size of the temperature step) after stability at the set temperature had been achieved.

## 3. Results and discussion

### 3.1. Room temperature structure for $\text{Nd}_{1/3}\text{NbO}_3$ and $\text{Pr}_{1/3}\text{NbO}_3$

A selection,  $1.85 < d < 2.45$  Å, of the neutron diffraction pattern recorded from  $\text{Nd}_{1/3}\text{NbO}_3$  at room temperature is shown in Fig. 1. The peaks in the figure are identified by indices based on the  $2 \times 2 \times 2$  cell. Peaks with all even indices correspond to peaks from the ideal cubic aristotype. The superlattice peaks are also indexed on the basis of the  $2 \times 2 \times 2$  cell, and marked as  $X$ -point (two even, one odd indices),  $R$ -point (all odd indices), or  $M$ -point (one even, two odd indices). Intensities at the  $X$ -points arise from  $A$ -site cation/vacancy ordering, and those at the  $R$ -points from out-of-phase (–) octahedral tilting. The very weak intensities at the  $M$ -points are due to  $X$ - and  $R$ -point distortions acting in concert [15]. Based on the arguments presented by Zhang et al. [13], the most likely structure for  $\text{Nd}_{1/3}\text{NbO}_3$  is either orthorhombic in space group  $Cmmm$

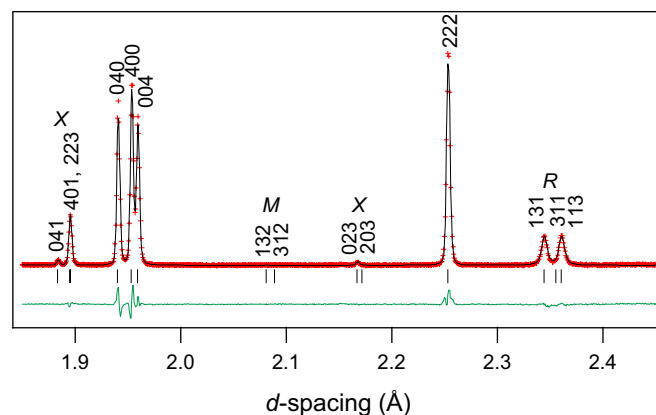


Fig. 1. Extract ( $1.85 < d < 2.45$  Å) from the neutron diffraction pattern recorded in the back-scattering detectors from  $\text{Nd}_{1/3}\text{NbO}_3$  at room temperature. The peaks are indexed on a cell of dimensions  $2 \times 2 \times 2$  (referred to edge of the cubic aristotype). Crosses represent the observed data. The continuous lines are fits obtained by the Rietveld method using the proposed structure in  $Cmmm$ , the vertical marks show the peak positions expected in this structure, and the line beneath the pattern records the difference between the observed pattern and that calculated in the Rietveld analysis.

<sup>1</sup>The ionic radii of  $\text{Ln}^{3+}$  quoted in this paper are those in 12-fold coordination as published by Shannon [12].

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