



Phase coexistence in NaTaO₃ at room temperature; a high resolution neutron powder diffraction study



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ARTICLE INFO

Article history:

Received 30 January 2015

Received in revised form

5 March 2015

Accepted 18 March 2015

Available online 19 March 2015

Keywords:

NaTaO₃

Crystal structure

Neutron diffraction

Phase transitions

ABSTRACT

Room temperature high resolution neutron powder diffraction data, measured in time-of-flight, from two independent samples of NaTaO₃ shows the presence of phase coexistence of two orthorhombic structures with space groups *Pbnm*, and *Cmcm*. The failure of earlier work to recognise the extent of the hysteresis associated with the high temperature (~763 K on heating) *Cmcm* – *Pbnm* phase transition, that extends down to room temperature, and probably to 0 K, is due to data having been collected at too low a real-space resolution to characterise the diagnostic pseudocubic fundamental and superlattice reflection multiplicities. The phase fraction of the *Cmcm* phase increases with increasing temperature from 45 weight % at 298 K, to 74 weight % at 758 K. Throughout the whole temperature interval 298 K–758 K, the volume per formula unit of the *Cmcm* phase exceeds that of the *Pbnm* phase by an almost constant ~0.01 Å³ suggesting the addition of pressure would suppress the volume fraction of the higher temperature phase. The crystal structure of both phases, determined from data collected at 298 K, are reported, with the atomic displacement parameters of the *Cmcm* phase being significantly larger than those associated with the *Pbnm* phase, probably reflecting a high degree of thermal and static disorder.

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1. Introduction

Identification of the correct unit cell metric and space group for hettotype phases of simple perovskite-structured compounds is problematic for two principal reasons. Firstly, the spontaneous strains that develop at zone-boundary phase transitions may be small [1], and hence it is necessary to collect data at the highest real-space resolution to permit analysis of the fundamental reflection multiplicities and separations. Secondly, the diagnostic superlattice reflections of the lower symmetry structures derive essentially from anion displacements [2], which in the case of oxide systems with heavy atoms in the dodecahedral and/or octahedral sites requires either sophisticated data collection strategies for X-ray powder diffraction, or the use of neutron diffraction, where the scattering length of oxygen has a comparable magnitude to those of the cations.

These zone-boundary phase transitions, frequently termed tilt

transitions in perovskite-structured phases, are a commonly observed phenomenon and occur when the crystal becomes unstable to a set of normal mode of vibrations of the aristotype phase [2]. For non-ferroelectric perovskite-structured compounds, without cation ordering of the dodecahedral and octahedral sites, these modes transform as basis vectors of either/or both the irreducible representations R_4^+ and M_3^+ [2–5]. In the former case, successive layers of octahedra rotate in the opposite sense (equivalent to an anti-phase rotation [4]), in the latter, successive layers of octahedra rotate in the same sense (equivalent to an in-phase rotation [4]). Superlattice reflections associated with these soft mode condensations are therefore observed in the diffraction patterns of hettotype phases at the R and/or M points of the pseudocubic Brillouin zone. Based on the earlier ideas of Megaw [6], Glazer used model building methods to systematize the permitted lattice metrics and space groups of perovskite-structures that exhibit these zone-boundary phase transitions [4]. More recently, these deductions have been reinvestigated and corrected using formal group theoretical techniques [3,5].

Perovskite-structured NaTaO₃ has been the subject of a number of studies, initially as a potentially ferroelectric material [7,8], as a

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model compound to study zone-boundary phase transitions [9,10], and latterly, as a photocatalyst for splitting water molecules as a clean and renewable source of hydrogen [11–14]. An early experimental determination of the dielectric constant suggested NaTaO₃ was ferroelectric with a Curie temperature of 748 K [7], however subsequent investigations found no evidence for ferroelectric behaviour [8,15]. Temperature-dependent optical birefringence studies showed the presence of 3 structural phase transitions, cubic – tetragonal at 903 K, tetragonal – orthorhombic at 853 K (indicated parallel to the cubic <100> ie pseudocubic orientation), and orthorhombic – orthorhombic at 753 K (one principal axis parallel to cubic <100> ie rhombic orientation) [8]. These transition temperatures were later confirmed by DTA [16] and neutron powder diffraction [17,18].

The earliest report of crystallographic analysis of NaTaO₃ used X-ray powder diffraction techniques and reported a unit cell $\sqrt{2}a \times a \times \sqrt{2}a$, where a is the lattice parameter of the aristotype phase [19]. A subsequent single crystal X-ray diffraction study determined the space group as polar $Pc2_1n$, in accord with the believed ferroelectric nature of the phase at the time, and observed a doubling of the unit cell b axis ($\sqrt{2}a \times 2a \times \sqrt{2}a$) [20]. The ambient temperature and pressure phase was later studied by X-ray powder diffraction [21] and a crystal structure was refined in the centrosymmetric space group $Pcmm$ (an alternate setting of Space Group (S.G.) No. 62), in keeping with the experimentally determined non-ferroelectric behaviour [8,15]. This structure was subsequently refined to higher precision in the anion coordinates using medium resolution neutron powder diffraction, and the two high temperature hettotype phases were identified, and their crystal structures reported in space groups $Bmmb$ (an alternate setting of S.G. No. 63) (803 K) and $P4/mbm$ (S.G. No. 127) (893 K) [18]. More recently, two contemporaneous studies of the temperature dependent structural crystallography of NaTaO₃ have been made with the aim of using it as a model system for studying zone boundary phase transitions in perovskite-structured phases [9,10]. Both studies utilised the advantages of neutron powder diffraction over X-ray powder diffraction but were carried out at significantly different real-space resolutions. The lower resolution investigation [10] carried out using the HB-4 diffractometer at the High Flux Isotope Reactor of the Oak Ridge National Laboratory, was in full agreement with the earlier investigation made on the D1a diffractometer at the Institut Laue-Langevin [18]. The higher resolution study carried out using the time-of-flight diffractometer HRPD on the ISIS spallation neutron source was in agreement with both studies at temperatures higher than the $Pcmm$ – $Bmmb$ phase transition temperature ~758 K, but not below [9]. Unfortunately no details of the discrepancy between the expected data from a perovskite structure in space group $Pcmm$ (or any equivalent setting of S.G. No. 62) and that experimentally observed were given in the paper [9]. Further evidence for a possible inconsistency between the crystal structures derived from the medium resolution neutron diffraction studies and correct crystal structure at room temperature has been afforded by ²³Na multiple-quantum magic-angle spinning (MQMAS) NMR [22]. Small discrepancies were observed between the experimentally observed MQMAS and MAS spectra and those calculated using the accepted room temperature crystal structure.

In this submission we report a re-evaluation of the original HRPD data [9] and furthermore, compare them with a data set collected on a sample of identical synthesis as that used in the HB-4 study.

2. Experimental section

The principal sources of the data that have been re-analysed for

this manuscript have already been described in detail [9], and we simply précis the methodology below. High resolution time-of-flight (TOF) neutron powder diffraction data were collected on a sample of commercial NaTaO₃ (Sigma–Aldrich, 99.9+% purity) in the TOF window 30–130 ms, at room temperature, and at 83 temperatures between 373 K and 1003 K. An additional TOF window, 100–200 ms, was also collected under ambient conditions to monitor the longer d -spacing reflections. The raw data were reduced as described previously to produce data sets in the TOF range 32–120 ms (~0.64–2.4 Å) and a single data set 102–190 ms (~2.04–3.8 Å) for profile refinement using the GSAS suite of programs. The intrinsic resolution of the instrument is to first order independent of Q ($4\pi\sin(\theta)/\lambda$), with $\Delta d/d = 4 \times 10^{-4}$. An instrument parameter file for the GSAS lineshape 4 which is suitable for use with the hkl -dependent line broadening functions of Stephens [23] was derived by fitting data collected on the NIST standard silicon powder SRM640b (data collected ~6 weeks after the NaTaO₃ experiment).

For comparison purposes, a second sample of NaTaO₃ was also measured at room temperature in the short (30–130 ms) TOF window. This sample, synthesised in the Chemistry Department, Sydney University, was prepared in an identical manner to that described in the high-temperature crystallographic study that used the medium resolution neutron powder diffractometer HB-4 [10].

3. Results and discussion

3.1. Crystallographic background

The results of the group theoretical analysis of the permitted space groups for simple perovskite-structured compounds [4] reduces structural characterisation to a two-step process [24]. Firstly, the tilt class is identified by the presence of diagnostic superlattice reflections on the surface of the pseudocubic Brillouin zone. These can be summarised as follows: superlattice reflections at the R point alone – anti-phase tilting; superlattice reflections at the M point alone – in-phase tilting; the presence of R and M point superlattice reflections – both anti-phase and in-phase tilting (Note in the case of both tilt systems being present, then superlattice reflections at the X point of the pseudocubic Brillouin zone are also observed [25]). The second step of the process requires determination of the pseudocubic lattice metric from an investigation of the multiplicities of the fundamental pseudocubic Bragg reflections, and it is in this process that high direct space resolution is a prerequisite. Taking the previously accepted sequence of phase transitions in NaTaO₃ for granted [18], and using space group settings of the two lowest temperature phases as $Pbnm$ (S.G. No. 62), and $Cmcm$ (S.G. No. 63), we expect to observe superlattice reflections at the R, M, and X points of the pseudocubic Brillouin zone from group theoretical arguments [4] ($Pbnm$: $a^-a^-c^+$; $Cmcm$: $a^0b^-c^+$ in Glazer notation [3]). The pseudocubic metric (subscript p) is related to the crystallographic unit cells by the matrix $\frac{1}{2} \frac{1}{2} 0 / -\frac{1}{2} \frac{1}{2} 0 / 0 \frac{1}{2} 0 \frac{1}{2}$ for space group $Pbnm$ ($a_p = b_p \neq c_p$, $\alpha_p = \beta_p = 90^\circ$, $\gamma_p \neq 90^\circ$), and $\frac{1}{2} 0 0 / 0 \frac{1}{2} 0 / 0 \frac{1}{2}$ for space group $Cmcm$ ($a_p \neq b_p \neq c_p$, $\alpha_p = \beta_p = \gamma_p = 90^\circ$). The pseudocubic fundamental reflection 111 would therefore be expected to be a singlet in $Cmcm$ (index 2 2 2 in the true orthorhombic unit cell) but a doublet in $Pbnm$ due to the monoclinic subcell metric (indices 0 2 2, 2 0 2 in the true orthorhombic unit cell).

3.2. Analysis of room temperature data

The data collected at room temperature from both HRPD and HB-4 only indicate superlattice reflections on the surface of the pseudocubic Brillouin zone (R, M, X points) and hence the

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